International Journal of Technology 11(2) 299-309 (2020)
Received January 2020 / Revised February 2020 / Accepted March 2020

International Journal of Technology

http://ijtech.eng.ui.ac.id

The Effect of Synthesis Condition of the Ability of Swelling, Adsorption, and Desorption of Zwitterionic Sulfobetaine-Based Gel

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Abstract. This study explored the ion adsorption of heavy metals using a copolymer gel containing zwitterionic betaine *N,N'*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) as the ion adsorbent agent and *N*-isopropylacrylamide (NIPAM) as the thermosensitive agent. We investigated the effect of ion monomer concentration and type and of temperature on the adsorption, desorption, and swelling properties and their correlation. A free-radical polymerization reaction was performed to prepare the thermosensitive NIPAM-co-DMAAPS gel using accelerators such as *N,N,N',N'*-tetramethylethylenediamine, ammonium peroxydisulfate as the initiator, and *N,N'*-methylenebisacrylamide at a concentration of 10 mmol/L as the cross-linker. An analysis was then performed on the gel's adsorption, desorption, and reversible adsorption-desorption properties using atomic absorption spectrophotometry. The results showed that the swelling degree and adsorption values increased as the temperature decreased in the gel with NIPAM:DMAAPS ratios of 9:1 and 8:2. In contrast, in a 7:3 ratio, the swelling degree increased significantly, and the adsorption ability decreased as the temperature increased. The higher the temperature, the smaller the quantity of Zn^{2+} and Pb^{2+} ions adsorbed and desorbed. The results indicate that in nitrate solution, Pb^{2+} ions are more easily adsorbed than Zn^{2+} ions.

Keywords: Adsorption; Desorption; Swelling; Thermosensitive

1. Introduction

Industrial development leads to increasing metal concentrations in the environment. This is a serious problem, given that heavy metals are non-biodegradable and persistent. Therefore, above certain concentrations, they harm aquatic ecosystems and human health. Various technologies have been successfully developed to decrease the heavy metal contents of industrial liquid waste.

One of these technologies is a conventional method of chemical precipitation and neutralization (El Samrani et al., 2008; Amaral Filho et al., 2016) . Although this method is commonly used, it can produce other waste in the form of sludge containing high heavy metal ion concentrations. Other methods are reverse osmosis (Chan and Dudeney, 2008),

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doi: 10.14716/ijtech.v11i2.3860

and nanofiltration (Cséfalvay et al., 2009), which involve separating the heavy metal content in liquid waste using membranes. However, such methods require high operational costs. In addition, using adsorbent-containing ligands, such as ion-exchange or chelating groups, also requires a strong acid or base in the process of cation or anion resin regeneration. This is a disadvantage because if the process is unsuccessful, it produces secondary waste in the form of a strong acid or base (Qdais and Moussa, 2004).

Kusrini et al. (2018) applied an adsorption technique with maximum iodine absorbance of 572.2 mg/g to remove commercial lanthanide ions from an aqueous solution using an adsorbent in the form of activated carbon extracted from a banana peels. Olufemi and Eniodunmo (2018) reported the adsorption of nickel (II) ions from aqueous solutions using banana peels and coconut shells. The optimal conditions were an adsorbent dose of 4.5 g, 120 minutes of contact time, and 25°C for the banana peels and an adsorbent dose of 4.5 g, 30 minutes of contact time, and 25°C for the coconut shells. The adsorption was better determined by the Langmuir isotherm, with coefficient of correlation values of 0.9821 for the banana peels and 0.9744 for the coconut shell.

