SYNTHESIS OF Fe IONIC-IMPRINTED POLYEUGENOL USING POLYETHYLENE GLYCOL DIGLYCIDILETHER AS CROSS-LINKING AGENT FOR SORPTION OF Fe(III)

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ABSTRACT

Fe-Ionic Imprinted Polymer (IIP) from polyeugenol as base polymer and polyethylene glycol diglycidyl ether (PEGDE) as cross-linking agent had been synthesized to adsorb Fe(III) from aqueous media. The non-imprinting material (NIP) and polyeugenol were used in the adsorption study as control. Synthesis work included polymerization, template uploading, crosslinking and template removal, optimized for different template ion upload pH and concentrations. The polymers were characterized by FTIR spectroscopy, XRD and SEM-EDX, followed by adsorption test to study the adsorption kinetics and isotherms for all adsorbents. Selective adsorption study of IIP was carried out using binary mixtures of Fe(III) and Cr(III), Pb(II), Cd(II). Experimental results showed that the optimum conditions for the synthesis was template upload pH of 3, Fe/polyeugenol ratio of 1 mg/g, while the optimum adsorption pH was 3. The adsorption mechanism of Fe(III) on all adsorbents was dominated by hydrogen bond formation. The adsorption kinetics followed the pseudo-second-order model while the equilibrium data was best explained by the Langmuir isotherm model. The adsorption capacity of Fe(III) on the IIP was 12.73 mg/g, higher than that of the other adsorbents. Results also show that IIP-Fe was more selective toward Fe than NIP by 2.69 (Cd), 1.66 (Cr) and 1.6 (Pb) fold, respectively.

Keywords: *polyeugenol; ionic imprinted Fe adsorbent; selective adsorption; PEGDE*

ABSTRAK

Dalam penelitian ini disintesis Ionik Imprinted Polimer Fe(III) menggunakan polieugenol sebagai polimer dasar dengan penautsilang PEGDE (Poli etilen Glikol diGlisidil Eter) untuk mengadsorpsi ion Fe(III) dari media air. Material non imprinting (NIP/tidak adanya Fe(III)) dan polieugenol juga digunakan dalam penelitian ini sebagai pembanding. Sintesis meliputi polimerisasi, upload templat, penautsilang dan pelepasan templat, variasi pH upload dan konsentrasi ion templat. Seluruh hasil polimer dikarakterisasi dengan spektrofotometer FTIR, difraksi sinar X (XRD), mikroskop elektron (SEM) dilanjutkan dengan uji adsorpsi untuk memperoleh kinetika adsorpsi dan isoterm adsorpsi. Selektifitas IIP Fe(III) diuji pada larutan campuran biner Fe(III) dengan Cr(III), Pb(II) dan Cd(II). Hasil penelitian menunjukkan kondisi optimal sintesis adalah pH upload 3, rasio Fe/polieugenol 1 mg/g dan optimum pH adsorpsi adalah 3. Mekanisme adsorpsi ion Fe(III) pada semua adsorben didominasi oleh ikatan hidrogen antara gugus OH dengan ion Fe(III). Adsorpsi ion Fe(III) pada semua adsorben mengikuti pseudo orde dua dan isoterm adsorpsi untuk semua adsorben lebih mengikuti Langmuir. Kapasitas adsorpsi ion Fe(III) pada material imprinting adalah 12,73 mg/g melebihi kapasitas adsorpsi material adsorben lain, IIP Fe lebih selektif daripada NIP sebesar 2,69 (Cd), 1,66 (Cr) dan 1.6 (Pb) kali.

Kata Kunci: *polieugenol; ionic imprinted polymer; adsorpsi selektif; PEGDE*

INTRODUCTION

The conventional methods for separating heavy metals especially iron from its solution usually include hydroxide precipitation, filtration, electrocoagulation, ion exchange techniques and adsorption. Adsorption is one of the physicochemical processes that occurs at the solid-phase and solid-gas interface, and has become an effective and economical method with great potential to be used for the separation, recovery as well as recycling of heavy metals from wastewater [1-3]. Due to the coexistence of other cations with dissolved

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Fe(III) in natural water, the separation as well as pre-concentration of Fe(III)before its determination needs to be done. Sorption based on sorbents having selectivity towards the target substance becomes very important and interesting. Therefore, it is very important to develop new sorbents that can be used for selective separation of trace amount of Fe(III) in ground water [2-4].

One of the latest techniques developed for the preparation of highly effective adsorbent is selective ion imprinting technique using ionic imprinted polymer (IIP), wherein the host molecule was prepared by consecutive addition and discharge of template molecules or ions. The polymer was then expected to be able to specifically recognize the target molecules or ions for adsorption. Today, heavy metal imprinted adsorbents used for the separation of selective heavy metal have attracted more attention, one of which is for the separation of Fe(III) [2-4]. The development of inexpensive adsorbent with high adsorption capacity had been the main goal of many studies. One interesting study is the use of biomaterials as adsorbent for heavy metal waste [5-6]. Biomaterials are very important because it is cheap, biodegradable and also biocompatible. They can be prepared from a number of different agricultural waste, corn husk, bagasse, rice husk, lignin, microbial biomass, chitosan [7-8] and eugenol.

