Thermosensitive and chitosan of crab (*Portunus pelagicus*) shells gel based adsorbent for reversible adsorption-desorption of several toxic metal ions

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**Abstract.** Indonesia experiences environmental pollution because of wastewater treatment problems. Such occurrence is affected by the heavy metal waste produced by the electroplating industry, one of them is ferrous and nickel. Thus, heavy metal waste needs to be regenerated through a method by using zwitterionic betaine gel. However, this method has weakness in the form of intra-intrachain associations which occurs and becomes the obstacle for the ionic group's ions adsorption ability by the charge group interaction. The purpose of this research was to increase the adsorption ability of the gel by removing the intra-intrachain copolymers association through conducting a synthesis of both the anionic gel N-isopropyl acrylamide (NIPAM) copolymerized with acrylic acid (NIPAM-co-acrylic acid) and cationic gel (NIPAM-co-chitosan), separately. The synthesis of the gels was conducted through a polymerization reaction using accelerator in the form of N,N,N',N'-tetramethylethylenediamine (TEMED), an initiator ammonium peroxodisulfate (APS) and a cross-linker in the form of N,N'-methylenebisacrylamide (MBAA). In this research, the metal ions adsorption by pH-thermosensitive gel was conducted in various pH and weight balance between NIPAM-co-anionic and NIPAM-co-cationic gel provided. The effects of the temperature and the conditions provided in the gel preparation were also investigated, including the effect of monomer concentration on the metal ions adsorption on the gel. The gel adsorption behavior is discussed by considering the swelling degree of the gel as well as the transition temperature of poly(NIPAM-co-chitosan) and poly(NIPAM-co-acrylic acid). According to the results of FTIR analysis, the vinyl group peak of the copolymer gel decreased compared with that of its constituent monomers, thus the copolymers synthesis was successful. Meanwhile, based on the swelling degree test using the electroplating waste solution, the higher the solution’s temperature, the lower the gel’s swelling degree. In addition, the higher synthesis temperature also caused the occurrence of gel porous. The adsorption ability of the gels that have positive and negative charge groups synthesized separately is better than zwitterionic gels. The gel can adsorb more heavy metal ions at higher adsorption temperatures.

1. **Introduction**

The rapid technology development in the industry produces an increase in product demand which requires an electroplating process. Therefore, it encourages the electroplating industry to produce products as consumer requests. This results in the increasing number of product demand which
requires an electroplating process. The increase in the electroplating industry also increases the heavy metal waste. The presence of heavy metals, especially the liquid waste form, becomes a problem that must be taken care seriously since it produces hazardous and toxic substances that can damage the aquatic ecosystem and its surrounding human life [14]. This toxicity results in acute and chronic poisoning. Recently, many cheaper and more effective approaches have been studied for technology development in order to decrease the amount of wastewater produced and increase the quality of effluents processed. Adsorption becomes one of the alternative treatments in the past years which has an intensified metal binding capacity [6]. Adsorption is a separation process of equilibrium recognized as an effective, efficient and economical method for water decontamination and analytical separation application.

Studies of the reduction of heavy metals by sulfobetaine zwitterionic polymer and gel have been carried out by several researchers previously. In general, zwitterionic betaine polymer has thermosensitive properties in aqueous solutions, thus when it is under Under Upper Critical Solution Temperature (UCST), Zwitterionic betaine polymers cannot dissolve in water, but it will dissolve at temperatures above UCST. At temperatures below UCST, collapsed coil due to the intra- and/or inter-chain interactions will happen by zwitterionic polymer. However, at temperatures above UCST, intra- and/or inter-chain interactions will be hampered due to the presence of thermal energy [15]. The polymer concentration and UCST are directly proportional, so the higher the concentration of the polymer, the higher enhancement the UCST of the zwitterionic polymer will be. An overcome of the enhancement in intra- and/or inter-chain interactions require higher thermal energy [15,16]. Poly (N-isopropyl acrylamide) or poly(NIPAM) is an example of thermosensitive polymers with a Low Critical Solution Temperature (LCST) of around 32°C [9]. NIPAM has a neutral charge so that it can transition from hydrophilic to hydrophobic and experience swelling at low temperatures and shrinking at high temperatures [1]. Most studies of sulfobetaine zwitterionic only emphasize on the synthesis and properties of polymer and gel solutions, for example, thermosensitive gel properties and swelling degrees.

