The effect of temperatures and monomer ratios on the characteristic of anionic and cationic gel-based adsorbents

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Abstract. Industrial development has caused the metal concentration in the environment to increase. This is a serious issue considering that heavy metals are stable and cannot naturally decompose. Therefore, wastewater should be processed before being disposed to the environment. Several technologies have been developed for removing heavy metal content in industrial liquid wastes. The adsorption method using solid adsorbent is a simple and effective method for separating heavy metal ions from electroplating wastes since they are eco-friendly and efficient. However, they produce secondary wastes and require high operational costs. The blending of cationic gel NIPAM-co-Chitosan and anionic gel NIPAM-co-Acrylic Acid is a potential candidate as a new alternative adsorbent. By this method, the secondary wastes can be eliminated, adsorbed ions simultaneously, and adsorb-desorb ions reversibly. NIPAM-co-Chi and NIPAM-co-Acrylic Acid are synthesized from a polymerization reaction using N, N, N', N'-tetramethylethylenediamine (TEMED) and sodium sulfite as accelerators, ammonium peroxodisulfate (APS) as an initiator, and N, N'-methylene bisacrylamide (MBAA) as a cross-linker. The gel was synthesized in a three-neck round flask for 6 hours. The product crush gel was then used for the adsorption and swelling degree test. The swelling degree test was performed by measuring the swelling gel volume before and after being soaked for 24 hours in target solutions. The gel obtained from the adsorption test was separated from the solution to be analyzed with Atomic Absorption Spectrophotometry (AAS). Based on the FTIR analysis of NIPAM-co-Chi and NIPAM-co-Acrylic Acid gels, there is no peak indicating the presence of vinyl C=C bonds. It can be concluded that the gel copolymer synthesis that was carried out was successful. The optimum results were obtained from the swelling degree analysis on electroplating waste at a concentration of 8:2.

1. Introduction

The rapid development of technology such as the automotive industry, electronic equipment, and construction has increased the demand for electroplating products. Meanwhile, the electroplating process itself produces waste containing heavy metal ions. Heavy metal ions in the waste are a serious problem if disposed of without pretreatment. Heavy metal ions are hazardous and toxic waste that could damage aquatic ecosystems and human life around them because they cannot be decomposed biologically [1].
One example of heavy metal ion pollution that attracted attention in Indonesia in 1996–2004 was the case of the Buyat Bay pollution. The pollution comes from mining activities on a large scale by PT. Newmont Minahasa Raya resulted in the marine ecosystem in Buyat Bay being damaged due to the discharge of 2000 tons of tailings every day [2]. In a study conducted by [3], the fish found in Buyat Bay contained types of heavy metals such as mercury 0.019 mg/kg, arsenic 0.5 mg/kg, cadmium 0.1 mg/kg, chromium 0.1 mg/kg, copper 1 mg/kg, and lead 0.1 mg/kg. The ion content has exceeded the maximum allowable limit in fishery products according to Indonesian National Standard (SNI) number 7387:2009. Water quality at any location close to the Industrial Estate has the potential to be polluted by heavy metal ions. In addition, according to the Governmental Regulation Number 82 of 2001, the quality of 30 rivers water in Indonesia did not qualify for the standard of drinking water first-class.

Various conventional methods have been carried out to regenerate heavy metal ions from solution, but these methods still have shortcomings. Some of these methods, such as precipitation and flotation, are uneconomical and produce large amounts of secondary waste and electrochemical, which require high operational costs. In addition, the coagulation method produces sludge. Ion exchange requires strong acid to regenerate the resin [4]. Of the methods described above, adsorption, especially biosorption, is the most effective and economical method [5]. One of the latest adsorption methods in separating heavy metals is by utilizing thermosensitive gel based on zwitterionic betaine [6]. According to [7], zwitterionic betaine is more promising in regenerating solid metal ions in waste because of the interaction between ions in waste and their positive and negative groups. However, one of the drawbacks of the zwitterionic betaine gel adsorption method is the presence of inter-intrachain associations limiting the gel's ability to absorb heavy metal ions.

