RESEARCH ARTICLE

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Role of Number of Imprinted Cavity on the Selectivity of the Imprinted Polymer

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Research on the effect of the number of imprinted cavities on the mechanisms of the selectivity of the imprinted polymer method was conducted. These imprinted materials studied were based on eugenol as a functional monomer while PEGDE (Polyethylene Glycol Diglycidyl Ether) and EDMA (Ethylene Glycol Dimethacrylate) used as cross linker. The first step of synthesis of material was by interacting the ion template Fe(III) on polyeugenol and polyeugenoxi acetate. The next step was locking the complex with cross linker PEGDE (polyeugenol) or EGDMA (polyeugenol and polyeugenoxi acetate). The macropolymer formed were then eliminated its Fe(III) using an acid to formed Ionic Imprinted Polymer (IIP). The IIP formed was then analyzed by SEM EDX to determine concentration of Fe (III) in the polymer. The results obtained show that the concentration of the Fe (III trapped in macropolymer was 1.5% in the interacted step with template. After being released by acid, 0.15; 0.6; 1.03; 1.06% of Fe (III) were still remaining in the polymer. The smaller the number of Fe (III) remaining in polymer, it can be expected that many imprinted cavity was formed. The more imprinted cavity formed, it can be obtained the higher degree of selectivity of adsorption.

Keywords: Imprinted Polymer, Eugenol, Selective Adsorption, Imprinted Cavity.

1. INTRODUCTION

Molecular imprinting is the latest technology, in which the materials synthesised containing areas (sites) receptor is very specific to the target compound. The application of MIP covers the development of sensors, membranes, polymer production adsorbent with special functions such as matrix release of the drug/drug release (matrix drug), separation of materials, biosensors, catalysts with specificity high,[1] stable, robust and resistant to range pH, solvent and temperature, in addition to the synthesis of MIP is also relatively inexpensive and easy.[2]

Development of cheap adsorbent are high adsorption capacity is a major goal of many studies. One interesting study is the use of biomaterials as adsorbent for metal ions and compounds. Biomaterials is very important because it is cheap and biodegradable, including waste taken from corn husk, bran, bagasse, lignin or from other sources), microbial biomass, chitosan,[3,4] and eugenol.

Indonesia with abundant natural resources, rich with natural ingredient compounds are not fully utilized. As a major essential oil-producing countries in the world, one of which is the clove leaf oil, Indonesia meet almost half of the world's needs clove oil in the early eighties.[5] Eugenol clove oil contains about 80–90% by weight.[6] Eugenol can be used as a starting material for the synthesis of a compound because of three functional groups attached to it, namely allyl group, hydroxyl and methoxy. Eugenol derivatives have been shown to be used for the carrier liquid membrane with a selectivity that can be adjusted depending of functional groups are included.[7–10]

In addition eugenol with its three functional groups also has potential as a functional monomer for the selective adsorption processes such as Molecularly Imprinted Polymers (MIP). Polyeugenol was used as functional polymers with Polyethylene Glycol Diglycidyl Ether (PEGDE) for the synthesis of MIP Fe (IIP Fe),[11] MIP phenol and MIP vanillin[12] and MIP Glucose[13] and also transport membranes for selective ion Fe.[14–17] Selectivity IIP (Ionic Imprinted Polymer) Fe was proven to adsorb Fe (III) > Pb (II) > Cr (III) ≫ Cd (II). MIP phenol was proven that adsorbed more phenol than the vanillin that has structure similarly with phenol. Likewise, MIP Glucose is able to adsorb more glucose than fructose, a compound with the same molecular weight and only distinguished by functional groups only.

