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Optimization of pH Conditions for Lead Adsorption using Ion-Imprinted Polymer (IIP) with EDTA as Ligand

Yuliani Permatasari, Maria Monica Sianita*

[a] Department of Chemistry, State University of Surabaya, Indonesia
*Corresponding author: mariamonica@unesa.ac.id
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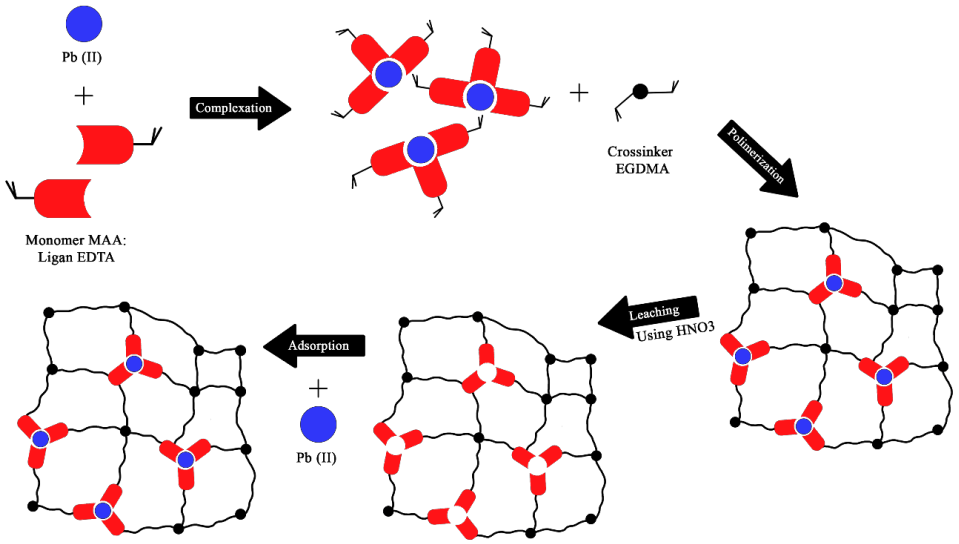
GRAPHICAL ABSTRACT



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ABSTRACT

Ion-imprinted polymers (IIPs) are selective adsorbents for heavy metal removal. In this study, IIPs were synthesized using Pb^{2+} as a template, EDTA as a ligand, methacrylic acid (MAA) as a monomer, and ethylene glycol dimethacrylate (EGDMA) as a crosslinker via precipitation polymerization in an ethanol-acetonitrile mixture with benzoyl peroxide (BPO) as an initiator at 70°C. FTIR analysis confirmed the successful synthesis of IIPs by identifying Pb-O vibrations at 530.1 cm^{-1} in the non-imprinted polymer (NIP), which disappeared in IIP after Pb^{2+} removal. SEM-EDX analysis showed IIP had more voids than NIP due to Pb^{2+} removal, with decreased Pb content from 1.85% to 0.18%. Adsorption was tested at pH 4–9, a 30-minute contact time, and an initial Pb^{2+} concentration of 50 ppm. The optimum pH was 7, with an adsorption capacity of 47.52 mg/g and a percentage recovery of 97.3%. This method offers higher selectivity, stability, and reusability due to the polymer matrix's specific Pb^{2+}-imprinted cavities than other adsorption methods. Adsorption occurred via electrostatic interactions and complex formation. These results demonstrate that IIPs are effective for Pb^{2+} removal, offering a promising solution for heavy metal pollution treatment.

1. INTRODUCTION

Industrial development in the modern era has many good and bad impacts on human life. One of the major negative impacts is environmental pollution due to the emergence of various kinds of hazardous waste, such as pollutants, pesticides, and heavy metals, that pose a high risk to human health [1, 2]. Toxic heavy metals such as lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu), mercury (Hg), and arsenic (As) are widely generated from the wastewater of smelting mining activities, the paint industry, metal plating industry, and other industries [3]. Lead (Pb) is the second most toxic heavy metal among 275 compounds, according to data from the Agency for Toxic Substances and Disease Registry (ATSDR) [4]. Even small amounts of lead exposure can indirectly impact public health due to its non-degradable nature, leading to continuous accumulation in the human body [5]. Prolonged lead exposure has been shown to cause damage to the kidneys, liver, nervous system, and reproductive system, as well as disrupt hemoglobin synthesis and binding in the blood [6].