Chitosan is a natural adsorbent for heavy metal ions such as Zn, Ni, Cu, Cr, and Pb. The amount of chitosan is abundant, placing it as the most abundant polymer after cellulose. Chitosan has high chemical reactivity due to amine and hydroxyl groups, so the use of chitosan in the adsorption process is extensive. Previous research conducted by [8] reported that desorption could be used to regenerate chitosan-based adsorbents. Low and high pH solutions can both be provided for the adsorption of cationic and anionic heavy metal compounds. The ions initially adsorbed cause a reverse reaction after the pH in the solution changes, resulting in the ions desorbed from the saturated adsorbent.

Acrylic acid is a weak acid that ionizes in water to form a carboxylic anion (-CH₂CHOO⁻) and is capable of binding water through hydrogen bonds. Poly(acrylic acid) contains a hydrophilic group (R-COOH) in its macromolecule which contributes to the exchange of cations in solution through the formation of a chelating complex with heavy metal ions [9]. NIPAM is a thermosensitive polymer with a transition temperature called LCST (Lower Critical Solution Temperature) at 32 °C [10]. NIPAM gel at temperatures below 32°C swells (hydrophilic), whereas the gel shrinks (hydrophobic) when it is above 32°C [11]. In the research by [9], poly(acrylic acid) are able to bind positive heavy metal ions such as lead(II) because of the anionic characteristics of carboxyl groups in their macromolecules.

Zwitterionic sulfobetaine polymer and gel have been studied numerously. However, the zwitterionic sulfobetaine has limited ability to adsorb ions from target solution as an adsorbent due to its inter-intra chain interaction [12][13][6][14][15]. Moreover, most previous researches on adsorbent gel only focused on the synthesis process and gel properties, including its thermosensitive and swelling degree [16].

Only a few studies have reported NIPAM copolymerization using chitosan and acrylic acid as the organic material. Therefore, this research utilized copolymers gel based on the blending cationic gel of NIPAM-co-Chi with anionic gel of NIPAM-co-AA. The gels are synthesized separately in order to reduce the entanglement resulted from the inter-interchain interaction. By this method, it is expected that the adsorption ability of the gel toward target ions (Cr⁶⁺) increases and heavy metal is adsorbed reversibly by temperature swing. Moreover, it is environmentally friendly since it does not cause secondary waste produced by the prior process and becomes more efficient and less expensive. This research investigates the effect of the ratio and temperature of the constituent monomers on the adsorption ability of the blend between NIPAM-co-Chi gel and NIPAM-co-AA gel. In addition, the swelling degree of the gel and adsorption isotherm is also elucidated.
2. Materials and method

2.1. Purification of N-isopropylacrylamide (NIPAM)

The primary monomer for copolymer gels employed in this research was N-isopropyl acrylamide synthesis (NIPAM; KJ Chemicals Co., Ltd., Japan). The purification of NIPAM was done through the recrystallization process using N-hexane. Initially, 510 mL of benzene and 300 grams of NIPAM were mixed until NIPAM was homogeneously dissolved. Next, the NIPAM and hexane solution was divided into six Erlenmeyer, then added with 1 L hexane. Then, the Erlenmeyer was covered with plastic film and placed inside the refrigerator for 24 h. The NIPAM crystal product is then separated with a vacuum filter and dried in a vacuum oven for two hours at 50°C. Finally, the crystal NIPAM produced was ready to be used for the synthesis of copolymers.