Adsorption mechanism is usually determined indirectly from the results of adsorption isotherms, desorption sequential and IR data. From the adsorption isotherms data and IR analysis we can assume that both IIP Fe and MIP phenol's selectivity because joint working mechanism between physical and chemical adsorption. But no research done to find out what the role of number of imprinted cavity towards selectivity of imprinted adsorption. This

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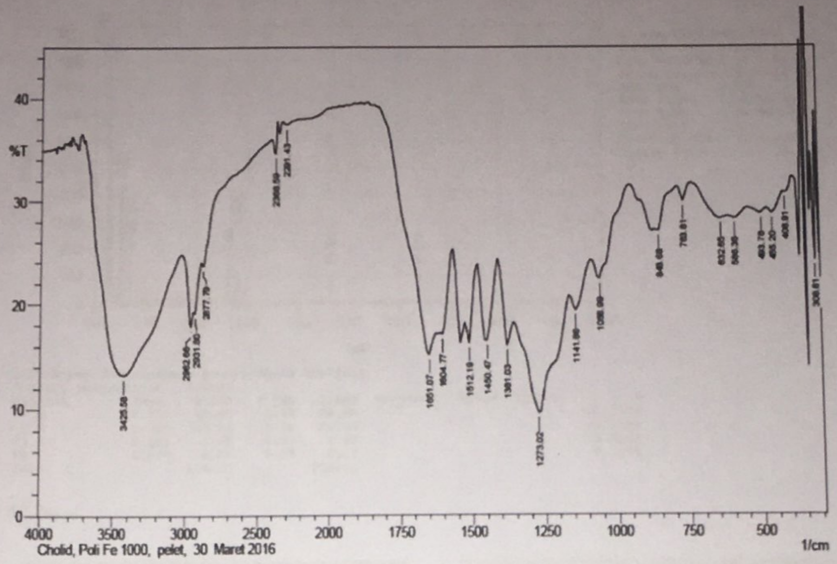


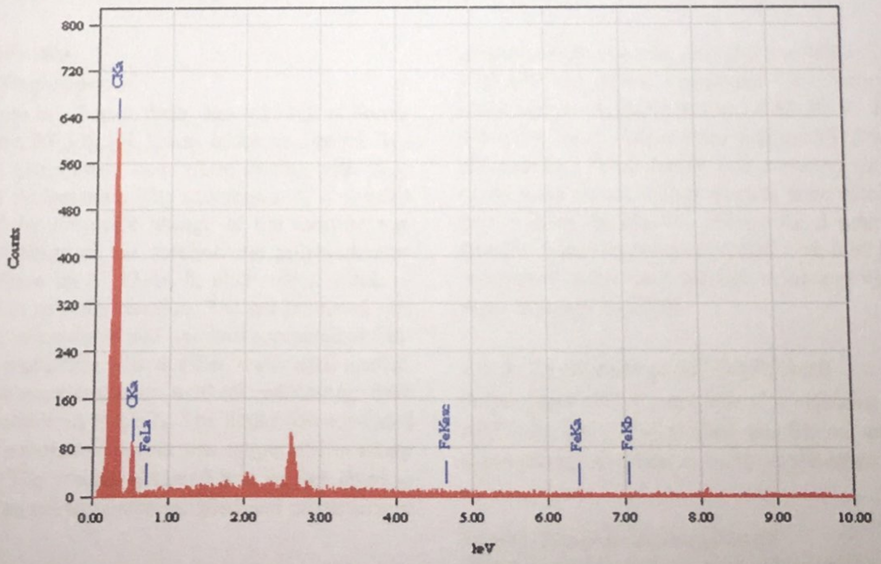
Fig. 1. FTIR spectra of polyeugenol after contacted to Fe(III) 1000 ppm.

study has aimed to determine the role of number of imprinted cavity towards selectivity of imprinted adsorption.

2. EXPERIMENTAL DETAILS

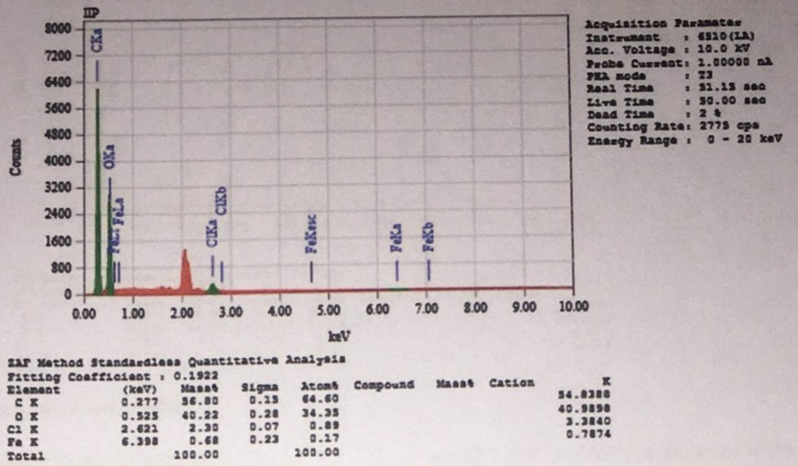
Materials. The materials were purchased from SIGMA-Aldrich, Eugenol, BF_3-diethylether while other reagents were purchased from E Merck, Germany, NaOH, chloroacetic acid, standard solution 1000 ppm $CrCl_3$, $PbCl_2$, $CdCl_2$. Chloroform, Methanol, Diethylether and demineralized water were purchased from Bratachem.

