Adsorption of Fe (III) metal ion by ionic imprinted polymer (IIP) method with poly (ethylene glycol) diglycidyl ether (PEGDE) as a crosslinker

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Abstract. The adsorption of Fe (III) metal ions in water media using the ionic imprinted polymer has been carried out with a polyeugenol base polymer and poly(ethylene glycol) diglycidyl ether (PEGDE) as the crosslinking agent. The adsorbent is in the form of Ionic Imprinted Polymer Fe (IIP-Fe), and Non-Imprinted Polymer (NIP) was also used as a comparison. The polymer results are characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX), and Fourier Transform Infrared (FTIR). The adsorption test was performed to obtain the adsorption kinetics by varying the contact time. Meanwhile, adsorption isotherm was performed by varying the concentration of adsorbate, and adsorption selectivity between binary metal ions of Fe(III)/Cr(III), F(III)/Zn(II), and Fe(III)/Ag(I). Also, the adsorption mechanism was studied using different solvents such as HCl, Aquades, KNO₃, and Na₂EDTA. The results of the filtrate in the adsorption test were characterized using AAS. The results showed the optimum time in kinetics was 60 minutes, the adsorption isotherm followed the Langmuir model with a large adsorption capacity of 23.640 mg/g on IIP-Fe and 17.636 mg/g on NIP. Adsorption selectivity towards Fe (III) metal ions in binary metal ions shows results in the order of Fe(III)/Zn(II)>Fe(III)/Cr(II)>Fe(III)/Ag(I), while the adsorption mechanism was dominated by hydrogen bonds.

1. Introduction
High levels of Fe (III) metal ions in waters could cause various health problems such as intestinal damage, Alzheimers, and Parkinsons [1]. One of the methods used to reduce levels of Fe (III) metal ions was through adsorption that is based on the adsorption of the substance (molecule or ion) (adsorbate) on the surface of the adsorbent [2]. However, the adsorption method has the disadvantage of being less selective of the target compound/ion. So, this research aims to enhance the effectiveness by using the Ionic Imprinted Polymer (IIP).

The working principle of IIP is the imprinted target ion in the adsorbent, where the polymer contains receptor sites that are specific to the target ion, the advantages of the IIP method are its high selectivity and easy preparation. Eugenol is a compound that has three active groups, namely allyl, hydroxy, and methoxy. Through the allyl group, eugenol can be polymerized into polyeugenol, and the hydroxyl group in eugenol can bind to metal ions, utilizing the eugenol as an ion-imprinted polymer [3]. The crosslinking agent used in this study was poly (ethylene glycol) diglycidyl ether (PEGDE) and the adsorbent pH was 3. In this study, PEGDE is used as the crosslinking agent, and the
2. Experimental

2.1. Equipment and materials
The tools used in this research are laboratory glasses equipment, reflux, filter paper, analytical balance, pH meter, UV – Vis Spectrophotometry (Shimadzu), AAS (Perkin Elmer), FTIR (Nicolette Avatar 360), and SEM (JSM-6510). The materials used are eugenol p.a (Sigma Aldrich), Na$_2$SO$_4$ (Merck), Concentrated HCl (Merck), NaOH p.a (Merck), Chloroform p.a (Merck), Methanol (Merck), KSCN (Merck), and Fe(NO$_3$)$_3$ (Merck).

2.2. Preparation method

2.2.1. Preparation method. Solid NaOH as much as 33 g was dissolved into 100 mL aquadest and mixed until homogenous. The solution was then moved into a bottle container as a stock solution. 8.33 mL HCl 12 M was dissolved into 100 mL aquadest, the mixture was then stored in a bottle container as a stock solution. KSCN 1 M solution was done by dissolving 24.3 g KSCN in 250 mL aquadest, the mixture was mixed inside the volumetric flask and then stored in a bottle container as a stock solution.

2.2.2. Synthesis of polyeugenol. Using a three-neck flask, 5.8 g of eugenol was added with 0.25 mL BF$_3$-diethyl ether every hour for 4 hours, stirred for 12-16 hours, and then 1 mL methanol was added. The formed gel was dissolved with chloroform and separated using a separating funnel. Aquadest was then added into the separating funnel continuously until it reached a neutral pH, decanted, and added with anhydrous Na$_2$SO$_4$ to remove the aquadest completely. Afterward, the gel was dried at room temperature and weighed. The product was then characterized by FTIR.