2.2. Synthesis of NIPAM-co-Chitosan (NIPAM-co-Chi) gel

The NIPAM-co-Chi gels were synthesized at various concentration ratios i.e., 6:4; 7:3; 8:2; 9:1 with total solution concentration of 1000 mmol/L. Furthermore, TEMED of 10 mmol/L and MBAA of 30 mmol/L were employed as the accelerator and cross-linker, respectively. In order to carry out this synthesis, a four neck flask filled with distilled water at 10°C was prepared. It was then continued by dissolving the materials including NIPAM, chitosan, MBAA, and TEMED accelerator into the flask until its total solution volume reached 100 mL through purging using N2 gas with a flow rate of 500 mL/min. After stirring this solution for 10 minutes, the monomer solution was further added by 2 mmol/L APS as an initiator in 20 mL distilled water by purging with N2 gas for 30 minutes. The cylinder mold was inserted once the solution had been thoroughly mixed. Polymerization reaction takes place for 6 hours.

2.3. Synthesis of NIPAM-co-Acrylic acid (NIPAM-co-AA) gel

The NIPAM-co-AA synthesis was done similarly to the NIPAM-co-Chi copolymers synthesis. However, in this case, the accelerator used was 10 mmol/L sodium sulfite (Na2SO3).

2.4. Adsorption analysis

In this study, the solution used in the adsorption process is electroplating waste obtained from the electroplating industry in Sidoarjo, East Java, Indonesia. The target solution for adsorption analysis is Cr6+ ion. The adsorption step is as follows: one gram of copolymer gel was added to a glass bottle containing 20 mL of a waste solution whose initial ion concentration has been analyzed previously by Atomic Absorption Spectroscopy (AAS). The glass bottles were then placed in a water bath and stirred for 3, 6, 9, and 12 hours at the temperature set to reach equilibrium adsorption. After the adsorption procedure, 10 minutes of centrifugation was done to separate the gel from the solution. Afterwards, a syringe filter was used to filter the gel. This solution was then analyzed using AAS to determine the ion concentration adsorbed by the copolymer gel. The time it takes to attain equilibrium adsorption is then utilized to assess the Cr6+ ions adsorption in the electroplating waste.

\[ Q = \frac{(C_o - C) \cdot V}{m} \]  

Where:

- \( Q \) : number of ions adsorbed by gel (mmol/gr)
- \( C_o \) : initial solution concentration (mmol/ml)
- \( C \) : solution concentration after adsorption (mmol/ml)
- \( V \) : total volume of solution (ml)
- \( m \) : gel’s weight (gr)

2.5. FTIR spectrum analysis

This analysis was done to identify the functional groups of constituent monomer and polymer products.
2.6. Swelling Degree (SD) analysis

In this research, the analysis of SD was done firstly by measuring the diameter of the gel cylinder to be inserted using a millimeter block at 70 °C and left for 24 hours to swell and reach equilibrium [17]. The calculation of SD was done by using the following equation:

\[
SD = \frac{d_{swell}^3}{d_{dry}^3}
\]  

(2)

According to the equation, dswell is the gel diameter after it reaches equilibrium swelling at a predetermined temperature (swollen gel diameter), while ddry is the dry gel diameter.

2.7. Visual analysis

The visual analysis aims to observe the transitions that occur before and after the gel is immersed inside the electroplating waste solution. An SLR camera interpreted images of copolymer gel at various temperatures of 10 °C, 30 °C, 50 °C, and 70 °C.

3. Result and discussion

This research aims to investigate isothermal equation adsorption Langmuir and Freundlich in adsorption of metal ions \(\text{Cr}^{6+}\) by copolymer gel of NIPAM-co-Acrylic acid (NIPAM-co-AA) by Atomic Absorption Spectroscopy (AAS). Results from AAS are then analyzed based on the empirical formula of Langmuir and Freundlich equations.

