Adsorption and Desorption of Na^+ and NO_3^- Ions on Thermosensitive NIPAM-*co*-DMAAPS Gel in Aqueous Solution

Eva Oktavia Ningrum[1,*], Agus Purwanto[2], Eka Octaviyatna Mulyadi[1], Dinny Islamiah Dewitasari[1], and Sumarno[1]

[1]Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Sukolilo Surabaya 60111, Indonesia

[2]Department of Chemical Engineering, Faculty of Engineering, Universitas Sebelas Maret, Jl. Ir. Sutami 36 A, Surakarta, Central Java 57126, Indonesia

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ABSTRACT

Adsorbent gel with the ability to absorb and to desorb Na^+ and NO_3^- ions simultaneously with temperature swing was synthesized by free radical copolymerization reaction of N-isopropylacrylamide (NIPAM) and N,N-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS). In this study, NIPAM acts as a thermosensitive agent and DMAAPS as an adsorbent agent. The purpose of this research is to investigate the effect of temperature and solution concentration on the swelling, adsorption, and desorption behaviors of NIPAM-co-DMAAPS gel. The relationship between adsorption and desorption behaviors of the gel was also elucidated. $NaNO_3$ solution was selected as the target solution in swelling, adsorption, and desorption test. It was observed that the swelling degree of the gel increased as temperature and solution concentration raised. The adsorption amount of ions decreased with the increase of temperature. In contrast, the amount of ions desorbed from the gel increased linearly with temperature.

Keywords: *thermosensitive; swelling degree; adsorption; desorption*

ABSTRAK

Gel adsorben yang memiliki kemampuan mengadsorpsi dan mendesorpsi ion secara simultan dengan perubahan suhu (temperature swing) dihasilkan melalui reaksi kopolimerisasi radikal bebas antara N-isopropylacrylamide (NIPAM), dan N,N-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS). NIPAM dipergunakan sebagai agen thermosensitive dan DMAAPS digunakan sebagai agen pengadsorpsi. Tujuan dari penelitian ini adalah untuk mempelajari pengaruh suhu dan konsentrasi larutan terhadap properti swelling, adsorpsi, dan desorpsi ion pada NIPAM-co-DMAAPS gel dan hubungan antara properti-properti tersebut. $NaNO_3$ dipergunakan sebagai larutan uji dalam mempelajari properti swelling, adsorpsi, dan desorpsi. Hasil penelitian menunjukkan bahwa swelling degree dari gel mengalami kenaikan dengan pertambahan suhu dan konsentrasi larutan. Selain itu, pada konsentrasi larutan yang tetap jumlah ion yang teradsorpsi menurun dengan peningkatan suhu namun jumlah ion yang terdesorpsi dari gel cenderung meningkat.

Kata Kunci: *thermosensitive; swelling degree; adsorpsi, desorpsi*

INTRODUCTION

Recently the biggest challenge confronting wastewater produced from industrial is about the removal of heavy metal ions. Various methods have been carried out to remove these metal ions such as neutralization [1], precipitation [2-3], and adsorption by an adsorbent containing chelating agents [4-5]. The conventional method such as precipitation and neutralization produce a new waste of sludge containing concentrated heavy metal ions. This challenge can be met by the incorporating adsorbent containing ligands that enable show the high adsorption capacity of heavy metal ions. Recently many works have been done to investigate the specific material as a potential candidate for the application of adsorbent [6-8].

Kumar et al. [9] used aniline formaldehyde condensate (AFC) coated on silica gel as an adsorbent to remove copper (Cu^{2+}) from aqueous solution under conditions of different initial Cu^{2+} concentration, adsorbent loading, pH and adsorption time. The main mechanism of copper removal was the coordination bond formation between the amine group and Cu^{2+} ion. Tao et al. [10] investigated the adsorption of Pb(II) from

* Corresponding author.
Email address : eva-oktavia@chem-eng.its.ac.id

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aqueous solution using chitosan/TiO_2 hybrid film (CTF) adsorbent. Batch experiments were carried out as a function of solution pH, adsorption time, Pb(II) concentration and temperature. The use of a zwitterionic hybrid polymer based on ring-opening polymerization of pyromellitic acid dianhydride (PMDA) and sol-gel process to remove Pb^{2+} from Pb^{2+}/Cu^{2+} mixed aqueous solution was investigated by Liu et al. [11].