Another adsorption method involves the use of a thermosensitive gel in the form of zwitterionic betaine, which can bind the anions and cations in liquid waste simultaneously (Ningrum et al., 2015 ; Ningrum et al., 2019a; Ningrum et al., 2019b). An interaction between negative and positive charges in the same repetition unit in zwitterionic sulfobetaine causes ion selectivity, making this method more attractive than others (Neagu et al., 2010). In general, zwitterionic betaine polymers are thermosensitive in water. They do not dissolve even at temperatures above the upper critical solution temperature (UCST). This means that when they are below the UCST and in water, they undergo coil collapse due to inter- and intra-chain interactions. Above the UCST, the inhibition caused by the inter- and intra-chain interactions can be overcome by the thermal energy produced. The increase in zwitterionic polymer concentration causes an increase in intra- and/or inter-chain interactions in the polymer, and thus higher thermal energy is needed to overcome the interaction, causing the polymer's UCST to increase (Takahashi et al., 2011). Zwitterionic betaine properties is also affected by interactions between zwitterionic containing charged groups and aqueous salt solutions (Kudaibergenov et al., 2006). Poly(*N*-isopropylacrylamide) (poly[NIPAM]) is a polymer with thermosensitive properties characterized by a low critical solution temperature (LCST) of 32°C (Ningrum et al., 2017a). NIPAM has a neutral charge and swells at low temperatures and shrinks at high temperatures because it changes from hydrophilic to hydrophobic.

Zwitterionic polymers have great potential in a wide range of biological and medical applications, such as antifouling coatings (Guo et al., 2015), blood contacting sensors (Yang et al., 2011; Joshi et al., 2015), drug delivery in vivo (Fang et al., 2011; Cao et al., 2012), separation membranes (Hadidi and Zydney, 2014; Tu et al., 2015), marine coatings (Aldred et al., 2010; Zheng et al., 2017), catalysts (Ajmal et al., 2015), and absorption dyes (Sahiner and Demirci, 2017). Liu et al. (2005) used a hybrid zwitterionic polymer for ion exchange membranes synthesized by sol–gel process on *N*-[3-(trimethoxysilyl) propyl] ethylene diamine, with 3-glycidoxypropyltrimethoxysilane, and by a reaction with γ-butyrolactone.

Ningrum et al. (2017b) conducted a study on the effect of monomer concentration on the adsorption and desorption properties of thermosensitive NIPAM and *N,N'*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) gel, comparing NIPAM:DMAAPS monomer ratios of 2:8, 1.5:8.5, and 1:9. The temperatures used during desorption and adsorption were 10, 30, 50, and 70°C, while the solution used was $NaNO_3$. The results showed that the higher the concentration and temperature of the $NaNO_3$ solution, the lower the NIPAM monomer concentration in the NIPAM-*co*-DMAAPS gel. In another study, Ningrum et al. (2020a) investigated the properties of an NIPAM-*co*-DMAAPS polymer gel, such as transition temperature, molecular structure, viscosity in water and $Zn(NO_3)_2$ solutions, and adsorption behavior. The poly (NIPAM-*co*-DMAAPS) in both water and the $Zn(NO_3)_2$ solution demonstrated a transition period of LCST. The higher the NIPAM monomer ratio, the lower the polymer's LCST. In addition, its transition temperature with a lower NIPAM concentration was not verified either in water or in the $Zn(NO_3)_2$ solution. Moreover, the higher the NIPAM concentration used in the preparation, the higher the polymer's viscosity, and the higher ion adsorption onto the gel, the higher the polymer transmittance.

