Synthesis of Fe(III)-IIPs (Ion Imprinted Polymers): Effect of 6M HCl Solvent on Extraction Variations in Cavity Formation of Fe(III)-IIPs

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Abstract. The heavy metal iron (Fe) is a pollutant that pollutes the aquatic environment and hurts health. Research on Fe(III)-IIPs aims to create an adsorbent capable of absorbing Fe ions by imprinting ionic IIPs (Ion Imprinted Polymers) using the cooling-heating method. Polymerization involves $Fe(NO_3)_3$, methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), benzoyl peroxide (BPO), and chloroform as analytes, functional monomers, cross-linkers, initiators and solvents. Fe(III)-IIPs were extracted using 6M HCl to remove the template from the polymer body involving varying times (18 hours and 12 hours) and repetitions (7 times and 10 times). HCl as a porogen solvent is more effective at removing Fe metal ions in the extraction process than other similar acid solutions such as HNO_3. Based on FTIR characterization testing, there was a 7% increase in transmittance percentage in Fe(III)-IIPs variation II. The test results of the best sample (Fe(III)-IIPs Variation II) were subjected to SEM characterization which produced 515 cavities <100 nm.

Keywords: Imprinted Polymer, Fe(III)-IIPs, Extraction, HCl 6M

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1. Introduction

Pollution in the aquatic environment occurs due to anthropogenic activities which have a negative impact on global ecology, including reduced biodiversity and ecosystem degradation [1], [2]. Water contaminated with heavy metals, if consumed continuously, will have negative impacts on health, such as diarrhea, chorea, respiratory system problems, and even liver failure. Heavy metals (Fe) are pollutants that have spread widely, especially in the aquatic environment and are toxic to humans and animals even at very small levels [1], [3], [4]. In Indonesia, the government designs regulations based on water use objectives according to WHO (World Health Organization), the concentration limit for Fe consumption is 0.3 mg/L [5]. In this case, a precise and efficient method is needed in the Fe separation process.

A number of studies related to adsorbent materials have focused on molecular separation through imprinting MIPs (Molecular Imprinted Polymers). Currently, ionic polymer imprinting is carried out in the separation of various heavy metals, one of which is Fe. The advantages of IIPs (Ion Imprinted Polymers) compared to other adsorbents are that the preparation process is efficient, can be stored for a long time without losing affinity for target ions, and has high selectivity for target ions at an affordable price [6], [7]. The synthesis of IIPs is carried out by involving templates, functional monomers, cross-linkers, porogens and initiators. In the polymerization of IIPs synthesis using the cooling-heating method with a shorter time efficiency than the nitrogen flow method [8]. The formation of cavities results from the extraction process to remove the template from the polymer body, leaving a cavity that is able to recognize the target ion based on the same physico-chemical properties as the analyte [9].

In previous research, especially regarding the separation of Fe(III)-IIPs ions, various extraction variations have been carried out such as composition and solution. However, there has been no research on Fe(III)-IIPs using 6M HCl in various repetitions of extraction with a shorter time used. In this research, the extraction process was carried out using 6M Hydrochloric Acid (HCl) with varying times (18 hours and 12 hours) and repetitions (7 times and 10 times). HCl as a porogen solvent is used in the extraction process because it is able to remove unwanted oxides and is more effective in removing Fe metal ions in the extraction process than other similar acid solutions such as HNO_3 [3]. Characterization of Fe(III)-IIPs has been carried out using fourier transform infrared (FTIR), x-ray diffraction (XRD), and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS).

Based on the description above, this research discusses the separation of Fe through ionic imprinting for environmental remediation. The characteristics of the Fe(III)-IIPs produced have been tested and provide information that the more extraction treatment given, the more cavities are formed and the shorter the time used.

2. Research Methods

2.1 Tools and Materials

The tools used are digital balances, mortar cups, magnetic stirrers, hot plates, refrigerators, furnaces, and others. The research carried out involved materials such as $Fe(NO_3)_3$ as an analyte, Methacrylic Acid (MAA) as a functional monomer, Ethylene Glycol Dimethacrylate (EGDMA) as a cross-linker, Benzoyl Peroxide (BPO) as an initiator and Chloroform as a non-polar organic solvent. Apart from that, there is Acetic Acid, Methanol, HCl, and Deionized Water as template cleaners, as well as Aquadest as a pure solvent. The resulting Fe(III)-IIPs samples will be characterized by XRD, FTIR, and SEM.