3.1. Adsorption analysis results

Some heavy metal ions in electroplating wastewater include iron, chromium, zinc, nickel, manganese, and copper. The quantity of waste generated in the electroplating process is not too large, but the level of toxicity is hazardous, especially chromium, nickel, and zinc [18]. The electroplating waste analysis using AAS in table 1 shows that the most dominating content in the sample is Chromium (Cr).

| No. | Metal Composition        | Analysis Results (ppm) |
|-----|--------------------------|------------------------|
| 1   | Zinc (Zn\(^{2+}\))       | 17.9                   |
| 2   | Nickel (Ni\(^{2+}\))     | 1336.47                |
| 3   | Copper (Cu\(^{2+}\))     | 19.84                  |
| 4   | Chromium (Cr\(^{6+}\))   | 2413.1                 |

Figure 1. Effect of time on \(\text{Cr}^{6+}\) adsorption on copolymer gels at 3, 6, 9, and 12 hours using blending gel concentrations ratio of 8:2 in electroplating waste solution.
Figure 1 shows the effect of adsorption time and the amount of Cr$^{6+}$ ions adsorbed in the first 24 hours. It can be seen that Cr$^{6+}$ ions adsorbed increased significantly in the first 6 hours. Then, it decreased slightly in the next 6 hours and remained constant in the remaining time. This can be explained because copolymer gel has a high adsorption ability in the first six hours. However, as time passed, the copolymer gel became saturated by ions. The results above determined that the time for the copolymer gel to reach adsorption equilibrium was above 12 hours. This study determined Langmuir and Freundlich isotherm equation in the Cr$^{6+}$ ions adsorption process from electroplating copolymer gel waste by blending NIPAM-co-Chitosan and NIPAM-co-AA gel. The method used to measure the adsorption process of Chrom metal is the Atomic Absorption Spectroscopy (AAS). The measurement results from the AAS were then analyzed further based on the empirical formula of the Langmuir and Freundlich equations. Results calculations as shown in tables 1 and 2.

| Time (hour) | Initial Cr$^{6+}$ (ppm) | Cr$^{6+}$ equilibrium (ppm) | Cr$^{6+}$ equilibrium (mg/g) |
|------------|--------------------------|-----------------------------|-------------------------------|
| 3          | 2513.1                   | 2453.4                      | 59.7                          |
| 6          | 2513.1                   | 564.10                      | 1948.99                       |
| 9          | 2513.1                   | 747.86                      | 1765.23                       |
| 12         | 2513.1                   | 709.40                      | 1803.69                       |

The adsorption isotherm model for Cr$^{6+}$ ions adsorption by copolymers gel was carried out using the Langmuir and Freundlich equations. The Langmuir Isotherm equation is as follows:

\[ Ce/(x/m) = 1/ab + 1/a Ce \]  

(3)

Meanwhile, for the Freundlich equation using equation:

\[ \log(x/m) = \log k + 1/n \log Ce \]  

(4)

Where:

- \( Ce = Cr^{6+} \) ions concentration in solution after being adsorbed
- \( x/m = \) mass of \( Cr^{6+} \) ions absorbed per gram of copolymer gel
- \( b = \) affinity parameter or Langmuir constant
- \( a = \) maximum adsorption capacity / power (mg/gram)

Values \( a \) and \( k \) indicate the adsorption capacity of \( Cr^{6+} \) by copolymer gels. The higher value of \( a \) in the Langmuir isotherm equation and \( k \) in the Freundlich isotherm equation shows higher adsorption capacity. The values of \( 1/ab \) and \( \log k \) are certainly strongly influenced by temperature, which affects the rate of adsorption. To determine the Langmuir and Freundlich isotherm equations, the values for \( x/m, Ce/(x/m) \), \( \log Ce/(x/m) \) and \( \log Ce \) are calculated as shown in table 3. From table 2, a graph was mapped using Excel to plot \( Ce/(x/m) \) versus \( Ce \) to obtain the Langmuir equation and plotted the \( \log (x/m) \) versus \( \log Ce \) to obtain the Freundlich equation.

| Time (hour) | Ce (ppm) | Co (ppm) | X/m | C/(X/m) | Logs (x/m) | Ce logs |
|-------------|----------|----------|-----|---------|------------|---------|
| 6 h         | 564.10   | 2513.1   | 38.97 | 14.47   | 1.59       | 2.75    |
| 9 h         | 747.86   | 2513.1   | 35.30 | 21.18   | 1.54       | 2.87    |
| 12 h        | 709.40   | 2513.1   | 36.07 | 19.66   | 1.55       | 2.85    |