Several studies have explored the copolymerization of polymers and thermosensitive zwitterionic sulfobetaine. The use of zwitterionic polymers can improve the selectivity of ions against adsorption since the cations and anions in the solution bind through both negative and positive charges (Ningrum, 2019; Ningrum et al., 2020b). These studies, however, generally focused only on the synthesis of gel and its properties. Therefore, this research aimed to improve the adsorption capability of gel by employing NIPAM and DMAAPS and copolymerizing them in various molar ratios such as 9:1, 8:2, and 7:3. DMAAPS was used as the ion adsorption agent because of its charged groups, while NIPAM acted as the desorption agent because it can change from hydrophilic to hydrophobic. NIPAM fills the space between DMAAPS molecules in the copolymer and allows further distances between them. Consequently, the interaction between charged groups of DMAAPS is weakened. The weak interaction between the charged groups causes the ions in the solution to pair easily with charged groups, as they are not engaged in inter- or intra-chain or intra-group interactions. Since they can adsorb and desorb ions, the gels can be used in reverse. In addition, at higher NIPAM concentrations, the gel is expected to be have higher swelling ability that will maximize the desorption and adsorption efficiency of the gel. In light of this, the effects of time, temperature, and monomer concentrations on the swelling degree, adsorption, and desorption in $Zn(NO_3)_2$ and $Pb(NO_3)_2$ solutions were investigated. The reversible adsorption-desorption of Zn^{2+} and Pb^{2+} in an aqueous solution with an NIPAM-*co*-DMAAPS gel were also examined.

2. Methods

2.1. Materials

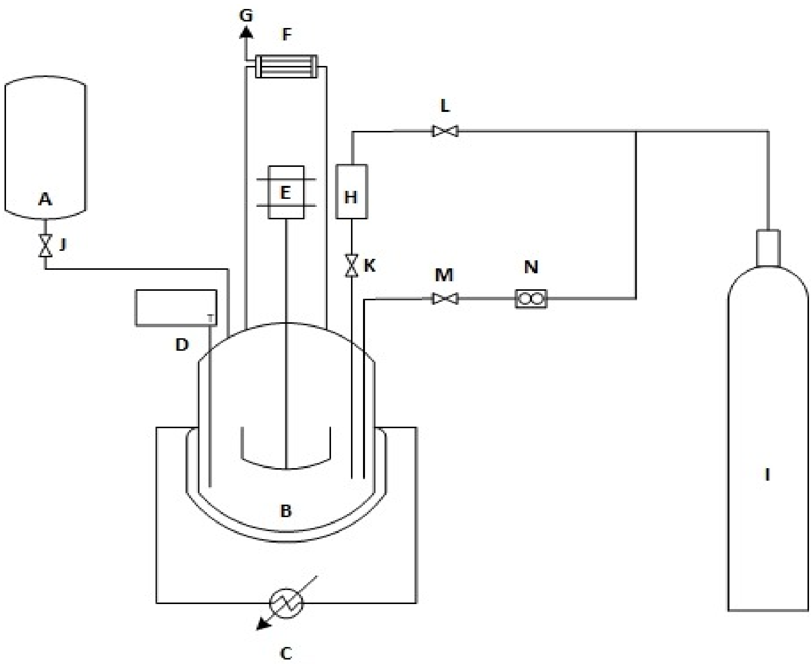
NIPAM (KJ Chemicals Co., Ltd., Japan) was synthesized for the gel copolymer. *N*-hexane was used to purify NIPAM in the recrystallization process. DMAAPS (KJ Chemicals Co., Ltd., Japan) was synthesized by the ring-opening reaction method introduced by Lee and Tsai (1994). In addition, *1,3*-propanesultone (PS; Tokyo Chemical Industry Co., Ltd., Japan) was used. An amount of 75 g of PS was mixed with 75 g of acetonitrile. The mixture was then added dropwise to a mixture of 100 g of DMAAPS and 200 g of acetonitrile for 90 minutes and then stirred at 30°C for 16 hours. The produced DMAAPS crystals were washed with 500 mL of acetone. The stirring then continued at room temperature for two days, producing white crystals, which were filtrated and washed with 500 mL of acetone and dried in a vacuum oven at 50°C for 24 hours.

The NIPAM-*co*-DMAAPS gel was synthesized by a free-radical polymerization reaction. DMAAPS, NIPAM, *N,N,N',N'*-tetramethylethylenediamine (TEMED), and *N,N'*-methylenebisacrylamide (MBAA) were added into distilled water until it reached a total solution volume of 100 mL. The solution was then poured in a four-necked separable flask and purged with nitrogen gas for 10 minutes to free up the dissolved oxygen. Then, 20 mL of ammonium peroxydisulfate (APS) solution with purging nitrogen gas added to the polymerization reactor. The nitrogen gas was kept flowing at 10°C for 6 hours during the polymerization reaction. Table 1 shows the gel copolymer synthesis conditions.