The adsorption ability of poly(DMAAPS) towards metal ions was found to be strongly dependent on the charge groups forming an ionic association (intra- and/or inter-chain association) with the metal ions, which also significantly affected their swelling and transition behavior [5]. DMAAPS was prepared differently from chitosan. N,N-dimethylaminopropylacrylamide (DMAPAA) and 1,3-propane sulfone (PS) are reacted through ring-opening reaction using the same method as in our previous study [2,4].

In Bagus and Chynintya’s research [1] regarding the synthesis and characterization of NIPAM-co-DMAAPS copolymer properties, it used a variation of monomer concentration ratio of NIPAM:DMAAPS, which are 9:1, 8:2 and 7:3 using a solution of Zn(NO₃)₂ [1]. From the research that has been carried out, it is known that at the ratio of 9:1 of monomer concentration, the thermosensitive phase transition properties of copolymers LCST in Zn(NO₃)₂ solution is 56°C. Meanwhile, at 8:2 and 7:3 monomer ratios, it is not detected. In the NIPAM-co-DMAAPS copolymer, the ions carried on by the copolymer are neutral ions so that the absorption of positive and negative ions in the waste solution resulting from the electroplating production process can be absorbed well from various sides of the ions contained in the waste. The poly(DMAAPS-co-NIPAM) has an intra-intrachain association so that the ionic group can be used to adsorb ions but its adsorption ability is hampered by the charge group interaction. In order to avoid the intra-intrachain association, gels are synthesized separately using NIPAM-co-chitosan and NIPAM-co-acrylic acid because NIPAM-co-chitosan tends to contain ions with positive charges, while NIPAM-co-acrylic acid contains ions with negative ions. When the gel is used to adsorb an electroplating waste, competition occurs between the ions from the polymer and ion from the waste solution. The NIPAM polymerization research with organic chitosan and acrylic acid material has not been developed much before. NIPAM gel is unique since it has a hydrophilic property at low temperatures and hydrophobic property at high temperatures in water so it can be used as an ion absorption agent with temperature changes. The purpose of this research is to increase the adsorption ability of the gel
by removing the intra-intrachain copolymers association through conducting a synthesis of both the anionic gel (NIPAM-co-acrylic acid) and cationic gel (NIPAM-co-chitosan), separately. So we developed a gel adsorbent to adsorb and regenerate heavy metal waste based on natural materials of NIPAM-co-chitosan and NIPAM-co-acrylic acid polymers. Heavy metals will be adsorbed reversibly. The comparison of the gel copolymer monomers concentration aims to increase the selectivity and quality of the heavy metal ions adsorption from electroplating waste. This hydrogel can remove metal ions in the form of hydroxides, anions, such as arsenic acid, nitrate acid and sulfate acid by adsorption on protonated amino groups. Besides being efficient and inexpensive, this adsorbent can also eliminate the secondary waste generated from the previous method.

Therefore, we developed a reversible and porous adsorbent gel to adsorb and regenerate heavy metal waste based on natural materials and thermosensitive NIPAM-co-chitosan and NIPAM-co-acrylic acid gels. Heavy metals were adsorbed reversibly with changes in temperature and pH. This adsorbent can also eliminate secondary waste so that it is more efficient and cheaper.