An excellent linearization graph proved the Langmuir Isotherm adsorption equation and Freundlich Isotherm adsorption equation test and determination coefficient \( R^2 \) of 0.9 (close to 1). Based on lvs 1 and 2, it can be seen that the adsorption equation for \( Cr^{6+} \) ions by the green copolymer gel fulfills the
adsorption equation.

Langmuir Isotherm had $R^2$ of 0.999969, while Freundlich Isotherm had $R^2 = 0.99901$. This indicates that Langmuir and Freundlich equations can be applied to the adsorption process of Cr$^{6+}$ metal ions by copolymer gels. In Langmuir equation, $Ce/(x/m) = 0.03631 Ce + 6.02425$, while the Freundlich equation shows that $\log (x/m) = -2.87693 Ce + 7.32858$ and the constant values of the two equations are shown in Table 3 below.

![Figure 2. The Langmuir and Freundlich isothermal equation.](image)

Based on the Freundlich equation model, multiple surface layers (multilayer) and heterogeneous sides implied that the binding energy was varied on each side, whereas the adsorption process on each adsorption side follows the Langmuir isotherm. Therefore, the determination of the maximum adsorption ability of the copolymer gel in Cr$^{6+}$ adsorption process was obtained through the Langmuir adsorption equation, since it was done on a single layer of adsorbed substance from Cr$^{6+}$ ions on each copolymer gel surface in mg units of chromium metal ions adsorbed/gram copolymer gel.

3.2. FTIR spectrum analysis
3.2.1. FTIR spectrum of NIPAM-co-Chi gel

![Figure 3. FTIR Spectrum of NIPAM, Chitosan, NIPAM-co-Chi of 9:1; 8:2; 7:3 and 6:4.](image)
Based on the FTIR analysis of NIPAM-co-Chi in figure 3, a wavelength range of 4000 cm$^{-1}$ to 500 cm$^{-1}$ was used. For NIPAM-co-Chi of 9:1, T syn of 10°C, the N–H, C–H, C=O, C=O bonds are shown by the light blue line at the wavelength of 3269.97 cm$^{-1}$, 2971.77 cm$^{-1}$, 1170.52 cm$^{-1}$, and 1626.31 cm$^{-1}$, respectively. Meanwhile, for NIPAM-co-Chi of 8:2 with a T syn of 10°C, the N–H, C–H, C=O, and C=O bonds are shown by green line at the wavelength of 3271.9 cm$^{-1}$, 2969.46 cm$^{-1}$, 1173.49 cm$^{-1}$, and 1634.62 cm$^{-1}$, respectively. For NIPAM-co-Chi of 7:3 with T syn of 10°C, the N–H, C–H, C=O, and C=O bonds are shown by the yellow line at the wavelength of 3281.48 cm$^{-1}$, 2972.11 cm$^{-1}$, 1170.45 cm$^{-1}$, and 1624.61 cm$^{-1}$, respectively. Furthermore, the red line shows NIPAM-co-Chi of 6:4 with a T syn of 10°C, N–H, C–H, C=O, C=O bonds at wavelength 3281.23 cm$^{-1}$, 2969.46 cm$^{-1}$, 1171.61 cm$^{-1}$, 1630.89 cm$^{-1}$, respectively.

In the NIPAM FTIR results, the vinyl bond (C=C) was seen at a wavelength of 961.92 cm$^{-1}$ (figure 2), however from the FTIR analysis results of NIPAM-co-Chi, there was no peak in the wavelength range of 900-1000 cm$^{-1}$, indicating the absence of a vinyl group (C=C) in the NIPAM spectra. This indicates that the copolymerization reaction between NIPAM and Chitosan has been successfully carried out to form the NIPAM-co-Chi copolymer. The difference between the functional groups of each constituent of the monomer and copolymer gel is seen in the absence of a vinyl C=C group after polymerization, which determines the success of the copolymerization reaction. The vinyl bond (C=C) is shown at a wavelength range from 900 to 1000 cm$^{-1}$.