Eugenol is one of native Indonesian natural products and has many functions, including for the separation of metal ions. Some examples are the conversion of eugenol into polyeugeniloxyacetate was used for the separation of heavy metal mixtures by solvent extraction method [9]; and its its conversion into eugenoxy acetate for the separation of Cr(III) using Bulk Liquid Membrane (BLM) method [10]. Eugenol polymer, polyeugenol, has been used as a BLM carrier with the order of Cr(III)»Fe(III)>Ni(II)»Zn>Cd (hard»medium>soft) [11]. In the present paper, we report the use of eugenol polymer chain, polyeugenol, as functional polymers for preparing Fe(III) imprinted adsorbents.

EXPERIMENTAL SECTION

Materials

The materials used in synthesis IIP included Eugenol, $BF_3O(C_2H_5)_2$ and PEGDE (Polyethyleneglycoldiglycidyl ether) were purchased from SIGMA-Aldrich, while other reagents were purchased from E Merck, Germany: anhydrate Na_2SO_4, fuming HNO_3, NaOH.$Fe(NO_3)_3$Methanol, chloroform, and demineralized water were purchased from Bratachem. Materials used in adsorption test included HCl 37%, Na_2EDTA, $Pb(NO_3)_2$ standard solution (1000 mg/L), $Fe(NO_3)_3$, $Cd(NO_3)_2$ were purchased from E Merck, Germany.

Instrumentation

The instruments used to characterization of IIP synthesized in this study were FTIR Spectrophotometer (Shimadzu 8201PC), XRD (Shimadzu XRD-8000), SEM EDX (JSM 6380 LA), and analytical balance (Mettler Tolendo AB54-S), DTA/TGA (BÄHR-Thermoanalyse GmbH - Simultaneous Thermal Analyzer STA 503), while the instruments used to analyze adsorption test was Atomic Absorption Spectrophotometer (Perkin Elmer).

Procedure

Synthesis of polymers
Polyeugenol. Eugenol (5.8 g) was put in a 3-neck flask, then 0.25 mL of boron trifluoride diethyl ether, $BF_3O(C_2H_5)_2$ 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 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 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.

Synthesis of IIP-Fe(III)
Polyeugenol (0.5 g) was stirred with (Fe(III) solution with different concentrations 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 crosslinked using PEGDE as the crosslinker 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 and dried at 115 °C in an oven for 6 h. The 0.2 gresin produced was further treated with 10 mL of eluent for several hours to release the Fe(III) ions and form the final product of IIP-Fe(III) adsorbent.

The performance of IIP synthesized for the adsorption of Fe(III) was optimized for two variables: the concentration as well as the upload pH of the template ions, whereas the following variables were kept constant: 50 mg adsorbent weight, 10 mL of the adsorbate solution, 10 mL of 50 mg/L Fe(III) for use in

the adsorption test, 22 mesh particle size, template removal using 1 M HNO_3 for 24 h, and crosslinker PEGDE/Fe(III) mole ratio of 1/1.

Variation of pH for template upload. To investigate the effects of pH during template upload, the following experimental conditions were used for adsorption: template ion concentration of 100 mg/L, pH was adjusted to 1-4 by adding HNO_3 and NaOH.

Variation of template ion concentrations. To study the effects of template ion concentration on IIP-Fe(III), adsorption experiments using Fe(III) solution were carried for IIP prepared by different initial concentrations of template: 25, 50, 100, 150, 200 and 300 mg/L. The experiments were carried out at pH 3 using 1 M HNO_3 as eluent.

Synthesis 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.

Synthesis NIP-HNO₃

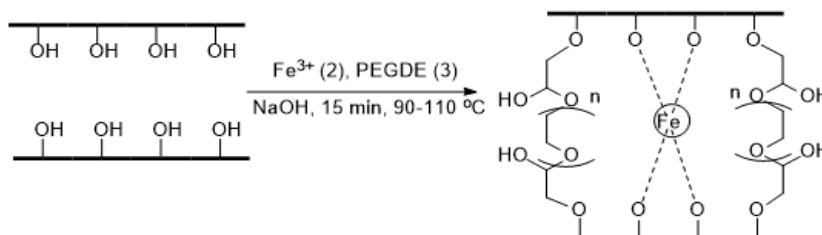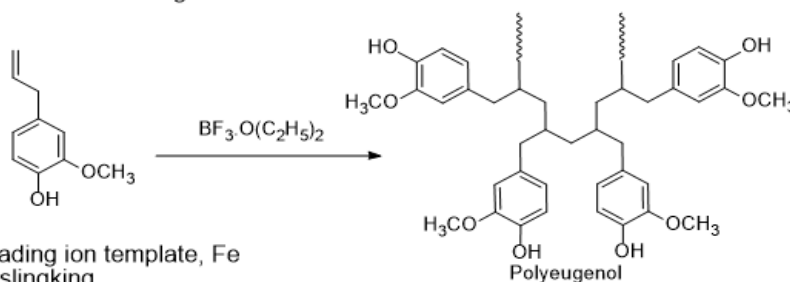The procedure for preparing NIP-HNO_3 was similar to that used to prepare NIP, however, at the end of the procedure, the polymer was soaked in 1 M HNO_3. NIP-HNO_3 was synthesized as the closest control (closest blank), and since IIP was synthesized using strong acid (HNO_3 1 M), NIP should also be exposed to acid.

Characterization. Characterization of IIP, NIP and also NIP HNO_3 adsorbents was done using FTIR, SEM, TGA/DTA.