Those findings were very useful for the separation and recovery of heavy metal ions from wastewater, but since the interaction between ligands and heavy metal ions are strong, the acid solution was usually used to regenerate the adsorbent. Therefore, the utilization of zwitterionic polymer will be promising for improving the ion selectivity toward the adsorption because the cations and anions in the solution can bond via both the negative and positive charges [12-14]. In this research, we intend to employ the NIPAM-*co*-DMAAPS gel to eliminate acidic waste produced in the previous method and to increase the adsorption ability toward ions. By copolymerization between NIPAM as thermosensitive polymer and zwitterionic betaine DMAAPS as adsorption agent, the adsorption and desorption mechanism can simply be controlled by tuning the temperature of the system. Based on the above reasons, the effect of temperature and solution concentration on the swelling degree, adsorption, and desorption behaviors of NIPAM-*co*-DMAAPS gel in $NaNO_3$ solution are investigated in the present study.

EXPERIMENTAL SECTION

Materials

N-isopropylacrylamide (NIPAM) and *N,N*-dimethylaminopropylacrylamide (DMAPAA) were purchased from KJ Chemicals Co., Ltd., Japan. DMAPAA was purified by vacuum distillation. *N,N'*-Methylenebisacrylamide (MBAA), *N,N,N',N'*-tetramethylethylene-diamine (TEMED), ammonium peroxodisulfate (APS) were kindly supplied by Sigma-Aldrich Co., USA. 1,3-Propanesultone (PS), acetonitrile, acetone, hexane, and $NaNO_3$ were purchased from Tokyo Chemical Industry Co., Ltd., Japan, Avantor Performance Material, Inc., USA, PT. Smart Lab., Indonesia, Anhui Fulltime Solvent and Reagent Co., Ltd., China, and PT. Merck Tbk., Indonesia, respectively.

Instrumentation

Fourier Transform Infra Red (FTIR, Thermo Fisher Scientific Nicolet IS10, USA) analysis was conducted to determine the functional groups and constituent monomers of DMAAPS, NIPAM, and also NIPAM-*co*-DMAAPS gel. In this analysis, the middle area of infrared radiation of a wavelength of 4000–500 cm^{-1} being used. In order to determine swelling degree (SD), the diameter of the gel after reach equilibrium at a certain temperature the diameter of the dry gel was measured by using millimeter block. Atomic Absorption Spectrophotometry (AAS, Model 210 VGP) was used to measure the concentration of ions in the initial and final solution. This concentration was then used to determine the adsorption and desorption ion by copolymer gel.

Procedure

Synthesis of DMAAPS

DMAAPS was synthesized by the same manner as that used in our previous studies [15-17], which was proposed by Lee and Tsai [18], by the ring-opening reaction of *N,N*-dimethylaminopropylacrylamide (DMAPAA, KJ Chemicals Co., Ltd., Japan) and 1,3-propanesultone (PS, Tokyo Chemical Industry Co., Ltd., Japan). A mixture of PS (75 g) or BS (79 g) and acetonitrile (75 g) was added dropwise with continuous stirring at 30 °C for 90 min into a mixture of DMAPAA (100 g) and acetonitrile (200 g). Stirring was continued for 16 h and the solution was then allowed to stand for 2 d. The precipitated white crystals of DMAAPS was collected by filtration, washed with 500 mL of acetone and finally dried under reduced pressure for 24 h. DMAAPS was used as an adsorbent agent.