Table 1 Composition for zwitterionic copolymer gel synthesis

		Concentration (mmol/L)
Monomer	DMAAPS	100, 200, 300
	NIPAM	900, 800, 700
Linker	MBAA	30
Accelerator	TEMED	10
Initiator	APS	2

To produce a gel cylinder, gel was synthesized in a four-necked separable flask using glass tubes 3 mm in diameter and 20 mm in length. Then, the gel produced by polymerization reaction in the glass tubes was cut into 3 mm length. This NIPAM-*co*-DMAAPS gel was washed with distilled water and then dried for several days on Teflon paper placed on a petri dish covered with a plastic film with small holes in it to prevent the gel from cracking due to evaporation. Other gel products were then cut into small pieces, washed, and dried in an oven. Then, to produce gels with a size of ≥ 90 μm, the gels were crushed and sieved. In the end, two types of gels were produced: cylindrical gels for swelling tests and crushed gels ≥ 90 μm in size for ion adsorption and desorption tests. The concentrations in the solutions after the adsorption and desorption processes were measured by atomic absorption spectrophotometry (AAS). The NIPAM-*co*-DMAAPS gel synthesis apparatus is shown in Figure 1.



(A) DMAAPS and NIPAM feed tank
(B) Polymerization batch reactor
(C) Heater
(D) Temperature controller and thermocouple
(E) Stirrer
(F) Condenser
(G) N_2 purge
(H) Initiator feed tank
(I) N_2 gas
(J, K, L, M) Valves
(N) Flowmeter

Figure 1 NIPAM-*co*-DMAAPS gel experiment setup

2.2. Swelling Degree Test

In the swelling degree test, a millimeter block was used to measure the diameter of the cylinder gel after it was developed until it reached the equilibrium swelling point in a solution at 10, 30, 50, and 70°C. Equation 1 was used to calculate the swelling degree.

$$\text{Swelling degree} = \frac{d_{swell^3}}{d_{dry^3}} \tag{1}$$

where d_{swell} is the gel diameter after it reached the equilibrium swelling point at a certain temperature (i.e., the swollen gel diameter) and d_{dry} is the dry gel diameter.

2.3. Adsorption/Desorption Test

$Zn(NO_3)_2$ and $Pb(NO_3)_2$ solutions were used in the adsorption and desorption processes. One gram of gel copolymer was added to 20 mL of aqueous solution (10 mmol/L) in a glass bottle. It was then stirred at various temperatures of 10, 30, 50 or 70°C for 15 hours until it reached the adsorption equilibrium point. Subsequently, the concentrations of cations and anions in the final solutions were analyzed by AAS after separating the gel by centrifugation for 10 minutes and filtration using a syringe filter.

After the adsorption, the gel that had previously been dried was placed into $Zn(NO_3)_2$ and $Pb(NO_3)_2$ solutions for the desorption test. Both solutions had the same concentration (10 mmol/L) and were stirred at various temperatures of 10, 30, 50 or 70°C for 15 hours. To determine the amount of ions adsorbed, Equation 2 was used.

$$Q = \frac{(C_0 - C)V}{m} \tag{2}$$

where Q is the quantity of ions (Pb^{2+} and Zn^{2+}) adsorbed on or desorbed from the gel copolymer, C_0 is the ion concentration (Pb^{2+} or Zn^{2+}) in the solution before the adsorption and desorption tests, C is the ion concentration (Pb^{2+} or Zn^{2+}) after the adsorption and desorption tests, V is the volume of the sample solution, and m is the weight of the dry gel.