2. Experimental Section

In this research, the materials used are N-isopropyl acrylamide (NIPAM), chitosan, acrylic acid, N,N,N',N'-tetramethylethylenediamine (TEMED) accelerator, sodium sulphite (Na$_2$SO$_3$), ammonium peroxodisulfate (APS) initiator, N,N'-methylenebisacrylamide (MBAA) crosslinkers, Benzene and N-hexane for the purification process of NIPAM, distillate water, nitrogen gas, and electroplating waste solution. Meanwhile, the tools used are polymerization reactor, magnetic stirrer, water bath, nitrogen tube, nitrogen inlet, stirrer, temperature controller, initiator in, heating mantle, distillation flask, Liebig condenser, Erlenmeyer, thermometer, retort stand, and clamp holder.

The N-isopropyl acrylamide synthesis (NIPAM; KJ Chemicals Co., Ltd., Japan) is the primary monomer for gel copolymers that was purified using the N-hexane gel recrystallization method. Meanwhile, the synthesis of acrylic acid for gel copolymers was purified using a distillation method. The process of making NIPAM-co-chitosan gel copolymers is N-isopropyl acrylamide (NIPAM), chitosan, N, N'-methylenebisacrylamide (MBAA), and N, N, N', N'-tetramethylethylenediamine (TEMED) were dissolved in demineralized water until the solution volume reaches 100 ml. Then, the solution was poured into a four-necked separable reactor whose temperature was set using temperature controller so that it is consistent on variables of temperatures of 10°C and 50°C. The solution is purged using ultra-high purity nitrogen gas to remove the oxygen contained in it for 10 minutes. Then, ammonium peroxodisulfate (APS) that was dissolved in distilled water of 20 ml was added into the initiator flask to be purged with nitrogen gas for 30 minutes. Then, the purged ammonium peroxodisulfate (APS) solution was mixed into the monomer solution while remaining purged with nitrogen gas. After the solution was mixed homogeneously, insert the cylinder mold and wait for 6 hours. The polymerization reaction takes place at temperatures of 10°C and 50°C. The making of NIPAM-co-acrylic acid copolymers is the same as the making of NIPAM-co-chitosan copolymers which is technically only different in the use of accelerators using sodium sulfite (Na$_2$SO$_3$) and initiators using ammonium persulfate (APS). The condition of the gel copolymers synthesis can be seen in the following table:

| Component   | Concentration (mmol/L) |
|-------------|------------------------|
| Monomer     |                        |
| NIPAM       | 800 600                |
| Chitosan    | 200 400                |
| Linker      |                        |
| MBAA        | 30                     |
| Accelerator |                        |
| TEMED       | 10                     |
| Initiator   |                        |
| APS         | 2                      |
Table 2. The Condition of NIPAM-co-acrylic acid gel copolymers synthesis

| Component | Concentration (mmol/L) |
|-----------|------------------------|
| Monomer   |                        |
| NIPAM     | 800 600                |
| Acrylic Acid | 200 400        |
| Linker    |                        |
| MBAA      | 30                     |
| Accelerator |                |
| Na₂SO₃    | 10                     |
| Initiator |                        |
| APS       | 2                      |

The gel formation reaction occurs for about 30 seconds and after the polymerization reaction, the gel formed in the cylindrical mold was cut off. The NIPAM-co-chitosan and NIPAM-co-acrylic acid gel copolymers were then washed with distilled water and dried for several days on Teflon paper spread on the petri dish. Petri dish was covered by plastic films that have been given small holes to reduce evaporation. This aims to prevent the occurrence of cracks in the gel by reducing the rate of drying. Then, the Fourier-transform Infrared Spectroscopy (FTIR) test was used to identify the functional groups in the compounds contained in the gel. In addition, a swelling degree test was used to measure the gel's ability in swelling in electroplating waste which was calculated using the equation:

\[
\text{Swelling Degree} = \frac{d_{\text{swell}}}{d_{\text{dry}}} \tag{1}
\]

In which \(d_{\text{swell}}\) shows the gel diameter which has reached the equilibrium swelling on a certain temperature (diameter of swollen gel) while \(d_{\text{dry}}\) shows the dry gel diameter.