2.2.3. Synthesis of ionic imprinted polymer (IIP). Polyeugenol as much as 0.5 gram was added with 10 mL of Fe(III) 50 ppm at pH 3 and stirred for 24 hours. Then, it was filtered, dried, and weighed. The obtained result was then added with 200 mL of 1 M NaOH and 2.88 g of 3 mol PEGDE (Mw 500), then it was stirred at 80-90°C for 15 minutes. Afterward, the results were neutralized and furnaced for 6 hours at 110°C. The formed adsorbent was then washed with HCl 0.5 M to detach the Fe (III) metal ion. The filtrate was characterized by UV-Vis spectrophotometry using KSCN as a complexing agent.

2.2.4. Synthesis of non-imprinted polymer (NIP). NIP adsorbent was synthesized using the same method as the IIP, without being introduced to the Fe (III) metal ion.

2.2.5. Adsorption kinetics. Adsorption by IIP-Fe and NIP adsorbent with 10 mL of 10 ppm Fe (III) adsorbate at pH 3 was done with the varied adsorption duration of 0, 5, 10, 15, 30, 60, 180, 360, and 720 minutes.

2.2.6. Adsorption isotherm. Adsorption isotherm was approached by adsorbing 10 mL of Fe (III) metal ion with the IIP-Fe and NIP adsorbent. The concentration of Fe (III) was varied by 5, 10, 25, 50, 100, dan 150 ppm.

2.2.7. Adsorption selectivity. Adsorption selectivity aimed to observe the influence of a metal ion competitor towards the selectivity performance of the IIP-Fe and NIP adsorbent towards Fe (III). The binary metal ions mixture used in this research were Fe(III)/Cr(III), Fe(III)/Zn(II), and Fe(III)/Ag(I), with the ratio of Fe(III) and competitor metal ion was 1 : 1, and 10 ppm in concentration.

polyeugenol ratio to PEGDE is 1:3. Fe (III) metal ion adsorption was also tested with the parameters of kinetics, isotherms, selectivity, and mechanisms.
2.2.8. Adsorption mechanism. The adsorption mechanism was done through desorption. The aim was to observe the interaction type between the Fe (III) metal ions and the adsorbent. Fe (III) metal ion release from IIP-Fe and NIP adsorbent in this desorption was done with 4 different solvents such as aquadest, Na2EDTA (0.1 M), KNO3 (0.1 M), and HCl (0.1 M).

3. Results and discussions

3.1. Synthesis of polyeugenol
Polyeugenol was characterized by FTIR. Eugenol was also characterized as a comparison. The formation of polyeugenol was proven with the disappearance of the allyl group from the eugenol on wave number 995 cm\(^{-1}\) and 910 cm\(^{-1}\) (Figure 1).

![Figure 1. The FTIR comparison eugenol and polyeugenol](image)

3.2. Synthesis of IIP
The filtrate resulted from the release of the Fe (III) metal ion template on the IIP-Fe adsorbent was characterized using UV-Vis spectrophotometers. The template release was done by washing the adsorbent using HCl until the filtrate is completely clean of Fe (III) metal ions which are marked when the red color fades and the absorbance value on the UV-Vis Spectrophotometer decreases (Figure 2).

![Figure 2. The absorbance value of Fe (III) metal ion release](image)

Poleugenol derivate compounds namely Polyeguenol-Fe, Polyegenol-Fe-PEGDE, NIP, and IIP were characterized by FTIR. The results showed the presence of a sharp and broad –OH group spectrum at 3448.72 cm\(^{-1}\) in the Polyegenol-Fe. Bending vibration of –CH was seen at 1350.17 cm\(^{-1}\), C=C aromatic stretch vibration was seen at 1625–1430 cm\(^{-1}\), and a sharp stretch vibration at 3000-
2926 cm\(^{-1}\) from the C(sp\(^2\))\(^{-}\)-H absorption band of the aromatic ring. The difference between the four spectra was that the Fe-O group was seen at wave number 462.91 cm\(^{-1}\) in polyeugenol-Fe, while it was not present in the rest of the other polyeugenol derivatives (Figure 3).