### 3.2.2. FTIR spectrum of NIPAM-co-AA gel

Based on the FTIR analysis of NIPAM-co-AA, a wavelength range of 4000 cm$^{-1}$ to 500 cm$^{-1}$ was used, since the reaction that occurs in NIPAM-co-AA synthesis is a polymerization reaction. For NIPAM-co-AA of 9:1 with T syn of 10°C, the N–H and C=O bonds are shown as the light blue line at wavelength of 3262.46 cm$^{-1}$ and 1636.2 cm$^{-1}$, respectively. Furthermore, for NIPAM-co-AA of 8:2 with a T syn of 10°C, N-H and C=O bonds are shown by the green line shown at a wavelength of 3263.12 cm$^{-1}$ and 1635.15 cm$^{-1}$, respectively. Meanwhile, for NIPAM-co-AA of 7:3 with a T syn of 10°C, N-H and C=O bonds are shown by the yellow line at a wavelength of 3268.42 cm$^{-1}$ and 1634.05 cm$^{-1}$, respectively.

Furthermore, for NIPAM-co-AA of 6:4 and T syn of 10°C, N-H and C=O bonds are shown as the
red line at a wavelength of 3273.12 cm\(^{-1}\) and 1624.7 cm\(^{-1}\), respectively. The synthesis of NIPAM-co-Chi and NIPAM-co-AA can be considered successful if there is no CH\(_2\) = CH vinyl group. However, sometimes unreacted monomers are still left in synthesis, so the C=C and C=O bonds remained are found in the FTIR analysis.

3.3. Swelling Degree Analysis

3.3.1. Swelling Degree of NIPAM-co-Chi gel

![Figure 5](image_url)

**Figure 5.** The effect of concentration on the swelling degree value of NIPAM-co-Chi at T syn of 10 °C.

Based on figure 5, it can be seen that NIPAM-co-Chi of 8:2 and T syn of 10°C with a swelling temperature (T swelling) of 10°C reached its optimum swelling degree. Based on the figure 5, it can be summed up that a high concentration of NIPAM and a low concentration of chitosan (9:1) does not produce a good swelling degree value. This is because the ability to bind ions to the gel is reduced so that even though the gel's ability to swell is high, the gel does not swell maximally. Likewise, with a low NIPAM concentration of 6:4 compared to chitosan, although the adsorption ability of chitosan is high, the gel's ability to swell is very low. This phenomenon is due to the thermosensitive nature of NIPAM in copolymer gel, i.e., change from hydrophilic to hydrophobic along with increasing temperature which causes NIPAM to shrink if the temperature is high. Such thermosensitive properties of NIPAM cause the decrease of swelling degree when it reaches a high temperature and cannot reach optimum swelling. Meanwhile, at a NIPAM: Chitosan ratio of 6:4, the swelling degree is minimal.

3.3.2. Swelling Degree of NIPAM-co-AA gel

![Figure 6](image_url)

**Figure 6.** The effect of concentration on the swelling degree value of NIPAM-co-AA at a T syn of 10 °C.
Figure 6 shows that the swelling degree is affected by temperature decrease, in which the higher the T swelling is, the smaller the swelling degree becomes. It can be concluded that with a high concentration of NIPAM, it does not produce a good swelling degree value because the ability to bind ions to the gel is reduced so that even though the ability of the gel to swell is high, the gel does not swell maximally. Likewise, with a low NIPAM concentration, the gel's ability to swell is very low despite the high adsorption ability of chitosan.

3.4 Visual Analysis

3.4.1 Visual Analysis of NIPAM-co-Chi gel

![Figure 7. NIPAM-co-Chi gel visual analysis at T swelling of 10°C.]