Instrumentation. The instruments used to characterization of polymer in this study were FTIR Spectrophotometer (Shimadzu 8201PC), analytical balance (Mettler Tolendo AB54-S), Atomic Absorption Spectrophotometer (Perkin Elmer), pH meter (HACH E C20), SEM EDX (JSM 6380 LA).



Element		(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
C K		0.277	98.13	0.23	99.68	C	98.13	0.00	98.6303	
O			0.42							
Fe K	*	6.398	1.45	3.72	0.32	FeO	1.87	24.00	1.3697	
Total			100.00		100.00		100.00	24.00		

Fig. 2. EDX spectra of polyeugenol after contacted to Fe(III) 1000 ppm and crosslink by PEGDE.



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Probe Current: 1.00000 nA
PHA mode      : T3
Real Time     : 51.15 sec
Live Time     : 50.00 sec
Dead Time     : 2 %
Counting Rate: 2775 cps
Energy Range :  0 - 20 keV
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1922
Element        (keV)   Mass%   Sigma   Atom%  Compound   Mass%  Cation         K
 C K           0.277   56.80    0.15   64.60                              54.8388
 O K           0.525   40.22    0.28   34.35                              40.9898
Cl K           2.621    2.30    0.07    0.89                               3.3840
Fe K           6.398    0.68    0.23    0.17                               0.7874
Total                 100.00          100.00
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Fig. 3. EDX spectra of IIP $Fe_{0.68}$.

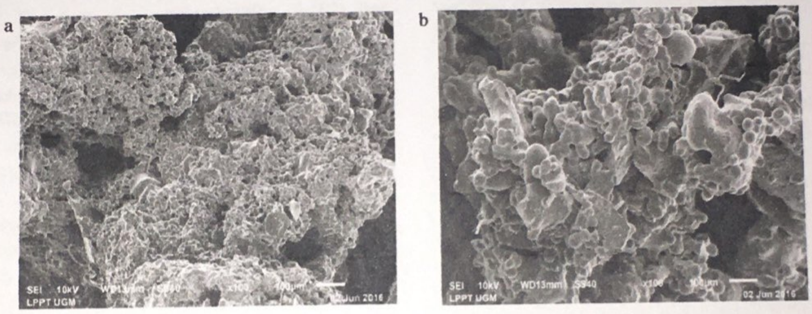


Fig. 4. SEM images of (a) Polyeugenol-Fe-PEGDE and (b) IIP Metal ion adsorption.

2.1. Polymer Synthesis

2.1.1. *Synthesis Polyeugenol*

Eugenol(5.8 g) was put in a 3-neck flask, then 0.25 mL of borontrifluoride diethylether, $BF_3O(C_2H_5)_2$ was added as catalyst. The addition was done 4 times every hour while stirring with magnetic stirrer at room temperature. The occurrence of a reaction can be characterized by the color change of the solution into red. After the last addition of the catalyst, the polymerization was allowed to continue up to 12–16 h, after which 1 mL of methanol was added to stop the reaction. The gel produced was dissolved in 100 mL chloroform and put into a separating funnel and then washed repeatedly with distilled water until neutral. The organic layer was transferred into a 50 mL erlenmeyer flask and added with 5 g anhydrous Na_2SO_4. The liquid was separated by decantation. Afterwards, the solvent was evaporated in rotary evaporator at 40 °C. The residue obtained was further dried in the desiccator, and was subsequently weighed and characterized using FT-IR.