Adsorption experiment. The adsorption properties studies were carried out using a batch method at the desired pH 1-4 for all of adsorbents, polyeugenol, IIP Fe, NIP and NIP HNO_3 of 50 mg was contacted with 10 mL of 50 mg/L Fe(III) solution for 24 h at a constant speed. The mixture was filtered with a fine filter paper and the concentration of Fe(III) in the filtrate was analyzed using Atomic Absorption Spectrometer (AAS). Variation of contact time (0-1440 min) was also done to determine the adsorption kinetics. The experiments were carried out for different Fe(III) concentrations (0-300 ppm) to determine the adsorption isotherms.

Adsorption mechanism of Fe(III) on adsorbents. Type of interaction between Fe(III) and the adsorbent was elucidated by performing sequential desorption of adsorbed Fe(III) in water, KNO_3 (0.1 M), HNO_3 (0.1 M) and 0.1 M Na_2EDTA, respectively [12].
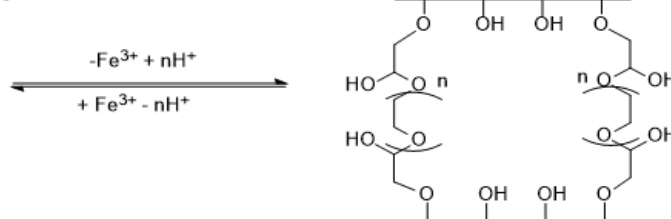

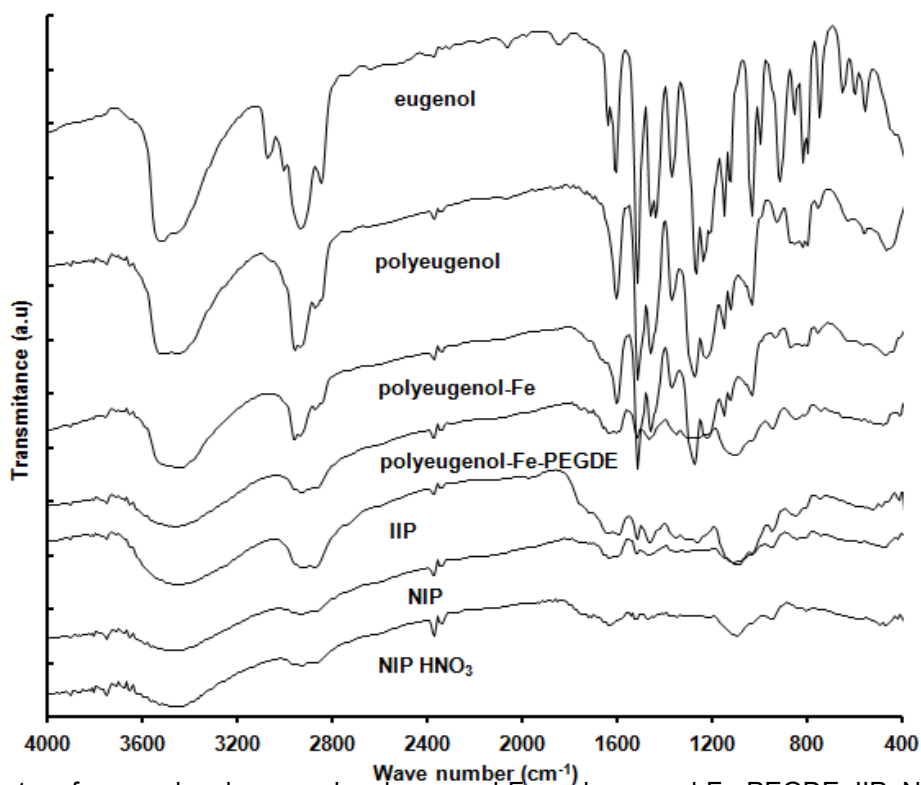**Fig 1.** Schematic synthesis IIP Fe

Fig 2. FTIR spectra of eugenol, polyeugenol, polyeugenol-Fe, polyeugenol-Fe-PEGDE, IIP, NIP, and NIP-HNO$_3$

Adsorption selectivity test. The study of adsorption selectivity is carried out by adding 0.05 g of adsorbent into each of 10 mL binary-solutions containing Fe(III)/Cd(II), Fe(III)/Cr(III), Fe(III)/Pb(II) using concentration of 10 mg/L for each ion. The adsorption experiments were carried out with batch system using a magnetic stirrer at pH 3.This study was carried out for both IIP and NIP-HNO$_3$.

RESULT AND DISCUSSION

Synthesis IIP Fe

The synthesis of IIP-Fe comprises of four stages, as can be seen in Fig. 1, starting with the polymerization of eugenol (stage 1). Eugenol was polymerized using BF$_3$ diethyl ether as catalyst, and resulted polyeugenol was characterized by FT-IR and NMR. From FTIR spectrum (Fig. 2), it can be seen that the eugenol vinyl group observed at 995.27 and 1635 cm^{-1} of allyl group can no longer be observed in the polyeugenol spectrum.

To determine how many *n* of eugenol molecules exist in the polyeugenol chain, gel permeation chromatography (GPC) analysis was done, which shows that the average Mr of polyeugenol is 1876, or about 11 times the monomer (Mr of eugenol is 164).

The next step was uploading Fe(III) into polyeugenol (stage 2). This was done by uploading

Fe(III) into the polyeugenol chain, followed by crosslinking using PEGDE (stage 3) and the release of Fe(III) using HNO$_3$ (stage 4). All of these stages can be characterized by IR as shown in Fig. 2. In the Fig. 2, the intensity of the absorption band of -OH in polyeugenol decreased as Fe(III) was loaded (Polyeugenol-Fe) and decreased further when it is "locked" with PEGDE (Polyeugenol-Fe-PEGDE). However, the intensity of this absorption band increased again after Polyeugenol-Fe-PEGDE polymer was discharged of its Fe with acid to produce IIP. The spectrum of IIP is sharper than that of NIP and NIP-HNO$_3$, which demonstrates the role of OH in the IIP.