Various methods have been developed to reduce heavy metal lead contamination in water, including precipitation, ion exchange, membrane filtration, phytoremediation, and adsorption [7]. Among these, the adsorption method is the most commonly used due to its advantages, such as high adsorption capacity, efficiency, and versatility in treating a wide range of pollutants [8]. The adsorption method using Ion-Imprinted Polymer (IIP) as an adsorbent is a technique being developed to reduce metal ion contamination in water efficiently [9]. This process involves using IIP to adsorb the template metal ions in the sample solution, with lead ions serving as the template.

Ion-imprinted polymer (IIP) is created using a metal ion template as a printed. The metal ion template is extracted from the formed polymer matrix, leaving behind a cavity or printed specific to the template metal ion. This allows the polymer to rebind the metal ion template selectively during adsorption [10]. IIP adsorbents offer several advantages, including high selectivity for template metal ions, stability during storage at room temperature, and reusability. The high selectivity of IIPs arises from a lock-and-key mechanism, which enables specific recognition of the template metal ion used in the polymer. The print formed within the polymer creates an active site on the template, allowing it to rebind the template metal ion selectively during adsorption [11]. These advantages make IIP widely applicable in analytical processes such as preconcentration and an adsorbent for removing toxic metals from water. One of the key factors influencing the adsorption process using IIP adsorbents is pH [12].

The pH (hydrogen potential), or acidity, is a parameter used to express the acidity of a solution [13]. The pH value influences the charge on the functional groups, whereas, in an acidic environment, H^+ ions compete with metal cations to bind to the adsorbent's functional groups. This competition can significantly reduce the adsorption capacity at low pH [14, 15]. In alkaline environments, the solubility of metals can decrease, leading to the precipitation of metal ions due to the formation of complexes with OH^- groups. This can result in suboptimal adsorption outcomes [16]. Adsorption using IIP as an adsorbent at excessively low or high pH can reduce its adsorption capacity. Therefore, optimizing the pH is essential to determine the optimum pH for adsorption when using IIP Pb as an adsorbent [17, 18].

This paper reports the development methods of Pb(II) adsorption using EDTA ligand-based ion-printed polymer synthesized using precipitation polymerization. The concentration of Pb(II) metal ions was analyzed using the atomic absorption spectrophotometer (AAS). Characterization of the IIP was investigated using Fourier transform infrared spectrophotometry (FTIR) and Scanning electron microscopy - Energy dispersive X-ray spectroscopy (SEM-EDX), and the experiment parameter was the pH of the solution [19]. This method enriched the trace amount of lead ions from aqueous solutions.

2. EXPERIMENTAL METHODS

2.1. Materials and apparantus

The tools used in this study were Erlenmeyer Pyrex 100 mL, Erlenmeyer screw cap Pyrex 100 mL, beaker glass Herma, volumetric flask Pyrex 100 mL, measuring cylinder, glass funnel, magnetic stirrer Daihan Scientific, vacuum filtration, plastic wrapping, reagent bottles, Buchner funnel, filter paper Whatman N0. 42, AAS (Atomic absorption spectroscopy) Shimadzu AA-700, FTIR (Fourier-

transform infrared spectroscopy) Spectrum Two N FT-NIR, and SEM-EDX (Scanning Electron Microscopy-Energy dispersive X-ray spectroscopy) Hitachi Flexsem 100.

The materials used in this study were $Pb(NO_3)_2$ Merck, *Ethylenediaminetetraacetic acid* (EDTA) Merck, ethanol pro analysis, acetonitrile Merck, *Ethylene glycol dimethacrylate* (EGDMA) Sigma Aldrich, *methacrylic acid* (MAA) Sigma Aldrich, *Benzoyl Peroxide* (BPO), aquadest, aquabidest Ikapharmindo Putramas, and phosphate buffer.

2.2. Preparation of Ion-Imprinted Polymer

The ion-imprinted polymer was synthesized using lead (Pb) as a template by precipitation polymerization method; IIP synthesis is produced from NIP or Non-Imprinted Polymer, which is extracted using 1M HNO_3 to remove template metal ions in the polymer matrix. In a glass, 0.1 mmol $Pb(NO_3)_2$ was added to 0.25 mmol EDTA ligand and dissolved in 60 mL ethanol-acetonitrile mixture (2:1), stirred with a magnetic stirrer for 30 minutes. 4 mmol methacrylic acid (MAA) as monomer, 20 mmol ethylene glycol dimethacrylate (EGDMA) as crosslinker, and 0.2 mmol BPO as initiator were added. The mixture was then flowed with nitrogen gas for 5 minutes, after which the mixture was covered using aluminium foil and carried out using a magnetic stirrer with a water system at 70°C. The polymer obtained was filtered, washed with ethanol and aquabidest, then oven-dried at 60°C until the weight was constant, and NIP or Non-Imprinted Polymer was obtained. Then, the Pb ions were leached from NIP using 100 mL of 1 M HNO3 in the magnetic stirrer for 30 minutes. The IIP was washed with aquabidest, filtered, and oven-dried at 60°C until the weight was constant.