2.1.2. *Synthesis Poly Eugenoxi Acetate*

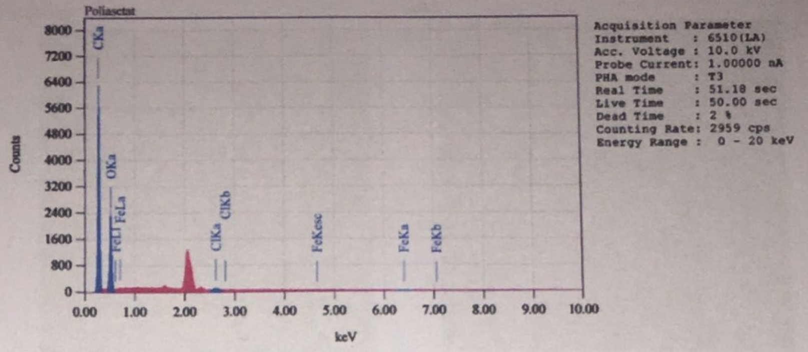
A total of 5 g of polyeugenol was added to the boiling flask size of 100 ml, and then added a solution of 17.5 mL NaOH 33% (33 g NaOH in 100 mL). Subsequently the mixture was stirred for approximately for 30 minutes, and added 12.5 mL of a 50% solution of chloroacetic acid (50 g in 100 mL water) slowly with a pipette and stirred constantly. The mixture was heated in a water bath with a temperature of 80–90 °C. Heating was carried out for 2 hours, then cooled and acidified with 6 M HCl until pH reached 1. Step further was extracted with diethylether for 3 times, each 50 mL. Ether extracts were combined and extracted with sodium bicarbonate 5%w/v for 3 times each 30 mL, and then the water layer was acidified with 6 M HCl to pH = 1. The subsequent steps were filtered, dried and weighted. The results were analyzed by FTIR.

2.1.3. *Synthesis of IIP-Fe-PEGDE*

Polyeugenol (0.5 g) was stirred at constant speed in 1000 ppm Fe(III) for 24 h. The product was filtered with a filter paper and subsequently air dried at room temperature. Polyeugenol-Fe(III)

Table I. **Selectivity IIP $Fe_{0.68}$PEGDE.**

	Selectivity	
Sample	IIP	NIP
Fe–Pb	0	1,34
Fe–Cd	0	0,82
Fe–Cr	0	0,76



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Acquisition Parameter
Instrument     : 6510(LA)
Acc. Voltage : 10.0 kV
Probe Current: 1.00000 nA
PHA mode       : T3
Real Time      : 51.18 sec
Live Time      : 50.00 sec
Dead Time      : 2 %
Counting Rate: 2959 cps
Energy Range :  0 - 20 keV
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2016
Element         (keV)    Mass%    Sigma    Atom%  Compound     Mass%  Cation          K
 C K            0.277    58.35     0.15    65.69                                59.6069
 O K            0.525    40.03     0.30    33.83                                38.4514
Cl K            2.621     0.59     0.05     0.23                                 0.8175
Fe K*           6.398     1.03     0.27     0.25                                 1.1242
Total                   100.00            100.00
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Fig. 7. EDX IIP Fe polyeugenoxi acetate-EDMA.

3. RESULTS AND DISCUSSION

3.1. Synthesis of IIP-Fe

The synthesis of IIP-Fe comprises of three steps after synthesis polyeugenol. The first step was uploading Fe(III) into polyeugenol followed by crosslinking using PEGDE (stage 2) and the release of Fe(III) using acid (step 3).[16] Polyeugenol synthesized was contacted with 1000 ppm Fe (III). The results are analyzed using FTIR. From FTIR spectrum (Fig. 1), it can be seen that spectrum of the bond O–Fe observed at 1038 cm^{-1}. The next step to synthesis IIP was crosslink by a cross linker (PEGDE) with 1:1 in comparison in mol. The final step was releasing Fe(III) trapped by acid and then characterized by EDX to know Fe(III) remained.

EDX analysis is used to determine the composition of polyeugenol-Fe-PEGDE and IIP especially content of Fe. Results of analysis of EDX analysis shows that the Fe content in the polyeugenol-Fe-PEGDE resin was 1.48% (Fig. 2), and reduced to 0.68% after treated with 0.5 M HCl (Fig. 3).