TGA analysis of polyeugenol, polyeugenol-PEGDE, polyeugenol-PEGDE+acid can be seen in Fig. 3. As shown in Fig. 3, polyeugenol experienced a weight loss of 90%, while polyeugenol-PEGDE (NIP) and polyeugenol-PEGDE+acid (NIP HNO$_3$) experienced weight loss of 80%, while IIP almost 100%. At 100 °C, there is a weight loss of about 5% in polyeugenol and polyeugenol-PEGDE+acid due to the release of water [13], the absence of weight loss in the polyeugenol-PEGDE may be due to its solidity. The next weight loss of 60-80% polymer observed at 200-400 °C can be correlated to the break/depolymerization of the benzene rings present
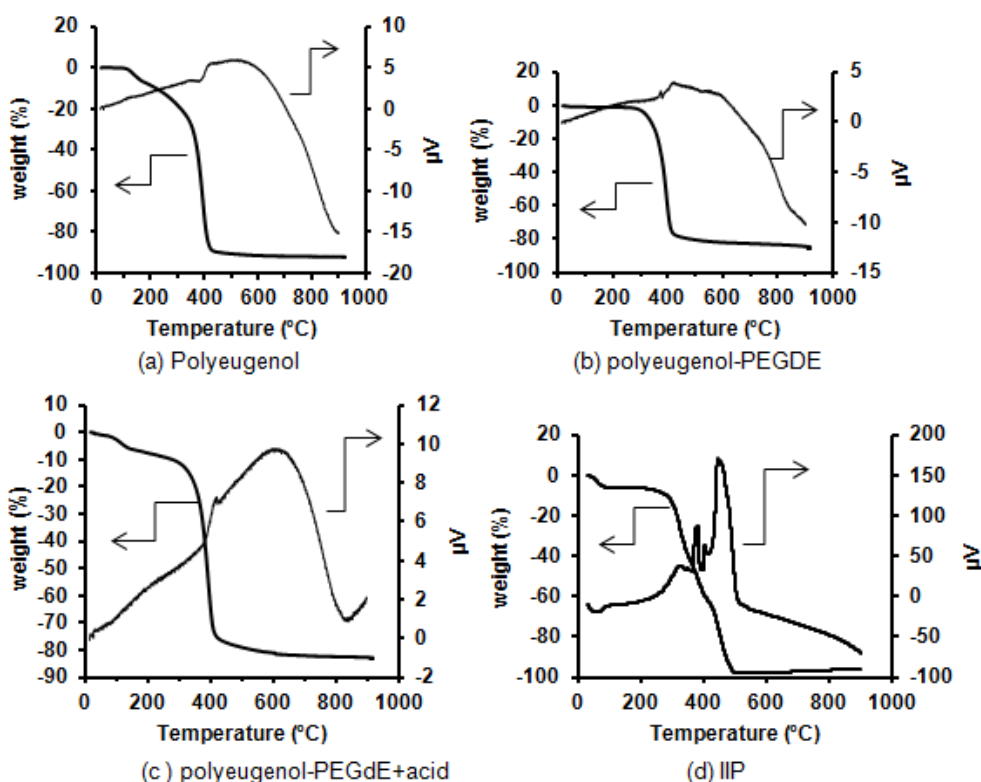
Fig 3. TGA-DTA curves of polyeugenol, polyeugenol-PEGDE (NIP), polyeugenol-PEGDE+acid (NIP HNO$_3$) and IIP
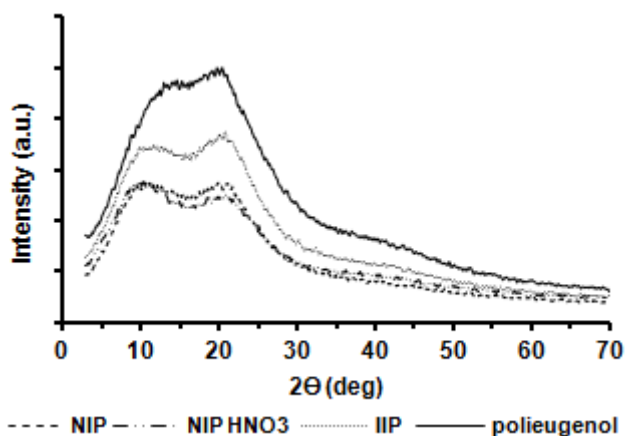

Fig 4. XRD patterns for polyeugenol, IIP, NIP HNO$_3$, and NIP

in the polymer chain. Next step weight change are 5% (polyeugenol) and 11% (poly-PEGDE and poly-PEGDE+acid). This change might be associated with the loss of -CO and -OCH$_3$. The smaller weight lost for polyeugenols compared to that of poly-PEGDE and poly-PEGDE+acid is due to fewer numbers of both groups in polyeugenol. From DTA analysis in Fig. 3, it can be seen that the three polymers have the same characteristics in that their degradations occurred as exothermic processes. Polyeugenol that was crosslinked by PEGDE

has higher degradation temperature than polyeugenol because they are more chemical stabile than polyeugenol.