2.3 Determination of Optimum pH of IIP Adsorption on Pb(II)

Optimization of pH conditions was performed for the adsorption method using the synthesized IIP as an adsorbent. A 0.5-gram sample of IIP Pb(II) was added to 50 mL of a 50 mg/L $Pb(NO_3)_2$ standard solution, with the pH varied from 4 to 9. The pH variation was achieved by adding 0.01 M phosphate buffer to dilute the standard solution. The adsorption process was carried out for 2 hours using a magnetic stirrer, followed by filtration. The filtrate was then analyzed using AAS. The adsorption process was performed in triplicate.

3. RESULTS AND DISCUSSIONS

The latest development of ion-imprinted polymer building materials was successfully synthesized using $Pb(NO_3)_2$ as the template metal and EDTA as the ligand. EDTA was chosen because it is an effective chelating agent for metals, allowing it to form stable complex bonds within the polymer matrix. In the synthesis process, methacrylic acid (MAA) was used as the monomer, ethylene glycol dimethacrylate (EGDMA) as the crosslinker, and benzoyl peroxide (BPO) as the initiator. The synthesized IIP was found to be a fine white powder. The polymerization reaction of IIP, shown in Figure 1, involves three steps: (1) formation of the Pb(II) metal ion complex with EDTA as the ligand, (2) polymerization with the monomer, crosslinker and BPO, and (3) removal of metal ions followed by rebinding of metal ions during the adsorption process.