2.4. Reversible Adsorption-Desorption Test

Reversible adsorption-desorption was defined as the ability of the gel to adsorb and desorb ions continually at 10 and 70°C, respectively, for 15 hours in 10 mmol/L of $Zn(NO_3)_2$ or $Pb(NO_3)_2$ solution. Once the adsorption experiment was completed, the solution temperature was increased to 70°C to desorb the ions previously adsorbed. The gel was utilized repeatedly to adsorb and desorb until it reached its saturation point, that is, the point at which it could not adsorb or desorb ions. The gel was separated from the solution by centrifugation for 10 minutes, filtrated by syringe filter, and finally the ion concentration in the solution was measured by AAS.

3. Results and Discussion

3.1. Effect of Time on the Swelling Degree of the NIPAM-co-DMAAPS Gel

Swelling degree, or volumetric swelling, is the ratio between swollen gel volume and dry gel volume. This study used NIPAM:DMAAPS ratios of 9:1, 8:2, and 7:3 with a total molarity of 1000 mmol/L. Figure 2 shows the times until the NIPAM-*co*-DMAAPS gel reached the equilibrium swelling point in the $Zn(NO_3)_2$ solution at various temperatures. In the NIPAM:DMAAPS ratios of 9:1 and 8:2, a significant increase was observed at 0–9 hours, and the gel reached the equilibrium swelling point at 9–15 hours (Figures 2a and 2b). These results indicate that the higher the temperature, the lower the swelling degree.

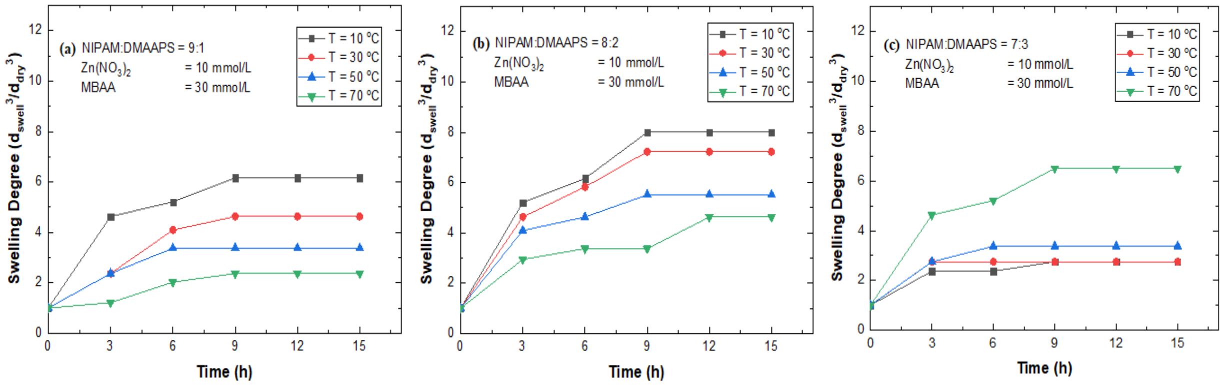


Figure 2 Equilibrium swelling of the NIPAM-*co*-DMAAPS gel in various time ranges and temperatures in NIPAM:DMAAPS ratios of: (a) 9:1; (b) 8:2; and (c) 7:3 in concentrations of 10 mmol/L of $Zn(NO_3)_2$ solution

In the NIPAM:DMAAPS ratio of 7:3, Figure 2c shows a significant increase in swelling at 70°C between 0 and 3 hours and then a slow increase in the next 3–9 hours until the gel reached the equilibrium swelling point at 9–15 hours. A significant increase occurred at temperatures of 10–50°C between 0 and 3 hours before the gel reached a constant value at 3–15 hours. These results show that the swelling degree increased in correlation with the increase in temperature. Furthermore, it can be concluded that swelling equilibrium can be achieved at 15 hours or more. Based on this, it was possible to determine the quantity of ions adsorbed on the NIPAM-*co*-DMAAPS gel.