IIP initially showed a similar phenomenon, wherein the weight loss at temperature range of 60-100 degrees occurred due to the loss of water, and at 200-400 degrees due to depolymerization of benzene rings. The deviation in the degradation pattern occurred at the temperature range of 400-500, which shows final weight loss as no further weight loss was observed after that. It is possible that the simultaneous degradation of remaining polyeugenol chain happened due to the imprinting process which produced many cavities inside the adsorbent. Hence, up to the temperature of 500 degrees, there were almost no compounds that are not degraded. This is in contrast with other polymers (polyeugenol 10%, NIP and NIP HNO$_3$ 15%). The result is confirmed by the DTA data, displaying exothermic reactions at the temperature of 400 and 500 degrees which indicate rapid degradation due to the cavity simultaneously generated during the imprinting process.

Fig. 4 shows the result of XRD analysis of polyeugenol, IIP, NIP-HNO$_3$ and NIP. Polyeugenol has better crystallinity than the IIP, NIP and NIP-HNO$_3$. Fig. 5 also shows that crosslinking with PEGDE seems to reduce the crystallinity of polyeugenol. The peak at 12.4° for polyeugenol shifted to lower range of 9.3°,
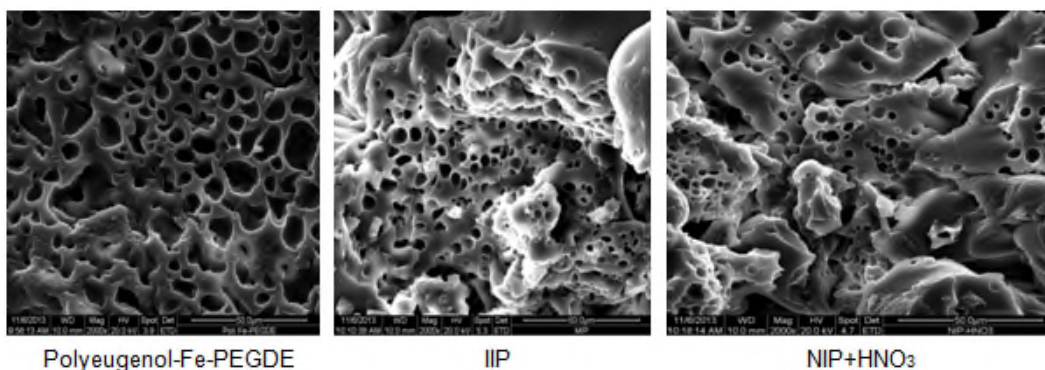
Polyeugenol-Fe-PEGDE   IIP   NIP+HNO₃

Fig 5. SEM of IIP, poly-Fe-PEGDE, and NIP-HNO$_3$ at 2000x magnification

Table 1. Variation of pH up load of template ion

pH	% adsorption during IIP synthesis	% Fe removed during IIP synthesis	% adsorption of Fe(III)
1	7.77	100.00	1.54
2	66.40	24.53	6.94
3	86.34	40.36	74.07
4	98.56	21.17	99.04

which indicates that the distance between polyeugenol chains increased [14]. NIP and NIP-HNO$_3$ both have similar crystallinity. This indicates that the addition of 1 M HNO$_3$ into the NIP does not affect the crystallinity of the NIP.

The results of SEM analysis are displayed in Fig. 5, which shows that when compared to Polyeugenol-Fe-PEGDE, the pore size of IIP is smaller, which might be correlated to the presence of loaded Fe(III) in Polyeugenol-Fe-PEGDE, as opposed to the relatively Fe-free pores in IIP. When compared to NIP-HNO$_3$, the pores in IIP are more uniformed and abundant, which is probably because the uploaded Fe was already released from the polymer matrices.

EDX analysis is used to determine the composition of poly-Fe-PEGDE and IIP. Results of analysis of EDX analysis shows that the Fe content in the poly-Fe-PEGDE resin was 1.58%, and was reduced to 0.14% after it was treated with HNO$_3$. This means that the acid was able to discharge as much as 91% of Fe content.

Effect of pH upload of template

pH plays a very important role in the synthesis of IIP, particularly in the binding/uploading of template ions (Fe(III)) on polyeugenol, which in turn will affect the % adsorption of Fe(III). This is because the more template ions (Fe) being uploaded, the greater the possibility of the formation of specific holes in the polymer. As shown in Table 1 the greater the pH, the more % Fe are uploaded, and the greater the % adsorption of Fe(III).

Table 1 shows uploading and adsorption percentage increases with the increase of pH, and it reaches a maximum at pH 4. This might be attributed to the changes in ionic state of acidic hydroxyl functional group and C-O of the adsorbent [15-16]. Above pH 4, white precipitate began to appear. At pH 4, Fe(III) formed yellowish colloid that can be filtered using filter paper, the colloid usually present until a maximum pH of 3.7 [17]. At pH solution lower than pKa, functional groups will be protonated, causing the adsorption percentage to decrease. At acidic condition, Fe(III) will exist as $[Fe(OH)]^{2+}$, $[Fe(OH)_2]^+$ and $[Fe_2(OH)_2]^{4+}$[18], and none of these ions are able to penetrate the resin pores of IIP, so that for the synthesized of IIP Fe(III) especially uploading of ion template Fe(III) in subsequent experiments were carried out at pH 3.

At pH 1 % Fe removed was the biggest because the concentration of Fe (III) which was uploaded was smallest and contrary with pH 3 and pH 4.