2.2 Polymer Synthesis

A total of 0.404 grams of $Fe(NO_3)_3$ was dissolved in chloroform (6.36 mL), then added sequentially MAA (0.4 mL), EGDMA (3.96 mL), and BPO (0.07 grams). After all the precursors were mixed, the pre-polymer solution was homogenized using a hot plate for 90 minutes at 25°C. Next, the solution was put into a vial and cooled using a refrigerator at -5°C for 1 hour. The pre-polymer solution is then subjected to a heating process using a furnace at a constant temperature of 75°C for 7 hours. A similar thing is done in the NIP synthesis, but without involving $Fe(NO_3)_3$ as an analyte.

2.3 Extraction of Fe(III)-IIPs

The resulting solid polymer is ground until it is fine so that it can be extracted to remove the template from the polymer body. Before extraction, the polymer powder is first washed (leached) by soaking in chloroform for 16 hours. Then the polymer was soaked again using methanol/acetic acid (1:20) three times for 1 hour. The polymer was then soaked again using methanol (3 mL) three times for 1 hour. Finally, the polymer was soaked using a methanol/aquadest solution (1:20) for 1 hour. Only then, the polymer is placed in an oven at 60°C for 1 hour. After being given a leaching treatment, the polymer was extracted using 6M HCl with 2 time variations, namely 18 hours for 7 repetitions and 12 hours for 10 repetitions. Then each was neutralized using deionized water (10 mL) until it reached neutral pH and dried using an oven at 60°C for 1 hour.

Fig.1. (a) NIP; Fe(III)-IIPs Extraction Results (b) Variation I; (c) Variation II

3. Results and Discussion

3.1 Fourier Transform Infrared (FTIR) Characterization

To determine the functional groups of a material, FTIR characterization is used with a number range of 4000-500 cm^{-1} and predicts the polymerization reactions that occur in NIP, Fe(III), and Fe(III)-IIPs polymers. The graph of the FTIR analysis results is shown in Figure 2.

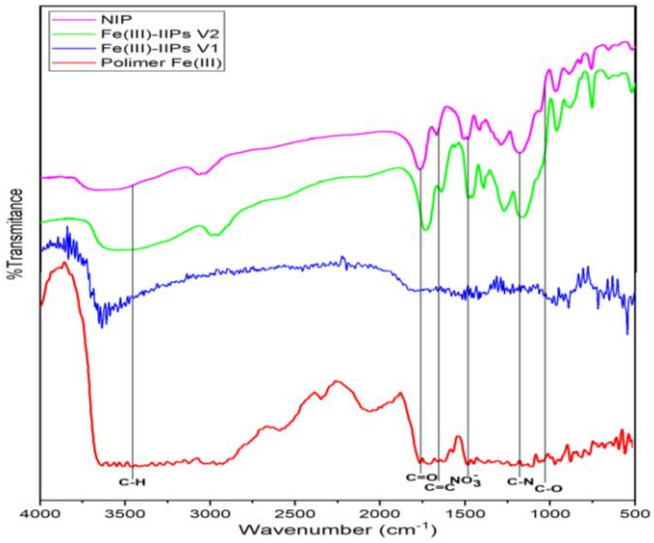

Fig.2. FTIR spectrum of Fe(III) polymer, Fe(III)-IIPs variations I and II, and NIP

In Figure 2, the functional groups found in Fe(III), Fe(III)-IIPs and NIP polymers are presented. The functional monomer chosen uses MAA because it can form hydrogen bonds and templates well. The hydrogen bonds formed to act as acceptors. The acceptor will accept the transfer of electrons from other compounds in the form of donors of the amino functional group and oxygen atoms in the carboxylic group. The number range 1700-1736 cm^{-1} indicates the presence of a C=O group in MAA which is classified as a carboxylic acid. Apart from that, the C-O functional group which is also classified as a carboxylic acid is shown in the wave number range 1030-1054 cm^{-1}. In this number range, it is shown that there is an EGDMA cross-linker and a BPO initiator [10]. The NO_3^- functional group from the common organic ion group is shown in the wave number range 1380-1350 cm^{-1}. This functional group indicates that there are Fe^{3+} metal ions in the material [11]. The transmittance value of each material tested using the FTIR spectrum is shown in Table 4.2.