Table 2 Percent adsorption of ions onto the gel with different NIPAM:DMAAPS ratios in concentrations of 10 mmol/L of nitrate solution at various temperatures

NIPAM:DMAAPS Ratio	Temperature (°C)	$Zn(NO_3)_2$		$Pb(NO_3)_2$	
		$C_0–C$ (mmol/L)	Percent Adsorption (mmol/g of gel)	$C_0–C$ (mmol/L)	Percent Adsorption (mmol/g of gel)
9:1	10	8.16	22.16	9.69	26.24
	30	8.13	22.09	9.66	26.19
	50	8.10	21.85	9.65	26.04
	70	7.91	21.36	9.60	25.99
8:2	10	8.23	12.50	9.78	14.80
	30	8.20	12.44	9.72	14.74
	50	8.12	12.29	9.69	14.65
	70	7.91	11.98	9.66	14.59
7:3	10	8.20	9.14	9.70	10.83
	30	8.15	9.10	9.69	10.80
	50	8.11	9.05	9.65	10.77
	70	7.89	8.80	9.64	10.76

Table 2 shows that the percent adsorption of both Zn^{2+} and Pb^{2+} decreased as the temperature increased and the NIPAM:DMAAPS ratio decreased. The rising temperature increased the thermal motion of the gel, causing the bond of the gel whose charge group was initially bound to Zn^{2+} and Pb^{2+} ions to break and the adsorption power to decrease.

3.2. Effect of the NIPAM Concentration on the Gel Copolymer's Adsorption and Swelling Degree

Figures 3a and 3b show the effect of the NIPAM monomer concentration on the NIPAM-*co*-DMAAPS swelling degree at various temperatures. Combined with Figures 2c and 2d, they show that the swelling degree and adsorption decreased when the temperature increased in the nitrate solution with NIPAM:DMAAPS ratio of 9:1 and 8:2. This occurred because poly(NIPAM) is a thermosensitive polymer with an LCST of around 32°C. This means that when it is dissolved in water, it swells at low temperatures and shrinks at high temperatures because it changes from hydrophilic to hydrophobic. Therefore, the NIPAM concentration in the NIPAM-*co*-DMAAPS gel has an increasingly hydrophobic effect as the temperature increases.