The effects of template ion concentration

As can be seen from Fig. 6, the saturated adsorption amount of IIP increases with the increase of Fe(III) concentration. This was due to increasing amount of imprinted cavities in IIP when Fe(III) was increased [20-21]. At Fe(III) concentration higher than 50 mg/L, the saturated adsorption amount of IIP slightly reduced. This indicates at 50 mg/L (ratio Fe/polyeugenol was 1 mg/g), the maximum amount of imprinted cavities has already been formed during the imprinting process, so that the imprinted cavities decreased despite the increase of template ion concentration. The decrease in the saturated adsorption amount of IIP might happen due to the "entrapment" of Fe(III) ions in the adsorbent so that they cannot be removed when treated with HNO$_3$. Therefore, template ion concentration of 50 mg/L was used for the following experiments.

Adsorption Experiments

Effect of pH on the adsorption of Fe(III)

The pH of adsorbate solution also plays an important role in the speciation of Fe ions in solution to allow for maximum adsorption by the adsorbent. The result can be seen in the Fig. 7. Fig. 7 shows that the higher the pH, the greater the adsorption percentage of Polyeugenol, NIP, and NIP-HNO₃ materials towards Fe(III).

The explanation of the effect of pH on the adsorption is the same as the explanation of the effect of pH on the synthesis of the IIP, so that for the subsequent experiments were carried out at pH 3.

Adsorption Kinetics

The adsorption kinetics of Fe(III) by IIP, NIP, NIP-HNO₃, and polyeugenol were studied at various contact time and optimum pH of 3. Initially, as shown in Fig. 8, the adsorption of Fe(III) (mg of Fe(III)/g of adsorbent) increased sharply because most of the active sites in the adsorbent were still vacant and unfilled by Fe(III). The adsorption equilibrium of IIP, NIP, NIP-HNO₃ were reached after 180 min (3 h) of stirring, since longer stirring time did not increase the adsorption. For polyeugenol however, the adsorption equilibrium was not reached until after 1400 min.

The adsorption kinetics was studied by data modeling into a pseudo first order (Lagergren) and pseudo second order. The pseudo first-order kinetics equation is formulated as: [23-24]

$$\ln\left(q_e - q_t\right) = \ln\left(q_e\right) - k_1\, t$$

where q_e and q_t is the adsorption capacity at equilibrium and at time t (mmol g^{-1}) and k_1 is the pseudo first-order rate constants 1 (min^{-1}).
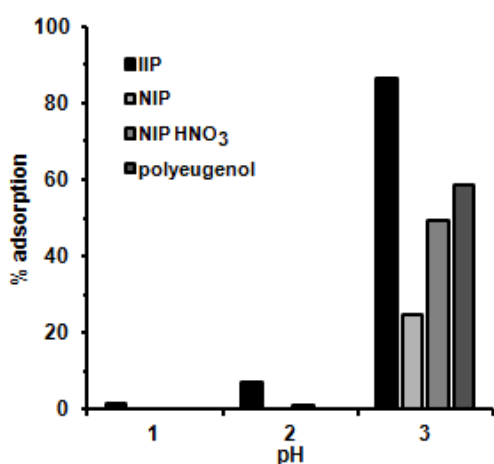
The pseudo second order kinetics equation is formulated as follow:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\, t \qquad (1)$$

where k_2 (g mmol^{-1} min^{-1}) is the pseudo second order rate constant.

Table 2 shows the adsorption kinetics parameters for Fe(III) by IIP, NIP, NIP-HNO₃ and polyeugenol. All adsorbents give very low correlation coefficient for $\ln(q_e-q_t)$ vs. t plot of pseudo-first-order equation, while the plot of t/qt vs. t showed very high correlation coefficient (> 0.974). The main assumption is that the rate determining step involves chemical adsorption involving valence force through the sharing or exchange of electrons between adsorbent and the trivalent metal ions. The rate constants (k_2) was the highest for IIP. The greater quantity of pores in IIP enables Fe(III) to reach the active sites more quickly and subsequently bound to the active groups of the adsorbent [25].
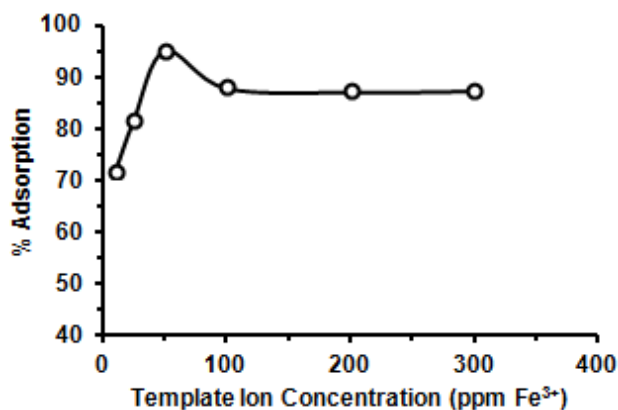