![Figure 3. Eugenol derivates FTIR comparison](image)

### 3.3. SEM-EDX characterization
SEM characterization was done to observe the morphologic of a compound (Figure 4). From the results as seen in figure 4 below, it can be seen that the porosity of IIP distributes uniformly with the average pore size of 3.078 µm, Poly eugenol-Fe-PEGDE has the average pore size of 2.468 µm, and the porosity is not uniform. Also, NIP showed an average pore size of 3.06 µm with disordered pore distribution.

![Figure 4. SEM comparison of eugenol derivates](image)

EDX characterization was used to observe the presence of Fe element from the Poly eugenol-Fe-PEGDE, IIP-Fe, and NIP adsorbent. The results showed that the Fe element content was at 2.2% in Poly eugenol-Fe-PEGDE, 0% in IIP, and 0% in NIP, which showed that HCl could release Fe(III) completely from Poly eugenol-Fe-PEGDE producing an IIP that could be readily used as an adsorbent.

### 3.4. Adsorption kinetics
The adsorption kinetics of Fe (III) by IIP-Fe and NIP was done at pH 3, the temperature of 29°C, and stirrer at 150 rpm. The time variation used were 0, 5, 10, 15, 30, 60, 180, 360, and 720 minutes. The adsorption results showed that the optimum duration was 60 minutes (1 hour) and as the stirring duration increase, it tends to be more constant, which is likely to occur because the IIP and NIP adsorbent has reached its optimum capacity (Figure 5).
Figure 5. Curve of Fe(III) adsorption by IIP-Fe and NIP adsorbent towards time variation.

The adsorption kinetics in this research was approached using the data modeling into first-order kinetic equation and second-order kinetics. Table 1 showed the adsorption kinetics parameter of Fe(III) in NIP dan IIP.

| Adsorbent | Pseudo-first-order | Pseudo-second-order |
|-----------|--------------------|---------------------|
|           | $q_e$ | $k_1$ | $R^2$ | $q_e$ | $k_2$ | $R^2$ |
| IIP       | 0.18887 | 0.000412 | 0.4238 | 2.040775 | 0.290066 | 0.9998 |
| NIP       | 0.37612 | 0.000216 | 0.0785 | 1.9996 | 0.055007 | 0.9998 |

All adsorbents gave low correlation coefficients for the $t$ vs log ($Q_e-Q_t$) plot in the pseudo-first-order, which are 0.4238 for IIP-Fe and 0.0785 for NIP. As for the pseudo-second-order, $t$ vs $t/Q_t$ plot gives a very high correlation of 0.9998, so it can be assumed that in addition to being influenced by the nature of the adsorbent, it is also influenced by the nature of the adsorbate (metal ion) [4]. For $k_1$ and $k_2$, IIP-Fe was higher than NIP. The $k_1$ value is 0.000412 L/min on IIP and 0.000216 on NIP, while $k_1$ on IIP-Fe is 0.290066 g/mg.min much higher than NIP, which is equal to NIP 0.055007 g/mg.min.

The $k_1$ and $k_2$ results from IIP-Fe were obtained as it was assumed that as more pores were open and the more distributed the porosity from the adsorbent were, the adsorption rate will increase, and the metal ion will be easier to be trapped in the adsorbent template. The kinetic equation results in this research are in accordance with a research that was done by Masykur in 2014, that IIP-Fe pore structure caused the metal ion to be fast-paced towards the active sites of the adsorbent and bonded [5].

3.5. Adsorption isotherm

The purpose of the adsorption isotherm was to show how a metal ion was distributed between a liquid and solid phase when the adsorption reached equilibrium. Isotherm data analysis was performed by adjusting the suitable isotherm model, the capacity of the adsorption was investigated by two models namely the Langmuir Isotherm and the Freundlich Isotherm. The adsorption isotherm indicates that when there is an initial increase in concentration, it will be followed by an increase in the amount of substance absorbed to reach equilibrium [6].