Preparation of NIPAM-co-DMAAPS gel

NIPAM as a thermosensitive agent was purified by recrystallization from hexane. NIPAM-*co*-DMAAPS gel with a molar ratio of NIPAM and DMAAPS 1:9 was synthesized through free radical polymerization reaction with the concentration of TEMED, APS, and MBAA were 10 mmol/L, 2 mmol/L, and 30 mmol/L, respectively. Firstly, NIPAM, DMAAPS, MBAA and TEMED, were dissolved in distilled water up to 100 mL. The monomer solution then poured into the four-necked separable flask. The solution was purged for 10 min using nitrogen gas to remove the dissolved oxygen, followed by addition of 20 mL APS which has been purging previously to the monomer solution. The polymerization reaction lasted for 6 hours at 15 °C with 500 mL/min flow of nitrogen gas during the reaction. Synthesis condition of NIPAM-*co*-DMAAPS gel is described in Table 1.

Characterizations

Fourier Transform Infra-Red (FTIR) analysis

Spectroscopy is a method observing the interaction of molecules with electromagnetic radiation in the wavelength range from 0.75 to 1000 μm or wave

Table 1. Synthesis condition of NIPAM-*co*-DMAAPS gel

		Concentration [mmol/L]
Monomer	*N,N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS)	900
	N-isopropylacrylamide (NIPAM)	100
Linker	*N,N'*-methylenebisacrylamide (MBAA)	30
Accelerator	*N,N,N',N'*-tetramethylethylenediamine (TEMED)	10
Initiator	Ammonium peroxodisulfate (APS)	2

Solvent: water; Reaction time: 6 h; Temperature: 15 °C

number 13000–10 cm^{-1}. Unit cm^{-1} is known as wavenumber (1/wavelength) which is a measurement unit for frequency. The working principle of infrared spectrophotometer deals with the interaction energy between materials. This analysis was conducted to determine the functional groups and constituent monomers of DMAAPS, NIPAM, and also NIPAM-*co*-DMAAPS gel. In this analysis, the middle area of infrared radiation of a wavelength of 4000–500 cm^{-1} being used.

Swelling Degree test (SD)

The cylindrical dry gel, which the diameter was determined using millimeter block, was immersed in water or nitrate solution at 50 °C, and the gel was allowed to swell and reach equilibrium swelling for 12 h. The temperature was incrementally reduced and the diameter of the swollen gel was measured again. This procedure was repeated until the temperature was reduced up to 10 °C. The temperatures used were 10, 30 and 50 °C. The solution used is $NaNO_3$ with a concentration of 2.5; 5; 7.5; and 10 mmol/L. Swelling degree of the gel is calculated using the following equation:

$$SD = \frac{d_{swell}^3}{d_{dry}^3} \quad (1)$$

where d_{swell} is the diameter of the gel after reach equilibrium at a certain temperature and d_{dry} is the diameter of the dry gel

Adsorption/Desorption test

In the adsorption test, 1 g of copolymer gel was added to the glass bottle contained 20 mL of $NaNO_3$ solution. Then glass bottles placed into a water bath accompanied by stirring for 12 h at a particular temperature to achieve adsorption equilibrium conditions. In order to determine the concentration of ions in solution after the adsorption process, the gels were separated from the solution by centrifuge and were filtered with a syringe filter. The filtrate concentration was then measured using Atomic Absorption Spectrophotometry (AAS).

In the desorption test, gel adsorption which had been dried previously was then placed into distilled water, followed by stirring for 12 h. The final solution was obtained by the similar method used in the adsorption test. The number of ions adsorbed to the gel was calculated from the concentration of ion before and after the adsorption process by using equation (2) as follows:

$$Q_a = \frac{(C_0 - C)V}{m} \quad (2)$$

Equation (3) is used to determine the number of ions desorbed from the gel:

$$Q_d = \frac{C \times V}{m} \quad (3)$$

where Q_a is the number of ions adsorbed, Q_d is the number of ions desorbed, C_o is the concentration of ions in solution before adsorption or desorption process, C is the concentration of ions in solution after the adsorption or desorption process, V is the volume of the solution, and m is weight of the dry gel (≥ 180 mesh).