Table 1. Percent Transmittance and functional groups of NIP functional groups, Fe(III) Polymers, and Fe(III)-IIPs

Functional Groups	NIP		Fe(III) Polymer		Fe(III)-IIPs			
					Variation I		Variation II	
	k (cm^{-1})	*T* (%)	*k* (cm^{-1})	*T* (%)	*k* (cm^{-1})	*T* (%)	*k* (cm^{-1})	*T* (%)
C-H	3568.76	8.9668	3469.46	0.0001	3645.92	0.1019	3569.74	0.9729
C=O	1739.94	12.4457	1700.98	0.0013	1714.48	0.1147	1736.66	1.5090
C=C	1637.59	18.1696	1633.48	0.0032	1633.48	0.1162	1633.48	2.6006
NO_3^-/CH-CH_3	1392.31	19.0060	1351.91	0.0030	1225.59	0.1119	1479.20	2.3789
C-N	1164.01	15.1443	1108.92	0.0001	1159.06	0.1104	1165.81	1.8620
C-O	1000.92	28.9691	1051.06	0.0019	1000.92	0.1099	1054.92	3.1724

Information:
k: Wave Number (cm^{-1})
Q: Transmittance (%)
Low infrared frequency absorption occurs when the resulting transmittance value is high. Meanwhile, a low transmittance value indicates that the infrared frequency absorption is high. The uneven distribution of nitrate ions affects the amount of transmittance produced by each functional group. The decrease in transmittance value between NIP and Fe(III) polymer indicates an interaction between the template and the monomer used.

3.2 X-Ray Diffraction (XRD) Characterization

XRD characterization produces a graph in the form of intensity against 2θ. Figure 3 shows that the resulting graph will show peaks indicating that constructive interference is occurring.

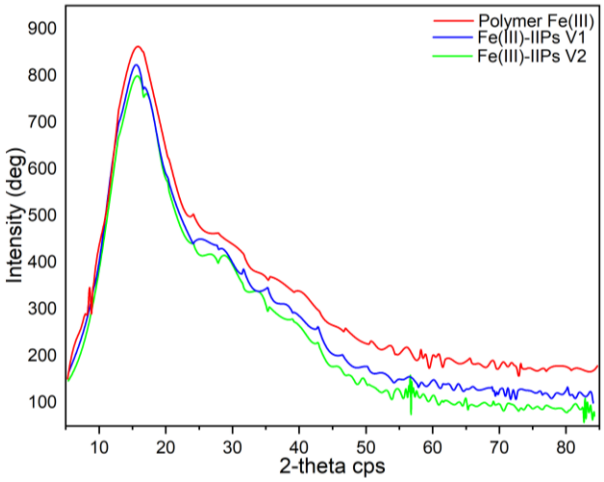

Fig.3. XRD test results of (a)Fe(III) polymer; (b)Fe(III)-IIPs Variation I; (c)Fe(III)-IIPs Variation II

A practical method for determining the average size of nanocrystallites in a material is X-ray diffraction. Through the Scherrer Equation, the crystal size distribution of Fe(III)-IIPs can be estimated from the XRD graph. Scherrer's equation is used to predict the crystalline size of a material. Based on the Scherrer equation, the resulting crystal size will be inversely proportional to the FWHM value, while the FWHM value is influenced by the intensity of each crystal plane. The higher the intensity produced, the smaller the FWHM value will be [12], [13]. Table 2 shows that the FWHM value for Fe(III)-IIPs variation II is smaller than for Fe(III) Polymer and Fe(III)-IIPs variation I. Based on the XRD results, there is an increase in the peak intensity of Fe(III)-IIPs variation II which indicates There is an increase in the number of atoms that causes diffraction in Fe(III)-IIPs variation II.

$$D = \frac{k\lambda}{B_0 \cos\theta} \quad (1)$$

Table 2. Results of Crystal Size Analysis for Each Sample

Sampel	2θ (^{0})	θ (^{0})	d (Å)	FWHM (^{0})	FWHM (*rad*)	D (*nm*)
Polimer Fe(III)	15.92	7.96	5.979	8.57	0.1494988	0.93682
Fe(III)-IIPs Variasi I	15.46	7.73	5.581	8.39	0.1463588	0.95692
Fe(III)-IIPs Variasi II	15.67	7.83	5.373	8.29	0.1446144	0.96846

3.3 Characterization of Scanning Electron Microscopy (SEM)

The IIPs material was then characterized by SEM to determine the surface morphology of the Fe(III) polymer, Fe(III)-IIPs variation I, and variation II. Based on the results of FTIR and XRD testing, the best results were shown by Fe(III)-IIPs variation II. In the FTIR test, it can be seen that many metal ions are transmitted so that the absorption value is greater than the Fe(III) and Fe(III)-IIPs polymer variation I. This is also reinforced by the intensity values and crystal size distribution of Fe(III)- IIPs variation II is more evenly distributed. Figure 4 shows the SEM imaging results and also the cavity size distribution of the adsorbent material.