3. Results and Discussion

**Scanning Electron Microscopy (SEM) Analysis**

Figure 1 shows the SEM images of NIPAM-co-chitosan with NIPAM:chitosan concentration of 8:2 with the synthesis temperature of 50°C. The image is an SEM image with a magnification of 500x. It can be seen that in the synthesis of a temperature of 50°C, there is a presence of porosity and aggregate. The formation of porosity occurs due to several things such as increased polymerization due to a decrease in solubility between NIPAM and chitosan, as it is known that NIPAM is LCST at 32°C, while chitosan dissolves in organic acid solution. Therefore, when the temperature of the synthesis was further away from the LCST, more porous was formed.
Fourier Transform Infra-Red (FTIR) Analysis

For FTIR NIPAM-co-acrylic acid analysis in the variable NIPAM concentration: 8:2 and 6:4 acrylic acid synthesized at 10°C, a 4000 cm⁻¹ wavelength range of up to 500 cm⁻¹ was used because of the reaction synthesis of NIPAM-co-acrylic acid is a polymerization reaction. In Figure 2 (▲), the FTIR result of NIPAM-co-acrylic acid with NIPAM:Acrylic acid concentration is 8:2 synthesized at 10°C, O-H bond is shown at a wavelength of 3359.64 cm⁻¹. The C-H bond is shown at a wavelength of 1722.99 cm⁻¹. In Figure 2 the red wave (■) is the FTIR result of NIPAM-co-acrylic acid with NIPAM:Acrylic acid is 6:4 with synthesized at 10°C, O-H bond is shown at a wavelength of 3347.82 cm⁻¹. The C-H bond is shown at a wavelength of 1721.125 cm⁻¹. Compared with NIPAM waves (purple, ●) and acrylic acid (blue, ●), FTIR NIPAM, which is a vinyl bond group C =O and C =C contained in the NIPAM waves and acrylic acid. The synthesis of NIPAM-co-acrylic acid in the ratio of concentrations of 8:2 and 6:4 at a temperature of 10°C can be successful because there are no vinyl group bonds discovered.

Figure 2. Result of FTIR of NIPAM-co-acrylic acid with concentration variables
Figure 3. Result of FTIR of NIPAM-co-chitosan with concentration variables

In Figure 3, the green wave (●) is the result of FTIR from NIPAM-co-chitosan with NIPAM:Chitosan concentration is 8:2 synthesized at 10°C, O -H bond is shown at a wavelength of 3271.9 cm⁻¹. The C – H bond is shown at a wavelength of 2969.46 cm⁻¹. Furthermore, the presence of C =O bonds is indicated by a wavelength of 1634.62 cm⁻¹. In Figure 3 the red wave (●) is the FTIR result of NIPAM-co-chitosan with the concentration of NIPAM:Chitosan is 6:4 synthesized at a temperature of 10°C, the C =O bond is shown with a wavelength of 1630.89 cm⁻¹. Compared with NIPAM waves (purple, ●) and chitosan (blue, ●), FTIR NIPAM-co-chitosan analysis results at a ratio of 8:2 and 6:4 with a synthesis of 10°C there is no vinyl group bond C =C contained in the NIPAM and chitosan waves but there are still vinyl group bonds C =O. The synthesis of NIPAM-co-chitosan at a concentration ratio of 8:2 and 6:4 synthesized at 10°C can be said to succeed if there is no vinyl group. But synthesis can also occur but not all vinyl reacts, so the FTIR test is still found in vinyl group bonds C =O.
Figure 4. Result of FTIR of NIPAM-co-acrylic acid with temperature variables