RESULT AND DISCUSSION

FTIR Test

In FTIR analysis, middle area of infrared radiation of a wavelength of 4000–500 cm^{-1} is used. NIPAM-*co*-DMAAPS gel is formed through a free radical polymerization reaction. Fig. 1(c) shows the result of spectrophotometric infrared rays analysis of NIPAM-*co*-DMAAPS gel. N-H bonds are shown at a wavelength of 3266 cm^{-1}. At wavelengths reach the point of 1635 cm^{-1} indicate the presence of C=O bond. C-N bond can be seen at wavelengths of 1185 cm^{-1}. While the S=O bond is shown at a wavelength of 1042 cm^{-1}. This group determines the constituent bonds of the copolymer, as shown in Fig. 2.

The success of copolymerization reaction can be determined by the existence of functional groups of each constituent monomers and the absence of the vinyl group CH_2=CH. Bonding vinyl (CH_2=CH) lies in the wavelength range between 950–1000 cm^{-1}. In NIPAM, vinyl bonding (CH_2=CH) shown at a wavelength of 960 cm^{-1} (Fig. 1(a)). In DMAAPS, vinyl bonding (CH_2=CH) being visible at a wavelength of 980 cm^{-1} (Fig. 1(b)). However, the results of NIPAM-*co*-DMAAPS gel FTIR analysis (Fig. 1(c)) shows no

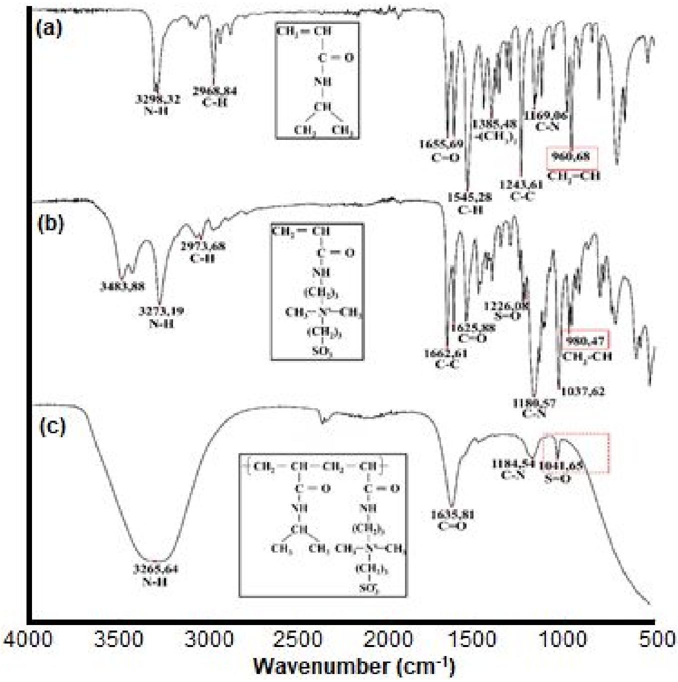

Fig 1. Infrared spectra: (a) NIPAM; (b) DMAAPS; (c) NIPAM-*co*-DMAAPS gel

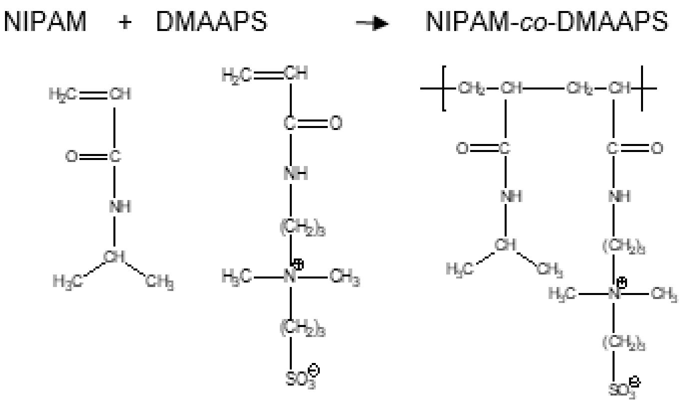

Fig 2. Copolymerization reaction of NIPAM-*co*-DMAAPS gel

indication of the CH_2=CH peak. It refers that copolymerization reaction between NIPAM and DMAAPS is successful.