![Figure 8. NIPAM-co-Chi gel visual analysis at T swelling of 30°C.]

Figure 9. NIPAM-co-Chi gel visual analysis at T swelling of 50°C.

Figure 10. NIPAM-co-Chi gel visual analysis at a T swelling of 70°C.

Figure 7 indicates the visual result of NIPAM-co-Chi gel with concentration variables of 6:4, 7:3, 8:2, and 9:1 with a T swelling of 10°C. Furthermore, figure 8 shows the visual result of NIPAM-co-Chi gel of 6:4, 7:3, 8:2, and 9:1 with a T swelling of 30°C. Then, figure 9 shows the visual result of NIPAM-co-Chi gel of 6:4, 7:3, 8:2, and 9:1 with a T swelling of 50°C. In addition, figure 10 shows the visual result of NIPAM-co-Chi gel of 6:4, 7:3, 8:2, and 9:1 with a T swelling of 70°C. Based on those four figures, the visual difference between the gel before and after being immersed inside the electroplating waste solution was shown.

The T swelling can affect the gel visual, such as the size of the gel. At a T swelling of 10°C, the gel optimally expands as indicated by larger gel size (figure 6). At a T swelling of 30°C, the gel swelled but was less than optimal (figure 7), so that the gel size slightly increased. At a T swelling of 50°C, the gel did not swell, so that the size of the gel before and after swelling analysis did not change (figure 8). Similarly, at a T swelling of 70°C, the gel did not swell, so that the size of the gel before and after swelling analysis did not change (figure 9). This is because NIPAM has a transition temperature called
LCST (Lower Critical Solution Temperature) at 32°C. NIPAM gel at a temperature below 32°C swells. And vice versa, when the temperature is above 32°C, it shrinks [19].

The T swelling can also affect the color of the gel. At T swelling of 10°C, the color of the gel changed, of which before the gel was put inside electroplating waste, it had a brownish yellow color from the yellowish-brown color of chitosan, while after immersion inside the electroplating waste, the color became dark blue because it had been mixed with dark blue-colored electroplating waste (figure 7). At a T swelling of 30°C, the color of the gel changed slightly to brownish-yellow which was more concentrated than before being added to the electroplating waste solution (figure 8). At a T swelling of 50°C, the color of the gel before and after immersion inside the electroplating waste solution did not change (figure 9). Furthermore, at a T swelling of 70°C, the color of the gel changed, of which before being immersed inside the electroplating waste, the gel had a brownish yellow color from the yellowish-brown color of chitosan, while the gel after being immersed into the electroplating waste was brownish blue (figure 10) since it was mixed with the electroplating waste which was dark blue and possesses high temperature.

The difference in the concentration of NIPAM and chitosan composition also affects the color of the gel. The NIPAM-co-Chi gel with a T swelling of 10°C with a concentration of 6:4 had a blue color close to milky white after being immersed into electroplating waste. Meanwhile, the NIPAM-co-Chi gel with a concentration of 9:1 had a clear blue color or was nearly transparent after being immersed inside electroplating waste (figure 7). The NIPAM-co-Chi gel with a T swelling of 30°C with a concentration of 6:4 had a darker brownish-yellow color after being immersed inside electroplating waste. Meanwhile, the NIPAM-co-Chi gel of 9:1 had a light brownish yellow color after being immersed into electroplating waste (figure 7). Likewise, for the NIPAM-co-Chi gel with T swellings of 50°C and 70°C. The higher the concentration of NIPAM composition, the color of the gel formed becomes nearly transparent. Conversely, the smaller the concentration of the NIPAM composition is, the color of the gel formed will be close to a milky white color.

3.4.2. Visual Analysis of NIPAM-co-AA gel

![Figure 11. NIPAM-co-AA gel visual analysis at T swelling of 10°C.](image-url)
Figure 12. NIPAM-co-AA gel visual analysis at T swelling of 30°C.