The Langmuir isotherm model is based on the assumption that the occurrence of adsorption is localized to the monolayer and all adsorption sites on the adsorbent are homogenous [7]. Adsorption energy describes the amount of electrostatic interaction energy and chemical bond energy between metal ions and adsorbents [8, 9]. The amount of energy released in physical adsorption ranges from -20 kJ/mol and below, and the energy released in chemical adsorption is quite high, between -40 kJ/mol.
to -800 kJ/mol [10]. According to the data in table 2 below, ΔG° IIP-Fe(III) value of -35.852 kJ/mol and ΔG° NIP-Fe(III) value of -35.531 kJ/mol, showed that Fe(III) metal ion adsorption in IIP-Fe and NIP are physical-chemical adsorption, and the template process increases the interaction strength between the Fe(III) metal ion and the adsorbent [11] (Table 2).

| Adsorbent | Qm (mg/g) | b (L/mol) | Kx10^{-7} (L/mol) | R² | ΔG (kJ/mol) | n | Kf' | R² |
|-----------|-----------|-----------|-------------------|----|-------------|---|-----|----|
| IIP       | 23.640    | 13.238    | 5.193             | 0.9051 | -35.852 | 2.382 | 1.239 | 0.597 |
| NIP       | 17.636    | 9.8765    | 5.9134            | 0.8679 | -35.531 | 1.785 | 0.496 | 0.567 |

3.6. Metal ion adsorption selectivity

The adsorption selectivity was carried out to find how selective the adsorbent was to Fe(III) adsorbate in a binary metal ion solution (Figure 6). Determination of adsorption selectivity was carried out by adding 50 mg of adsorbent into 10 mL of binary metal ion solution Fe(III)/Ag(I), Fe(III)/Cr(III), and Fe(III)/Zn(II) with each ion concentration of 10 mg/L.

The highest Fe(III) adsorption selectivity of Fe(III)/Zn(II) > Fe(III)/Cr(III) > Fe(III)/Ag(I) showed that the formed adsorbent (IIP-Fe adsorbent) has the characteristics that match the metal ion template used during printing process [12]. The highest selectivity adsorption ability is by the Fe(III)/Zn(II) binary solution. It is higher compared to Fe(III)/Cr(III) binary solution, which indicates the formed adsorbent has the same characteristics as the metal ion template used in the templating process and also according to the HSAB theory, where hard acid will tend to bond with soft base, and soft acid will tend to bond with hard base [13]. Cr(III) metal ion is a hard acid, Zn(II) is included in borderline acids, and Ag(I) is included in soft acids [14]. Fe(III)/Ag(I) is the least selective because Ag(I) has the biggest radius than Zn(II) and Cr(III), which could hinder the Fe(III) metal ion to enter the template sites, resulting in a lower Fe(III) selectivity ability [13].

3.7. Adsorption mechanism of Fe(III) metal ions in IIP and NIP

The adsorption mechanism of IIP-Fe and NIP adsorbent towards Fe(III) was done through desorption towards each adsorbent that has been previously used to adsorb Fe(III) metal ion. The desorption solution is used to dissolve the absorbed metal both physically (trapping) and chemically (ion exchange, hydrogen bond formation, and complex formation).
The solvent used in the desorption process was aquadest that showed a trapping mechanism, 0.1 M KNO$_3$ that showed ion-exchange mechanism, 0.1 M HCl that showed hydrogen bond formation, and Na$_2$EDTA that showed a complex formation mechanism. As seen in figure 7, the highest desorption process is shown by the 0.1 M HCl solution towards NIP and IIP-Fe, so it can be concluded that the Fe(III) metal ion adsorption mechanism is chemical adsorption because it happens through hydrogen bond formation.

![Figure 7. Desorption percentage of Fe (III) with various solvent towards IIP-Fe and NIP](image)

**4. Conclusion**

IIP-Fe and NIP have been successfully synthesized, both of it followed the pseudo-second-order, and adsorption isotherm followed the Langmuir model. Fe(III) metal ion adsorption capacity on IIP-Fe is 23.640 mg/g and 17.636 mg/g on NIP, with the rate on IIP-Fe and NIP are 0.290 g/mg.min and 0.055 g/mg.min, respectively. Adsorption of Fe(III) by IIP-Fe and NIP followed the chemical-physical adsorption model with Gibbs energy of -35.851 kJ/mol and -35.831 kJ/mol, respectively. IIP-Fe adsorption selectivity coefficient is bigger than NIP in metal ion binary solution with the order as Fe(III)/Zn(II)>Fe(III)/Cr(III)>Fe(III)/Ag(I), while the Fe(III) adsorption mechanism on NIP and IIP-Fe are dominated with a hydrogen bond.

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