Fig 6. Adsorption trends of Fe^{3+} in various concentrations of Fe^{3+}

Fig 7. The effects of pH on the % adsorption of Fe(III) by polyeugenol, NIP, NIP-HNO₃, and IIP
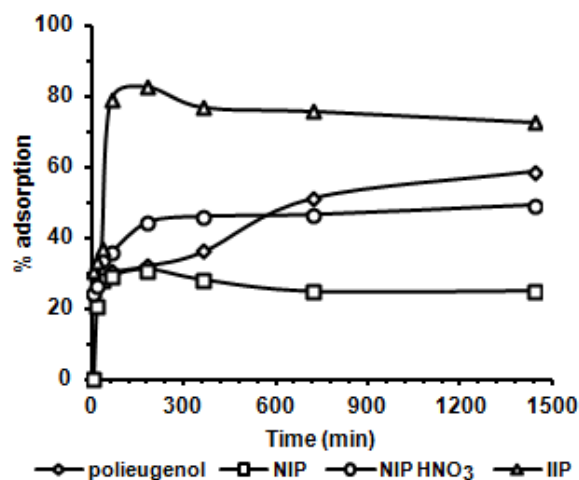

Fig 8. % adsorption of IIP and NIP resins at different contact time

Table 2. Kinetics parameters for the adsorption of Fe(III) by IIP, NIP, NIP HNO$_3$ and polyeugenol

Adsorbent	Parameter					
	Pseudo-first order			Pseudo-second order		
	q_{e1} (mg/g)	k_1 (L/min)	R^2	q_{e2} (mg/g)	k_2 (g/mg min)	R^2
IIP	0.721	0.0004	0.173	7.35	0.1706	0.998
NIP	0.774	0.000006	0.006	2.45	-0.0330	0.998
NIP HNO$_3$	1.353	0.0010	0.934	4.98	0.0073	0.998
polyeugenol	3.004	0.0006	0.819	5.75	0.0022	0.974

Table 3. Langmuir and Freundlich isotherm constants for Fe(III) ions adsorption at solution pH value of 3 and 25 °C at 3 h contact time

Adsorbent	Langmuir isotherm parameters					Freundlich isotherm parameters		
	b	K		R^2	ΔG	KF	n	R^2
	(mg/g)	(L/mg)	(L/mol)x10^4		(kJ/mol)	(mg/g)		
IIP	12.73	0.1362	0.7626	0.976	-22.1	1.979	6.579	0.458
NIP	8.63	0.0156	0.0873	0.910	-16.8	1.327	3.584	0.651
NIP HNO$_3$	9.33	0.1059	0.5929	0.973	-21.5	1.576	7.042	0.282
polyeugenol	10.37	0.0289	0.1622	0.967	-18.3	1.145	0.1351	0.583

Adsorption Isotherms

The adsorption isotherms can be seen in Table 3. In a two-state system comprising of an adsorbent and a solution, adsorption will cause the solute to move from the solution onto the surface of adsorbents and the remaining solutes in the solution are in a dynamic equilibrium with the solutes present on the adsorbent surface. Plotting the concentration of the solute in the adsorbent q_e (mg/g) as a function of solute concentration in the solution C_e (mg/L) at equilibrium will produce the adsorption isotherm graph. The adsorption isotherm can be used to obtain information about the interaction between adsorbate molecules and the adsorbent. To understand and clarify the adsorption process, Langmuir and Freundlich adsorption model were used in this study.

Langmuir isotherm equation is often used as an adsorption model on a homogeneous surface wherein the interaction between adsorbed molecules is negligible, as shown in the following equation: [5]

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \qquad (2)$$

where q_e is the amount of adsorption at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), q_{max} is the adsorption capacity (mg/g) and b is the adsorption intensity known as the Langmuir coefficient (mg/L) which is equivalent to the binding site affinity.

Freundlich adsorption isotherm equation is an equation based on heterogeneous surface which suggests that the binding sites are not equivalent and free, as illustrated by the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (3)$$

Where K_F and $1/n$ are constants related to adsorption capacity and adsorption intensity.

As can be seen in Table 3, IIP, NIP, NIP-HNO$_3$ and polyeugenol have the same adsorption properties following Langmuir adsorption models. This means that the adsorption occurs on anhomogeneous surface. Table 3 also shows that IIP has the highest adsorption capacity than the others (12.73 mg/g); with NIP, NIP-HNO$_3$ and polyeugenol having adsorption capacities of 8.63, 9.33 and 10.37 mg/g, respectively. The amount of pores that is suitable for Fe(III) enables IIP to have the highest adsorption capacity.

The adsorption energy equation can be written as follows:

$$E_{ads} = -\Delta G° = RT \ln K \qquad (4)$$

where R is the universal gas constant (8.314 J K^{-1}mol^{-1}), T is the temperature in Kelvin(K)and ΔG° is Gibbs free energy. Free energy for physical adsorption (physisorption) is generally below -20 kJ/mol, the combination of physisorption and chemical adsorption (chemisorption) is in the range of -20 to -80 kJ/mol, while chemisorption has values ranges from -80 to -400 kJ/mol [9]. From Table 3, it can be seen that ΔG° values for IIP, NIP-HNO$_3$ are -22.1 and -21.5 kJ/mol, respectively, while the others have values under -20 kJ/mol. This suggests that the adsorption of Fe(III) on both IIP and NIP-HNO$_3$ is a combination of physical and chemical adsorption, while the adsorption on NIP and polyeugenol can be classified as physical adsorption. Table 3 also shows that the imprinting process increases the interaction strength between Fe(III) and the adsorbent.
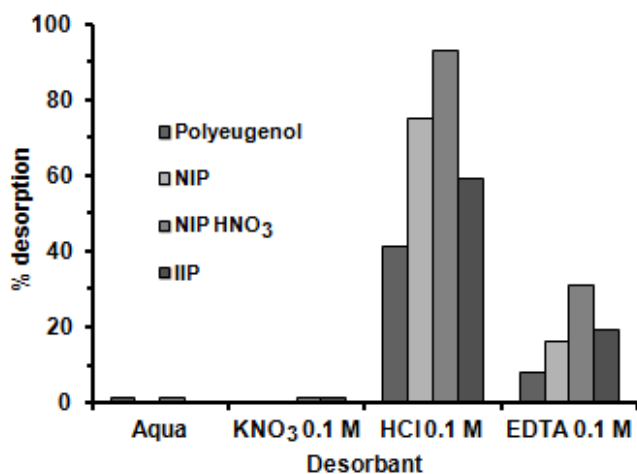
Fig 9. Types of interaction in the adsorption of Fe(III) by polyeugenol, NIP, NIP HNO$_3$ and IIP