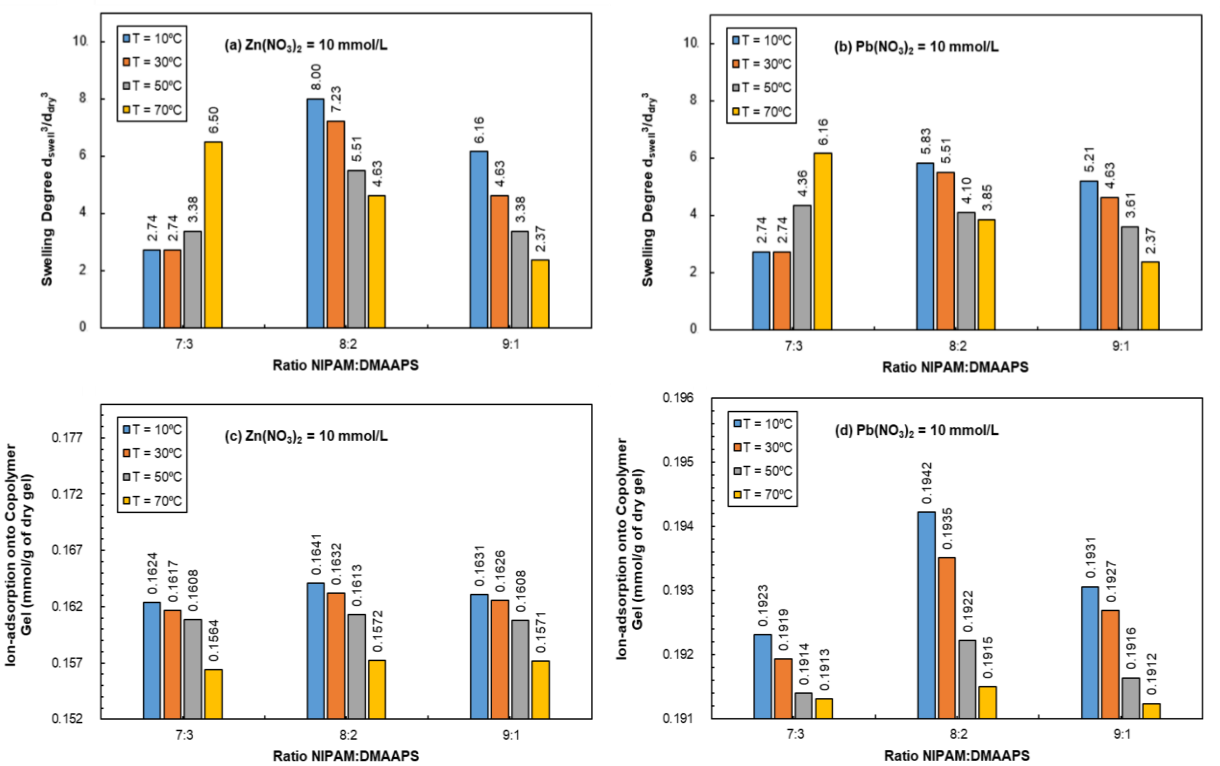


Figure 3 Effect of NIPAM concentration on the NIPAM-*co*-DMAAPS gel swelling degree with various NIPAM:DMAAPS ratios in concentrations of 10 mmol/L of (a) $Zn(NO_3)_2$ solution and (b) $Pb(NO_3)_2$ solution; effect of NIPAM concentration on the adsorption of (c) Zn^{2+} ions on the NIPAM-*co*-DMAAPS gel in concentrations of 10 mmol/L of $Zn(NO_3)_2$ solution and (d) Pb^{2+} ions on the NIPAM-*co*-DMAAPS gel in concentrations of 10 mmol/L of $Pb(NO_3)_2$ solution

In addition, a significant increase was observed in the swelling degree in the nitrate solution at 70°C with the NIPAM:DMAAPS ratio of 7:3 (Figures 3a and 3b). This phenomenon is at odds with the theory that poly(NIPAM) gels tend to swell below the LCST of 32°C and shrink above the transition temperature. This occurred because of the higher relative DMAAPS concentration, whose solubility was affected by the temperature at NIPAM:DMAAPS ratio of 7:3. Hence, the higher the temperature, the higher the solubility. However, in the case of a higher swelling degree, this characteristic is strongly influenced by the gel's ability to adsorb water, not the strongly charged–group DMAAPS bond in the solution.

As the temperature increased, the quantity of ions adsorbed onto the gels with various monomer ratios decreased. Moreover, at lower temperatures, intra-group pairing of SO_3^- and N^+ dominated the interactions within the gel, and such pairings were enough to block the gel's ability to adsorb water. Consequently, the quantity of ions adsorbed onto the copolymer gel was limited. Thermal motion at higher temperatures weakened the pairing between Zn^{2+} and NO_3^- in the solutions with SO_3^- and N^+ in the gels, respectively. In addition, the gel's shrinking at higher temperatures, particularly in the NIPAM:DMAAPS molar ratios of 9:1 and 8:2 (Figures 3a and 3b) resulted in a stronger interaction between sulfobetaine groups. This phenomenon caused the amount of ions adsorbed onto the gel to decrease.

Moreover, as Figures 3c and 3d show, the amount of Pb^{2+} ions adsorbed was higher than that of Zn^{2+} ions. This phenomenon is explained by the Hofmeister series of cations as follows (Collins and Washabaugh, 1985):

$$H^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > Li^+$$

Based on their atomic diameter, ions can be classified into two groups: kosmotropes and chaotropes. Kosmotropes are on the left side of the series, while chaotropes are on the right side. Zn^{2+} is considered a kosmotrope, as its atomic diameter (74 pm) is close to that of Mg^{2+} (72 pm), and has greater hydration potential than Pb^{2+}, whose atomic diameter is 119 pm. Therefore, it is more difficult for sulfobetadine groups in the copolymer gel to adsorb it.