Analysis of SEM towards both polymer indicate that IIP has size cavity bigger than polyeugenol-Fe-PEGDE (Fig. 4). It can be happened because acid that releases Fe(III). To determine the selectivity of the adsorbent IIP, then performed a series of experiments used to adsorb Fe in binary solution contain Fe, Pb, Cd and Cr). 0.05 g of IIP was contacted to the solution with an each concentration of 10 ppm. The result can be seen from Table I.

Table II. Selectivity IIP Fe$_{0.11}$PEGDE at 10 ppm binary solution in each.

	Polyeugenol-EDMA			Polyeugenoxi acetate-EDMA		
Adsorbent	Fe/Cd	Fe/Pb	Fe/Cr	Fe/Cd	Fe/Pb	Fe/Cr
IIP	0	0	0	0	0.93	0.35
NIP	0	0.21	0.05	0	1.64	0.75

Table III. Selectivity IIP Fe$_{0.11}$PEGDE at 10 ppm binary solution in each.

	Selectivity		
Adsorbent	Fe(III)/Cd(II)	Fe(III)/Cr(III)	Fe(III)/Pb(II)
IIP	23.1	5.8	0.8
NIP	8.6	3.5	0.5

Table I show that selectivity NIP was better than IIP. This occurred because the content of Fe in polymer was still high and give contra productive.

3.2. Synthesis of Polyeugenoxy Acetate

Polieugenoksi acetate synthesis was carried out with the addition of NaOH and chloroacetic acid. Through a hydroxyl group, polyeugenol react with bases to form salts polyeugenolat. Proton in OH is easily separated because of the anion stabilized by the resonance of the benzene ring. NaOH is added created in order to produce excess salt as possible. Polyeugenol at sodium salt formed is reacted with chloroacetic acid to form acetic acid polieugenoksi.

Polyeugenoxi acetate which has been formed are purified by extraction using diethylether to remove impurities that are polar and extraction with NaHCO$_3$ to remove impurities that are nonpolar. Polieugenoksi acetic acid synthesized shaped colored precipitate blackish brown of 5 grams polyeugenol polieugenoksi obtained 4.56 g of acetic acid (yield 91.2%).

3.3. FTIR Analysis of the Synthesized Polieugenoxy Acetate

FTIR analysis results can be seen in Figure 5. In the FTIR spectra contained absorption bands 3448.72 cm^{-1} which indicate a hydroxyl group (O–H). Absorption bands in the range 3000–2800 cm^{-1} is a saturated carbon cluster (Csp^3-H), an absorption band 1604 and 1512 cm^{-1} are aromatic group (C=C), an absorption band 1419 cm^{-1} indicates a methylene group (–CH$_2$–) and an absorption band in the absorption band 864 cm^{-1} indicate

Table IV. Selectivity IIP Fe$_{0.11}$PEGDE at 50 ppm binary solution in each.

	Selectivity		
Adsorbent	Fe(III)/Cr(III)	Fe(III)/Cd(II)	Fe(III)/Pb(II)
IIP	5,50	21 × 10^5	10,60
NIP	1,50	116	12,70

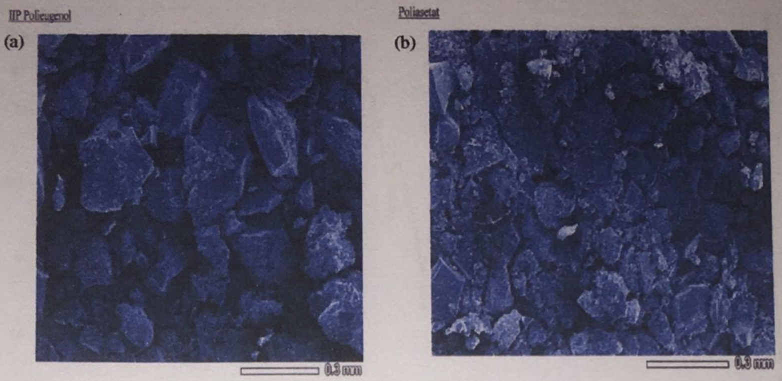
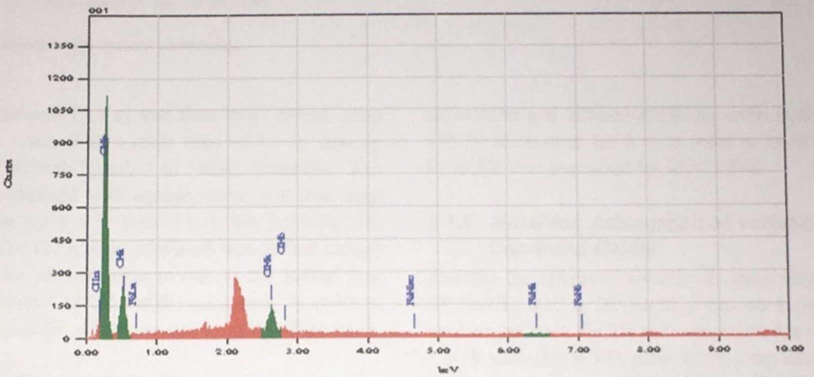