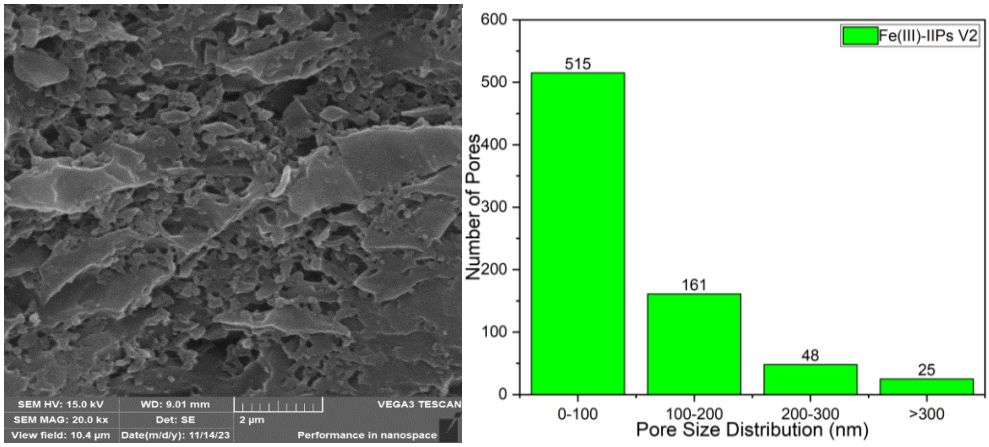

Fig.4. Fe(III)-IIPs Variation II (a) 20.0 kx SEM Imaging Results; (b) Cavity Distribution

The resulting SEM images were analyzed using Image J Software with the assistance of Origin Software. The SEM imaging results show the number and size of cavities formed as a result of the repeated extraction process of IIPs material. Based on the output data from Image J processing in

Figure 3b, it was found that the number of cavities formed on a scale <100 nm was 515 cavities. This indicates that there are a lot of nitrate ions that are removed during the extraction process so the adsorption distribution is more even compared to Fe(III) and Fe(III)-IIPs polymer variation I. The formation of cavities occurs due to the extraction process or removal of Fe(III) metal ions. When the active substance binds to HCl as an extraction solvent, the active substance Fe(III) will be lifted from the polymer body and leave a template that can recognize molecules with the same chemical-physical structure as the analyte ion or target Fe(III). HCl can cause the breakdown of interactions between Fe^{3+} ions and polymer particles so that Fe^{3+} ions can be better eluted from the polymer body [14].

4. Conclusion

Based on the results of XRD, FTIR, and SEM characterization tests, the best sample is Fe(III)-IIPs variation II. This can be observed directly or indirectly in the material. To the naked eye, the color produced in Fe(III)-IIPs variation II material is whiter than Fe(III)-IIPs variation I, similar to NIP (without involving a template). In FTIR characterization, the transmittance value of Fe(III)-IIPs variation II is higher than other adsorbents, which indicates the greater absorption produced. This absorption indicates that more nitrate ions (NO_3^-) have been adsorbed evenly. Comparison of the FWHM values of Fe(III) and Fe(III)-IIPs polymer variations I and II in XRD characterization shows that Fe(III)-IIPs variation II has better mechanical properties than the two. Apart from that, SEM characterization shows that the pore size distribution produced in the Fe(III)-IIPs variation II sample on a scale of <100 nm is 515 cavities. Based on the SEM imaging results, there are many cavities formed after the extraction process using 6M HCl solvent. This indicates that through many repetitions in a short time, it is possible to remove Fe^{3+} ions from the polymer body more effectively through the variation of extraction used. The HCl solution has better performance compared to other acid solutions in the extraction process. The use of HCl can cause a breakdown in the interaction between Fe^{3+} ions and polymer particles so that the Fe^{3+} ions can be lifted from the polymer body and leave a cavity to recognize the target ion based on the chemical-physical properties of the metal ion.

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