In Figure 4, the green wave (▲) is the FTIR result of NIPAM-co-acrylic acid with NIPAM:acrylic acid concentration is 8:2 synthesized at 10°C, O-H bond is shown at wavelength 3359.64 cm⁻¹. The C–H bond is shown at a wavelength of 1722.99 cm⁻¹. In Figure 4 the red wave (■) is the FTIR result of NIPAM-co-acrylic acid with NIPAM:acrylic acid concentration is 8:2 synthesized at 50°C, C–H bond is shown at a wavelength of 1718.63 cm⁻¹. Compared to NIPAM waves (purple, ●) and acrylic acid (blue, ◆), FTIR of NIPAM-co-acrylic acid analysis results at a ratio of 8:2 synthesized at temperatures of 10°C and 50°C there are no vinyl group bonds C =O and C =C contained in the NIPAM and acrylic acid waves. So the synthesis of NIPAM-co-acrylic acid at a concentration ratio of 8:2 synthesized at temperatures of 10°C and 50°C can be said to be successful because there are no vinyl group bonds.
In Figure 5, the green wave (▲) is the result of FTIR from NIPAM-co-chitosan with NIPAM:Chitosan concentration is 8:2 synthesized at 10°C. O-H bond is shown at a wavelength of 3271.9 cm\(^{-1}\). The C-H bond is shown at wavelengths of 2969.46 cm\(^{-1}\) and 1385.08 cm\(^{-1}\). Furthermore, the presence of C=O bonds is indicated by a wavelength of 1634.62 cm\(^{-1}\). In Figure 5 the red wave (■) is the result of FTIR from NIPAM-co-chitosan with the concentration of NIPAM:Chitosan is 8:2 synthesized at a temperature of 50°C. C-H bond is shown at wavelength 1454.15 cm\(^{-1}\). The C=O bond is indicated by a wavelength of 1632.13 cm\(^{-1}\). Compared to the NIPAM waves (purple, ●) and chitosan (blue, ◆), the results of FTIR NIPAM-co-chitosan analysis at a concentration ratio of 8:2 synthesized at temperatures of 10°C and 50°C there are no vinyl group bonds C=C contained in the NIPAM and chitosan waves but there are still vinyl group bonds C=O. The synthesis of NIPAM-co-chitosan at a concentration ratio of 8:2 synthesized at temperatures of 10°C and 50°C can be said to succeed if there is no vinyl group. But synthesis can also occur but not all vinyl reacts, so the FTIR test is still found in vinyl group bonds C=O.
Swelling Degree Analysis

Figure 6. The effect of concentration on swelling degree value on NIPAM-co-chitosan concentration of 8:2 and 6:4 at a temperature of 10°C.

Figure 7. The effect of temperature on swelling degree value on NIPAM-co-chitosan concentration of 8:2 at a temperature 10°C and 50°C.

From Figures 6 and 7, it is seen that the best swelling degree of NIPAM-co-chitosan is 8:2 at a temperature of 10°C with a swelling temperature of 10°C. From Figure 6, it can be concluded that the higher the concentration of NIPAM, the higher the swelling degree value. This is due to the nature of thermosensitive NIPAM on gel copolymers which have hydrophobicity to temperature changes, where at high temperatures NIPAM gel will shrink [18]. It is the nature of the thermosensitive NIPAM that causes the swelling degree value at high temperatures to decrease and cannot experience maximum swelling.
Figure 8. The effect of concentration on swelling degree value on NIPAM-co-acrylic acid concentration of 8:2 and 6:4 at a temperature of 10°C.

Figure 9. The effect of temperature on swelling degree value on NIPAM-co-acrylic acid concentration of 8:2 at temperature 10°C and 50°C.