Fig. 8. SEM IIP polyeugenol-EDMA (a) and IIP polyeugenoxi acetate-EDMA (b).



Element		(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
C K		0.277	70.19	0.16	77.57			66.2404	
O K		0.525	24.79	0.89	20.57			22.9319	
Cl K		2.621	4.92	0.44	1.84			10.6440	
Fe K	*	6.398	0.11	2.50	0.03			0.1837	
Total			100.00		100.00				

Fig. 9. EDX IIP IIP $Fe_{0.11}$PEGDE.

that the substituted aromatic. Acid carbonyl group indicated by absorption at 1720 cm^{-1}.

Based on the absorption bands in FTIR spectra can be concluded that the compounds analyzed contained substituted aromatic nucleus, the OH group, methylene, aromatic, saturated carbon and carbonyl acid.

3.4. Synthesis IIP $Fe_{1.06}$ EDMA

Polyeugenol and polyeugenoxiacetic acid were crosslinked by ethylene glycol diglycidil ether with AIBN (2,2 azobis) as a initiator. Characterization polymerization of polyeugenol and polyeugenoxi acetate will be published in other articles. IIP Fe EDMA produced after polyeugenol-Fe_{1000}-EDMA was released by acid and measured Fe content in polymer using EDX.

As shown in both EDX (Figs. 6 and 7) Fe content in bulk polymer was still very high, more than 1%. It can be occurred because releasing by acid were not effective.

3.4.1. Metal Ion Adsorption

To determine the selectivity of the adsorbent IIP, 0.05 g of IIP was contacted to the solution with each concentration of 10 ppm. The result can be seen Table II. Table II shows that selectivity NIP was better than IIP. It was occurred because the content Fe in polymer (IIP) was still high (1.06% and 1.03%) and give contra productive.

3.4.2. Analysis of SEM

SEM images of two EDMA polymers shows that no pores in that. As shown in Figure 8. While that, IIP $Fe_{0.11}$ PEGDE was obtained by acidified poly-Fe-PEGDE using 1 M HNO_3. The result was check Fe content using EDX (Fig. 9). Figure 9 showed that % mass Fe was just 0.11%.

Metal ion adsorption.

4. CONCLUSION

This study shows that the amount of imprinted cavity determine selectivity. The amount of imprinted cavity can be showed by EDX measurements. When a content of remaining template Fe in polymer was high it can be produced a poor selective adsorption. And the otherwise, can be produced a rich selective. In conclusion the amount of imprinted cavity can determine selectivity.

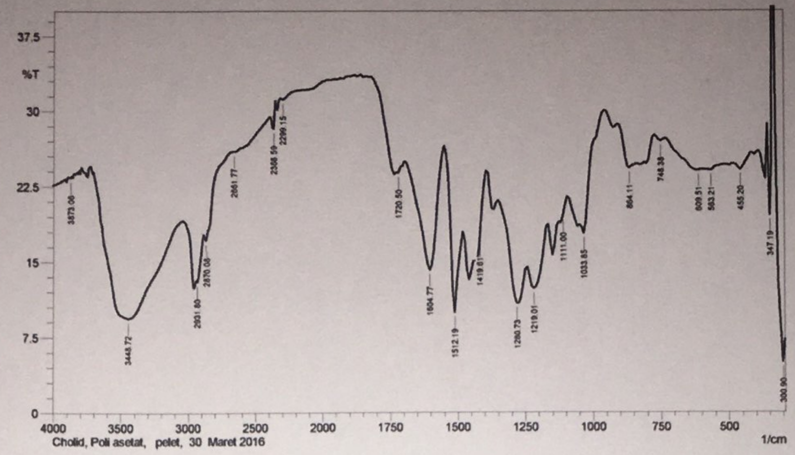


Fig. 5. FTIR spectra polieugenoksi acetate compounds.