Swelling Degree of NIPAM-co-DMAAPS Gel

Swelling degree of NIPAM-*co*-DMAAPS gel in various $NaNO_3$ solution concentrations and temperatures is shown in Fig. 3. It can be seen that the swelling degree of NIPAM-*co*-DMAAPS gel in $NaNO_3$ solution was directly proportional to the concentration of the solution and swelling degree NIPAM-*co*-DMAAPS gel reached the highest value at 10 mmol/L of $NaNO_3$ solution.

NIPAM-*co*-DMAAPS gel is a hydrophilic copolymer having a zwitterion in the side chain. The existence of Na^+ ions from solution causes the weakening or even breaking the interaction of intra- or intra-chain between the charged group N^+ and SO_3^- in copolymers with $NaNO_3$ solution. This can be explained as follows: Ion Na^+ and NO_3^- in higher concentrations will interfere with the interaction of N^+ and SO_3^- that binds to NO_3^- and Na^+ of the solution. The higher the concentration of the solution, the bonds of N^+ and SO_3^- are easily broken. Thus, the distance between units becomes greater that caused the polymer network gel further expand and enhance the swelling ability of NIPAM-*co*-DMAAPS gel [19].

Adsorption and Desorption Behaviors of NIPAM-co-DMAAPS Gel

Adsorption can be defined as reversible binding molecules and atoms of the gas phase and liquid on the surface, highly porous adsorbent media. The reverse process called desorption. In adsorption, adsorption matter accumulates on the adsorbent, which is then loaded with adsorbate. In this adsorption and desorption study, the crush gels with mesh size ≥ 180 mesh were used.

Fig. 4 shows adsorption behavior of NIPAM-*co*-DMAAPS gel in various $NaNO_3$ solution concentrations and temperatures. It can be seen that the higher the concentration of $NaNO_3$ the amount of ion adsorbed by the copolymer gel also increased. It is caused by the large number of Na^+ and NO_3^- in a $NaNO_3$ solution that attacks the charged group of sulfobetaine (SO_3^- and N^+) in copolymer gel. Moreover, at higher temperature, the adsorption amount of ion is slightly decreased at fixed solution concentration. The phenomenon above can be explained as follows. At higher temperature, thermal motion weakens the interaction between the charged groups of DMAAPS (N^+ and SO_3^-) and cation Na^+ and anion (NO_3^-) from $NaNO_3$ solution [15-17,20], as a result, the adsorption ability of copolymer decreased as temperature increased. The adsorption are less influenced by temperature change because gels prepared using high cross-linker concentration, the interaction is dominated by intra-group ionic pairs that is quite strong to be broken by thermal motion.

Fig. 5 shows desorption behavior of NIPAM-*co*-DMAAPS gel in various $NaNO_3$ solution concentrations and temperatures. It can be seen that the higher the temperature and concentration of the solution used, the amount of ion desorbed from the gel also increased. This result can be explained by fact that increasing temperature leads to the breakages of the charge groups associations of DMAAPS and ions from $NaNO_3$, therefore the ions are easily released from the copolymer gel, consequently, the desorption amount of ion from the gel increased.