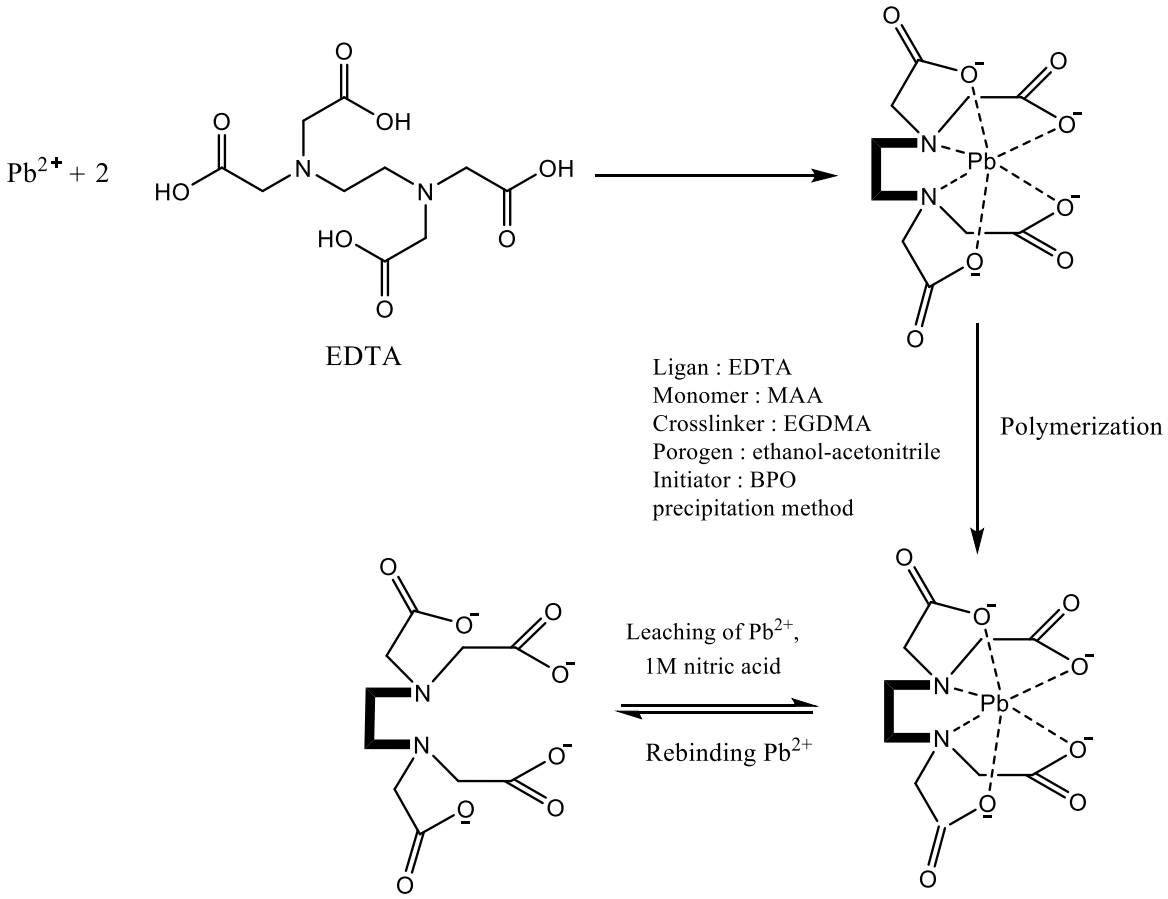

Figure 1. Illustration of IIP Formation

3.1 Characterization of IIP

FTIR characterization was conducted at wavelengths ranging from 400 to 4000 cm^{-1} for NIP and IIP samples (Figure 2). In the NIP sample, the wavenumber at 530.1 cm^{-1} corresponds to Pb-O vibrations. However, in the IIP sample, no Pb-O functional group was observed because the Pb(II) metal ions were successfully removed. The infrared spectrum showed a vibration at 1728.3 cm^{-1}, which is associated with the C=O carbonyl group. In comparison, a wavenumber at 1453.7 cm^{-1} indicated the presence of a C=C bond, and a wavenumber at 1144.7 cm^{-1} corresponded to the C-O-C bond, a characteristic peak of the crosslinker (EGDMA) [9]. A relatively weak IR absorption band at 3546.2 cm^{-1} showed the stretching vibration of the -OH bond from the carboxyl group, and the stretching vibration at 1728.3 cm^{-1} again indicated the carbonyl group (C=O), which is characteristic of EDTA.

Functional Group	Wave Number (Cm^{-1})	
	Reference [9, 18]	Research results
Pb-O	531	530,1
C-O	1065 - 1075	1042,5
O-H	3538	3546,2
C=O	1651 - 1740	1728,3
C=C	1468 - 1557	1453,7
C-O-C	1147	1144,7
C-H	720	752,9

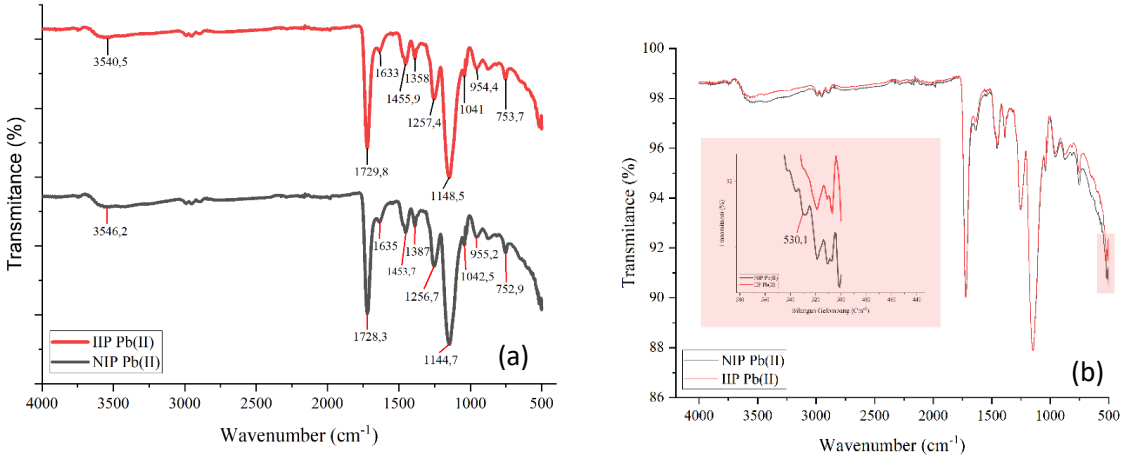

Figure 2. FTIR Spectra of NIP (a) and IIP (b)

SEM-EDX characterization combines two analytical methods used to study metallic materials. It was performed on NIP and IIP samples at a magnification of 20.000x, as shown in Figure 3. The results revealed a clear difference between the NIP and IIP samples. The surface morphology of the particles showed that IIP had more voids than NIP. This is because the Pb(II) ions were successfully removed from the polymer matrix, leaving behind molds or cavities.