produced from this process (0.3 g) was then cross linked using PEGDE as the cross linker with a mole ratio of 1:1 by heating for 15 min at 80–90 °C with 20 mL 1 M NaOH as catalyst. The product was then neutralized with aquademinaralised and dried at 115 °C in an oven for 6 h.% mass Fe in this polymer was measured by EDX. The 0.2 g resin produced was further treated with 10 mL of acid for several hours to release the Fe(III) ions and form the final product of IIP–Fe(III) adsorbent. In order to know how many % mass Fe in IIP was measured by SEM EDX.

2.1.4. Synthesis of IIP-Fe-EDMA

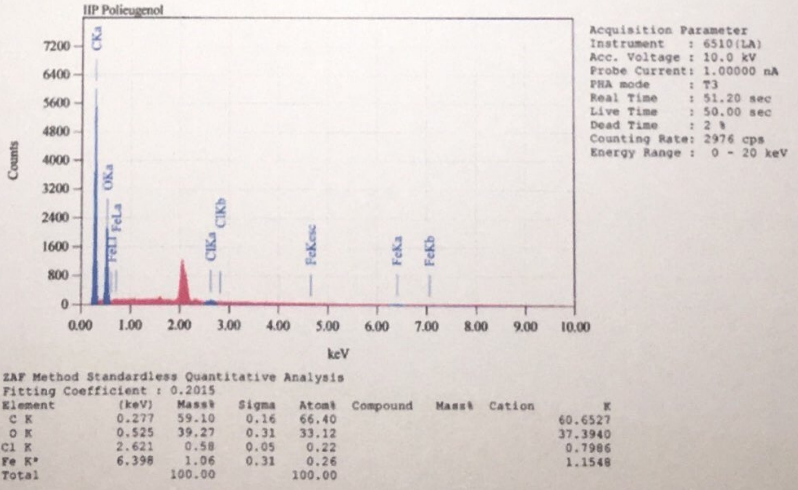
Polyeugenol (0.5 g) was stirred at constant speed in 1000 ppm Fe(III) for 24 h. The product was filtered with a filter paper and subsequently air dried at room temperature. Polyeugenol-Fe(III) produced from this process (0.3 g) was then cross linked using EDMA as the cross linker with 0.4 mL EDMA (5 mol), 1.67 mL chloroform and initiator AIBN as much as 0.48 mL and dried at 115 °C in an oven for 6 h. In order to know how many % mass Fe in IIP was measured by SEM EDX.

2.1.5. Metal ion Adsorption at Variation of Number of Imprinted Cavity

To study the effects of number of cavity imprinted on selectivity IIP-Fe(III), 0.05 g IIP-Fe(III)$_x$ was contacted to 10 mL binary solution between Fe(III) and competitor ion with 10 ppm in each. x is % mass Fe in IIP. After filtered the adsorbate was analysed by AAS to know metal ion concentration left.

2.1.6. Synthesis of NIP

NIP was synthesized using the same procedure as the IIP, but without using Fe (III) at the beginning. NIP was synthesized and used in the adsorption experiments as control.



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Real Time      : 51.20 sec
Live Time      : 50.00 sec
Dead Time      : 2 %
Counting Rate: 2976 cps
Energy Range :  0 - 20 keV
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2015
Element        (keV)   Mass%   Sigma   Atom%  Compound   Mass%  Cation          K
 C K           0.277   59.10    0.16   66.40                              60.6527
 O K           0.525   39.27    0.31   33.12                              37.3940
Cl K           2.621    0.58    0.05    0.22                               0.7986
Fe K*          6.398    1.06    0.31    0.26                               1.1548
Total                 100.00          100.00
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Fig. 6. EDX IIP Fe polyeugenol EDMA.

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