3.3. *Effect of Reversible Adsorption-Desorption on Ion Concentration*

Figure 4 shows the gel's capability of reversible adsorption-desorption after having been used over a certain period until it reached its saturation point. After the adsorption experiment had been completed, the solution's temperature was raised from 10 to 70°C to desorb the ions previously adsorbed. The same process was repeated for the second and third reversible adsorption-desorption tests. Reversibility 1 in Figure 4 shows the quantity of ions desorbed in the nitrate solution after 15 hours. In the first 15 hours, the desorption in the $Zn(NO_3)_2$ solution first increased and reached a constant value in the third reversibility test, where the final concentration was 0.0018 mmol/g of dry gel. This means that NIPAM drove the bonds between Zn^{2+} and NO_3^- with charged groups (N^+ and SO_3^-) in the gel copolymer in the first 15 hours at 70°C, thus weakening the bonds. However, over time, these copolymer bonds were located at the saturation point of desorption; thus, the copolymer gel stabilized, as it could not desorb further. A significant increase also occurred in the $Pb(NO_3)_2$ solution at 15 hours and subsequently decreased to a concentration of 0.0675 mmol/g of dry gel.

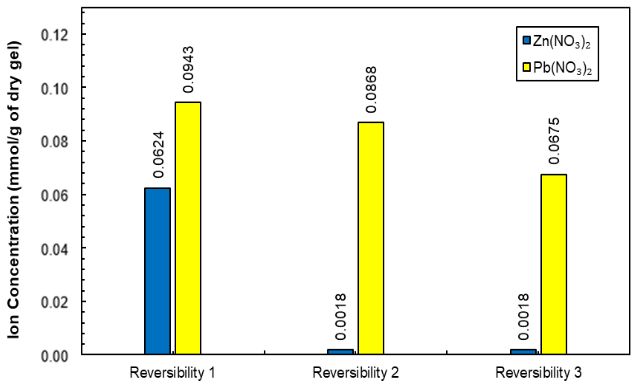


Figure 4 Reversible adsorption-desorption of copolymer gel in nitrate solutions with an 8:2 NIPAM:DMAAPS ratio at 70°C

4. Conclusions

The copolymer gel took more than 15 hours to reach the swelling degree equilibrium and desorption and adsorption points. In the NIPAM:DMAAPS ratios of 9:1 and 8:2, the swelling degree increased as the temperature decreased. In contrast, the 7:3 ratio resulted in a higher swelling degree as the temperature increased. In the nitrate solution, the swelling degree and adsorption ability of the 9:1 and 8:2 ratios decreased with an increase in temperature. Conversely, in the 7:3 ratio, the swelling degree increased significantly, while the adsorption capability decreased with a temperature increase. Furthermore, in the 9:1 ratio and a temperature of 10°C, the gel's adsorption ability reached its highest values of 22.16% (Zn^{2+}) and 26.24% (Pb^{2+}). It can be concluded that the higher the temperature, the lower the quantity of Zn^{2+} and Pb^{2+} ions adsorbed and desorbed. In nitrate solution, Pb^{2+} ions are more easily adsorbed than Zn^{2+} ions. An ion concentration of 0.0018 mmol/g of dry gel was obtained from the reversible adsorption-desorption test using an 8:2 NIPAM:DMAAPS ratio in the $Zn(NO_3)_2$ solution, while the $Pb(NO_3)_2$ solution reached an ion concentration of 0.0675 mmol/g of dry gel.

Acknowledgements

This research was supported by Penelitian Dasar 2019 research grant under contract number 853/PKS/ITS/2019 from the Ministry of Research, Technology, & Higher Education of Indonesia for ten consecutive months.

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