From Figures 8 and 9, it is seen that the best swelling degree of NIPAM-co-acrylic acid is 8:2 at a temperature of 10°C with a swelling temperature of 10°C. From Figure 8, it can be concluded that the higher the concentration of NIPAM, the higher the swelling degree value. This is due to the nature of thermosensitive NIPAM on gel copolymers which have hydrophobicity to temperature changes, where at high temperatures NIPAM gel will shrink [18]. It is the nature of the thermosensitive NIPAM that causes the swelling degree value at high temperatures to decrease and cannot experience maximum swelling.
Adsorption Equilibrium

Figure 10. Effect of time on gel copolymer adsorption with variations of time 3, 6, 9, and 12 hours at gel concentration 8: 2 in electroplating waste solution

Figure 10 shows the relationship between the time of gel copolymer adsorption with the amount of adsorption of Ni$^{2+}$ ions in susceptible adsorption time of 0-24 hours. In the first 6 hours, the number of adsorbed Ni$^{2+}$ ions increased significantly, then 6-12 hours slightly experienced a subsequent decrease in constant. This is because, during the first 6 hours the gel copolymer has high gel copolymer adsorption power, but with increasing time the gel copolymer bond in adsorbing is increasingly saturated. From the results above it is determined that the time for gel copolymers to achieve equilibrium adsorption is above 12 hours. From the results of adsorption equilibrium it is determined that the time for gel copolymers to achieve equilibrium adsorption is above 12 hours.

Adsorption ability of NIPAM-co-chitosan and NIPAM-co-acrylic acid gel

Figure 11. The amount of Ni (II) and Fe (II) ions adsorbed onto the gel monomer concentration 9:1 in solution at various temperatures

Figure 12. The amount of Ni (II) and Fe (II) ions adsorbed onto the gel monomer concentration 8:2 in solution at various temperatures
Figure 13. The amount of Ni (II) and Fe (II) ions adsorbed onto the gel monomer concentration 7:3 in solution at various temperatures.

Figure 14. The amount of Ni (II) and Fe (II) ions adsorbed onto the gel monomer concentration 6:4 in solution at various temperatures.

Figure 11-14 shows that the greatest amount of Fe$^{2+}$ ions absorbed into the gel occurs in the gel on monomer concentration 6:4 at a temperature of 50°C as much as 0.122 mmol /g gel. At 50°C NIPAM shrink as shown in Figure 6-9. The amount of ions absorbed is greater than that absorbed by NIPAM-co-DMAAPS as did Bagus and Chinintya [1]. In Bagus and Chinintya's research [1] the best temperature to absorb more ions occurs at the lowest temperature (10°C) because at that temperature NIPAM as a spacer agent swells according to its natural properties. In this study, more ions are absorbed in 50°C proving that the inter/intra-chain bonds that inhibit ionic binding have no significant effect even though NIPAM with more amounts than other monomers shrinks. When the temperature rises to 70°C a force occurs which causes bonds between the ion charged group and the heavy metal ions weaken.

While in Ni metal ions, ideal conditions occur at the same temperature which is 50°C but the NIPAM concentration is greater that is 8:2. The ideal conditions of Fe and Ni are certainly different due to the influence of the Hofmeister cation sequence. The number of ions absorbed under the same operating conditions by Fe is greater because Ni$^{2+}$ ions have a large hydration ability so that the bonding ability with metal ions is smaller. When compared with Fe$^{2+}$ and Ni$^{2+}$, the Fe$^{2+}$ radius is much larger than the Ni$^{2+}$ radius, so that Fe$^{2+}$ metals more easily absorb ions than Ni$^{2+}$ [19].

4. Conclusions

Based on the discussion of FTIR analysis, vinyl groups were still found but in a small number. It can be considered that the synthesis of copolymers was qualified because the final results of the synthesis formed a gel even though not all vinyl reacted. Meanwhile, based on the swelling degree test, the higher the temperature of the solution, the lower the swelling degree value. In addition, the formation of porosity occurred because of the higher temperature of the synthesis. The adsorption ability of the gels that have positive and negative charge groups synthesized separately was better than zwitterionic gels. The gel can adsorb more heavy metal ions at higher adsorption temperatures.
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