Fig 10. Selectivity coefficient of NIP HNO$_3$ and IIP towards Fe(III)

Adsorption Mechanism of Fe(III) on Polyeugenol, NIP, NIP-HNO$_3$ and IIP

To determine the mechanisms involved in the adsorption process of Fe(III) on polyeugenol, NIP, NIP-HNO$_3$ and IIP, a series of desorption experiments were carried out sequentially using the adsorbents that have been previously used for the adsorption of Fe(III) from its solution. The sequential desorption will be able to dissolve the metal ions that have been previously adsorbed, both physically (entrapment mechanism) and chemically (ion exchange mechanism, hydrogen bonding formation and complex formation) [12].

Solvents used in this sequential desorption process distilled water for the entrapment mechanism, 0.1 M KNO$_3$ ion exchange mechanism, 0.1 M HCl for hydrogen bond formation mechanism and Na$_2$EDTA for complex formation mechanism.

It can be seen in Fig. 9 that the adsorption process in all adsorbents is dominated by the formation of hydrogen bond as well as complex formation.

Based on Fig. 9, it can be seen that adsorption mechanism of Fe(III) on the adsorbents (polyeugenol, NIP, NIP-HNO$_3$ and IIP) does not occur in physically, but chemically. The adsorption mechanism of Fe(III) on polyeugenol, NIP, NIP-HNO$_3$ and IIP generally occurs through the formation of hydrogen bonds mechanism and complex formation between adsorbates and the active sites of the adsorbents. This can be seen from the high percentage of Fe(III) being desorbed when dissolved in 0.1 M HCl and 0.1 M Na$_2$EDTA. However, when IIP-Fe compared to the blanks (NIP-HNO$_3$), it can be seen that there is significant difference between the two, probably due to the contributions of specific pores in IIP-Fe as a direct result of the imprinting process.
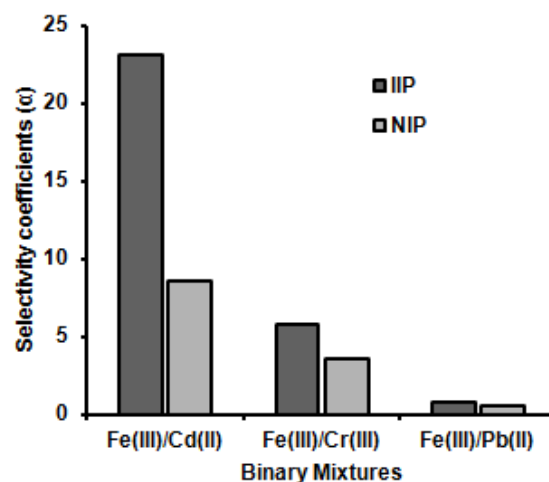
Adsorption Selectivity

The coefficient of selectivity (α) is determined by using the following equation:[26]

$$\alpha_{(M1/M2)} = D_{M1}/D_{M2}$$

where the distribution ratio $D = Q/C_e$; Q is the adsorption capacity (mmol/g), C_e is the adsorbate concentration in the aqueous phase at equilibrium (mmol/L), and α is the selectivity coefficient.

It can be seen from Fig. 10 that the selectivity of IIP towards Fe(III) is better than HNO$_3$-NIP, with the following selectivity sequence: Cd^{2+}(2.69 fold) > Cr^{3+}(1.66 fold) > Pb^{2+}(1.6 fold) or medium > hard > soft. The selectivity for Fe(III)/Cd(II) mixture is the highest because Fe(III) can be classified as hard acid, while Cd^{2+} is a soft acid. The active sites containing hydroxyl groups can also be classified as hard base, thus it is understandable that the selectivity towards Fe(III)/Cd(II) is higher than towards Fe(III)/Cr(III). The adsorption selectivity towards Fe(III)/Pb(II) is the smallest, probably because there are more hydroxyl groups in NIP-HNO$_3$ than in IIP, so that NIP-HNO$_3$ was able to bind with Pb(II) [25].

CONCLUSION

In the present study, IIP-Fe had been synthesized using Fe(III) as a template ion, eugenol derivatives (polyeugenol) as polymer and PEGDE (Polyethylene glycol diethyl ether) as a cross-link agent. The adsorption capacity of IIP-Fe towards Fe(III) is higher than that of polyeugenol, NIP and NIP-HNO$_3$. The interaction between Fe(III) and Fe-IIP is dominated by the formation of hydrogen bonds. The adsorption process is best described using the pseudo second-order kinetics model and Langmuir isotherm. The selectivity of IIP-Fe towards Fe(III) ions were compared

to that of NIP-HNO$_3$ using Cd(II), Cr (III) and Pb(II) as competitive ions, and it was obtained that IIP-Fe is more selective than NIP-HNO$_3$.

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