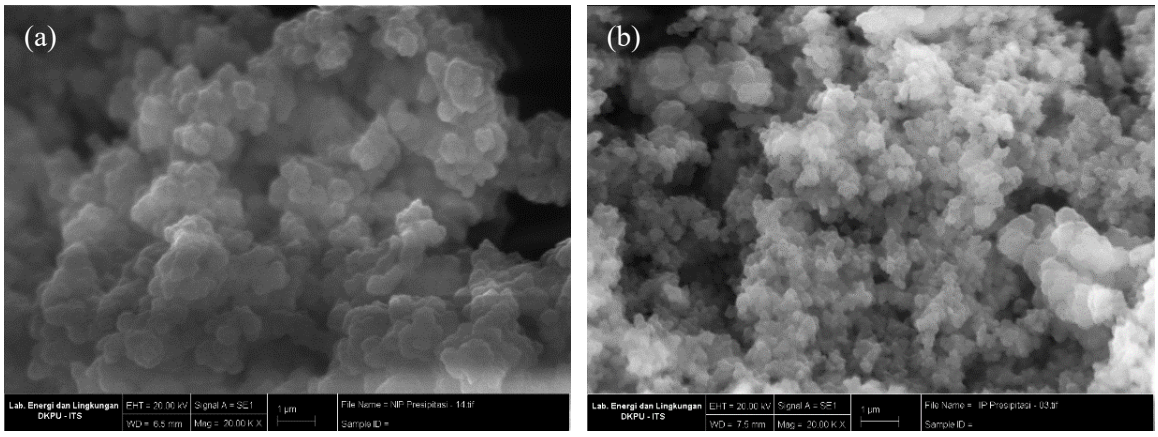

Figure 3. Characterization of IIP Pb(II) (a) SEM images of NIP (20.000x magnification) (b) SEM images of IIP (20.000x magnification).

The EDX characterization results provided elemental mapping data, as shown in Figure 4, illustrating the distribution of elements in the sample, including Pb, SE, C, and O. The percentage of Pb atoms in the NIP sample was 1.85%. In contrast, in the IIP sample, it was significantly reduced to 0.18%. This decrease in Pb content in the IIP indicates that the Pb metal ions were successfully removed during synthesis.

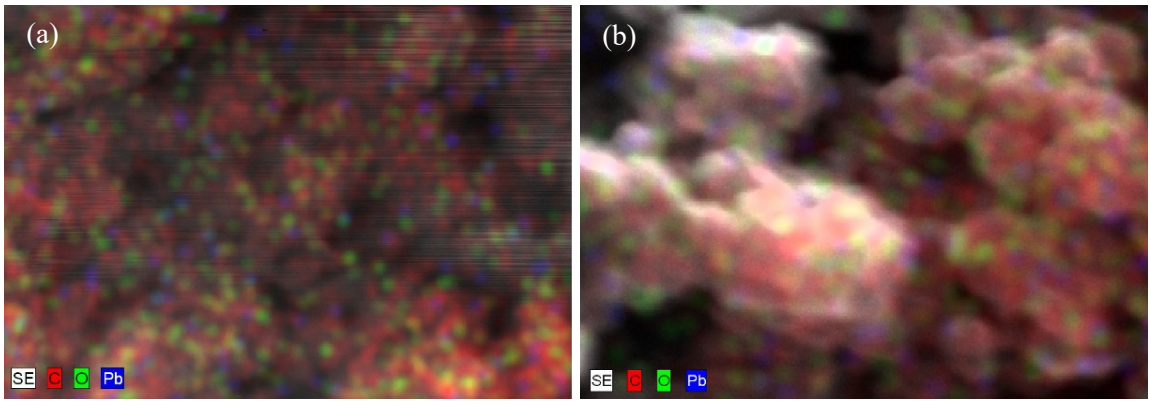

Figure 4. (a) EDX elemental mapping of NIP (b) EDX elemental mapping of IIP

3.2 Optimum pH condition of adsorption IIP

The pH is a crucial parameter influencing the adsorption process when using IIP as an adsorbent. This is because the pH of the solution affects the charge interactions between metal cations and the functional groups of the adsorbent. The adsorption capacity is determined from the filtrate results, which are analyzed using AAS and then calculated using the following equation [20]:

$$Qe = \frac{(Co-Ce)}{m} \text{ x } V \quad (1)$$

The adsorption of Pb(II) metal ions to determine the optimum pH was conducted within the pH range of 4 to 9 using a 50 mg/L $Pb(NO_3)_2$ solution, with three replications. The average adsorption capacity is presented in Table 1 and Figure 5. The results showed that the adsorption of Pb(II) metal ions increased from pH 4 to 6, reaching its peak at pH 7, and then decreased at pH 8 and 9. At low pH, the high concentration of H^+ ions in the solution competes with Pb^{2+} cations for binding to the functional groups of the adsorbent, thereby reducing the adsorption capacity. The optimum pH for Pb(II) metal ion adsorption was pH 7. Above pH 7, the adsorption capacity decreases due to OH^- ions, which can form complexes with metal cations. At alkaline pH, $Pb(OH)^+$ and $Pb(OH)_2$ complexes dominate in the solution, and the IIP functional groups cannot effectively adsorb these complexes. The complex reactions occurring are as follows:

$$Pb^{2+}(aq) + OH^-(aq) \rightarrow Pb(OH)^+(aq)$$
$$Pb(OH)^+(aq) + OH^-(aq) \rightarrow Pb(OH)_2(s)$$

TABLE I. Adsorption capability of Pb(II) using IIP as adsorben

pH	Pb Concentration (C)		Qe[#c] (mg/L)
	Co[#a] (mg/L)	Ce[#b] (mg/L	
4	50,24	7,28	42,96
5	50,48	5,79	44,69
6	50,32	4,4	45,92
7	50,16	2,64	47,52
8	45,52	5,31	40,21
9	45,2	6,46	38,74

[a]Concentration before adsorption; [b]Concentration after adsorption; [c]Adsorption capability

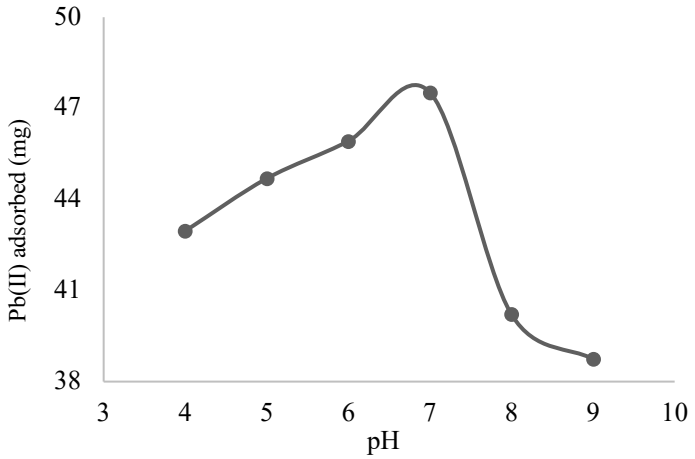

Figure 5. Influence of pH on the adsorption of Pb(II) on IIP

TABLE II. Percent recovery to determine the accuracy of the method

Actual conc. (mg/L)	Conc. obtained (mg/L)	Recovery (%)
5	5,024	100,48
	5,048	100,96
	5,032	100,64
	5,016	100,32
	4,552	91,04
	4,52	90,4
Average		97,3

A $Pb(NO_3)_2$ standard solution with a concentration of 5 mg/L, adjusted to varying pH levels, was analyzed using AAS to determine the method's accuracy. Table 2 shows the percent recovery value as 97,3%, which means the method can accurately analyze 97,3% of the actual value.

4. CONCLUSIONS

A novel EDTA ligand-based ion-imprinted polymer (IIP) adsorbent for the adsorption of Pb(II) metal ions was successfully synthesized via a precipitation polymerization method. Methacrylic acid served as the monomer, ethylene glycol dimethacrylate (EGDMA) as the crosslinker, and benzoyl peroxide (BPO) as the initiator in the polymerization reaction. FTIR characterization confirmed the successful synthesis of IIPs by identifying relevant functional groups, including Pb-O. Furthermore, SEM-EDX analysis revealed significant differences between non-imprinted polymer (NIP) and IIP, with IIP exhibiting more voids due to the removal of Pb(II) ions, forming molds in the polymer matrix. The optimum pH for the adsorption method was pH 7, achieving an average adsorption capacity of 47.52 mg/L and a percent recovery of 97.3%.

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