Figure 13. NIPAM-co-AA gel visual analysis at T swelling of 50°C.
Figure 14. NIPAM-co-AA gel visual analysis at T swelling of 70°C.

Figure 11 shows the visual result of NIPAM-co-AA gel of 6:4, 7:3, 8:2, and 9:1 with a T swelling of 10°C. Figure 12 shows the visual result of NIPAM-co-AA gel with concentration variables of 6:4, 7:3, 8:2, and 9:1 with a T swelling of 30°C. Then, figure 13 shows the visual result of NIPAM-co-AA gel of 6:4, 7:3, 8:2, and 9:1 with a T swelling of 50°C. Furthermore, figure 14 shows the visual result of NIPAM-co-AA gel of 6:4, 7:3, 8:2, and 9:1 with a T swelling of 70°C. Based on these four figures, the visual difference between the gel before and after being immersed inside the electroplating waste solution was shown.

The T swelling can affect the visual gel, including the size of the gel. At a T swelling of 10°C, the gel significantly swelled as indicated by the larger gel size (figure 11). At a T swelling of 30°C, the gel swelled but was less than optimal (figure 12) so that the gel size only slightly increased. At a T swelling of 50°C, the gel did not swell so that the size of the gel before and after the swelling analysis did not change (figure 13). The same occurred at the T swelling of 70°C. This is because NIPAM has a transition temperature called LCST (Lower Critical Solution Temperature) at 32°C. NIPAM gel at temperatures below 32°C swells, and vice versa, when the temperature is above 32°C, it shrinks [19].

The T swelling can also affect the color of the gel. At a T swelling of 10°C, the gel color, which previously had a clear/transparent color from the transparent color of acrylic acid. However, after immersion inside the electroplating waste, the color became blue since it was mixed with the electroplating waste that had dark blue color (figure 11). At a T swelling of 30°C, the color of the gel remained transparent white after being immersed inside the electroplating waste solution (figure 12). At a T swelling of 50°C, the color of the gel before and after being added to the electroplating waste solution became white but not transparent/milky white (figure 13). And at a T swelling of 70°C, the gel color changed, of which before being immersed into the electroplating waste, the gel had a transparent white color. After immersion into the electroplating waste, it became milky white (figure 14) due to swelling at a high temperature.

In addition, there was an effect provided by NIPA concentration differences on the gel color. The NIPAM-co-Chi gel of 6:4 with a T swelling of 10°C had a blue color close to milky white after being immersed into electroplating waste. Meanwhile, the NIPAM-co-AA gel of 9:1 after being immersed inside electroplating waste had a clear blue color or was nearly transparent (figure 7). The NIPAM-co-AA gel of 6:4 with a T swelling of 30°C after being immersed inside electroplating waste had a clear white color. Furthermore, NIPAM-co-AA gel with a concentration of 9:1 had a clear transparent color after being immersed inside electroplating waste (figure 8). The higher the concentration of NIPAM composition is, the color the gel formed becomes nearly transparent.
4. Conclusion
FTIR spectrum analysis of the NIPAM-co-Chi and NIPAM-co-AA shows that the gels have several bonds including N-H, C-H, C=O, C-O, along with the absence of vinyl C=C bonds. Therefore, it can be concluded that the NIPAM-co-Chi and NIPAM-co-AA was successfully synthesized. The higher the ratio of NIPAM monomers is, the properties of NIPAM tend to dominate so that when the copolymer temperature is under LCST, it is hydrophilic, and above LCST, it is hydrophobic, as seen from the change of the transparent gel to milky white. The results of the swelling degree analysis of NIPAM-co-Chi and NIPAM-co-AA were optimum at a concentration of 8:2, synthesized at 10 °C with a T swelling of 10°C. In comparison, the concentration of NIPAM that is too high or too low compared to chitosan or acrylic acid did not produce the optimum swelling degree due to the reduced ability to bind ions in the gel.

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