The relationship between adsorption on desorption behavior of the gel is shown in Fig. 6. The result shows that the number of ions adsorbed decreased slightly with increasing temperature. However, the desorption ability increased with increasing temperature. This desorption occurred because at high temperatures the thermal motion weakens the paired bonding interactions of ions Na^+ and NO_3^-, with N^+ and SO_3^- in copolymer gel. With increasing temperature, the ions Na^+ and NO_3^- binding charged with sulfobetaine group (N^+ and SO_3^-) in copolymer gel weakened, thus ions of Na^+ and NO_3^- copolymer gel then desorbed into the distilled water. In contrary, for adsorption thermal motion weaken the bond ions paired chain between the charged groups of the copolymer gel itself and also weaken the bonding between Na^+ and NO_3^- in a solution of $NaNO_3$ and charged groups in the copolymer gel, thus reduce the ions adsorbed from $NaNO_3$ solution by copolymer gel at higher temperatures.

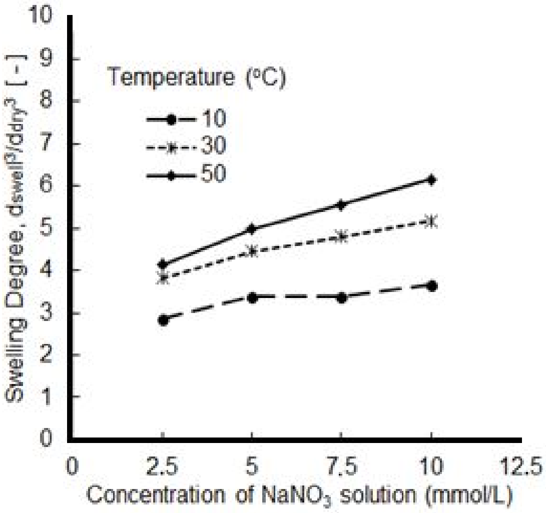

Fig 3. Swelling degree of NIPAM-*co*-DMAAPS gel in various $NaNO_3$ solution concentrations and temperatures

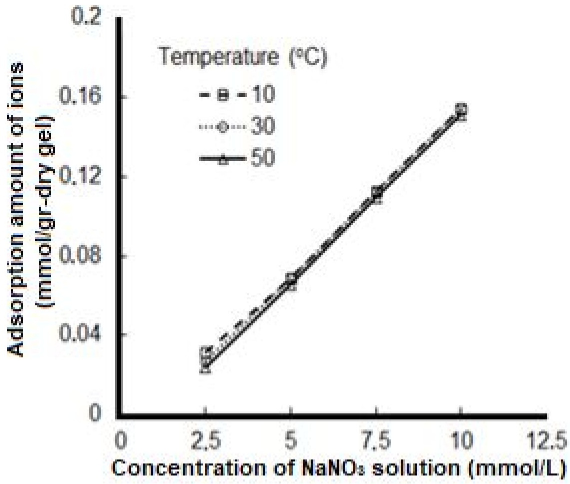

Fig 4. Adsorption behavior of NIPAM-*co*-DMAAPS gel in various $NaNO_3$ solution concentrations and temperatures

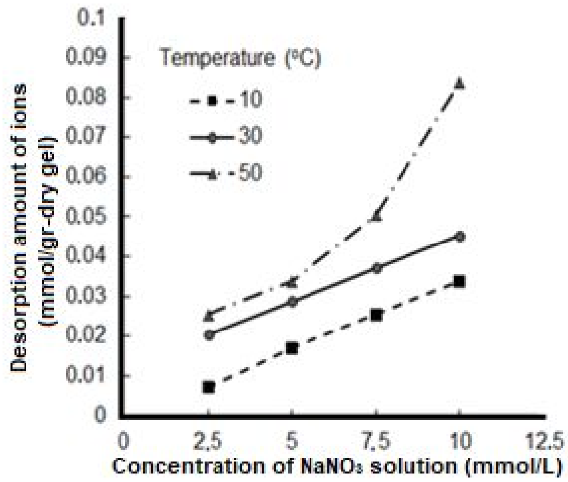

Fig 5. Desorption behavior of NIPAM-*co*-DMAAPS gel in various $NaNO_3$ solution concentrations and temperatures

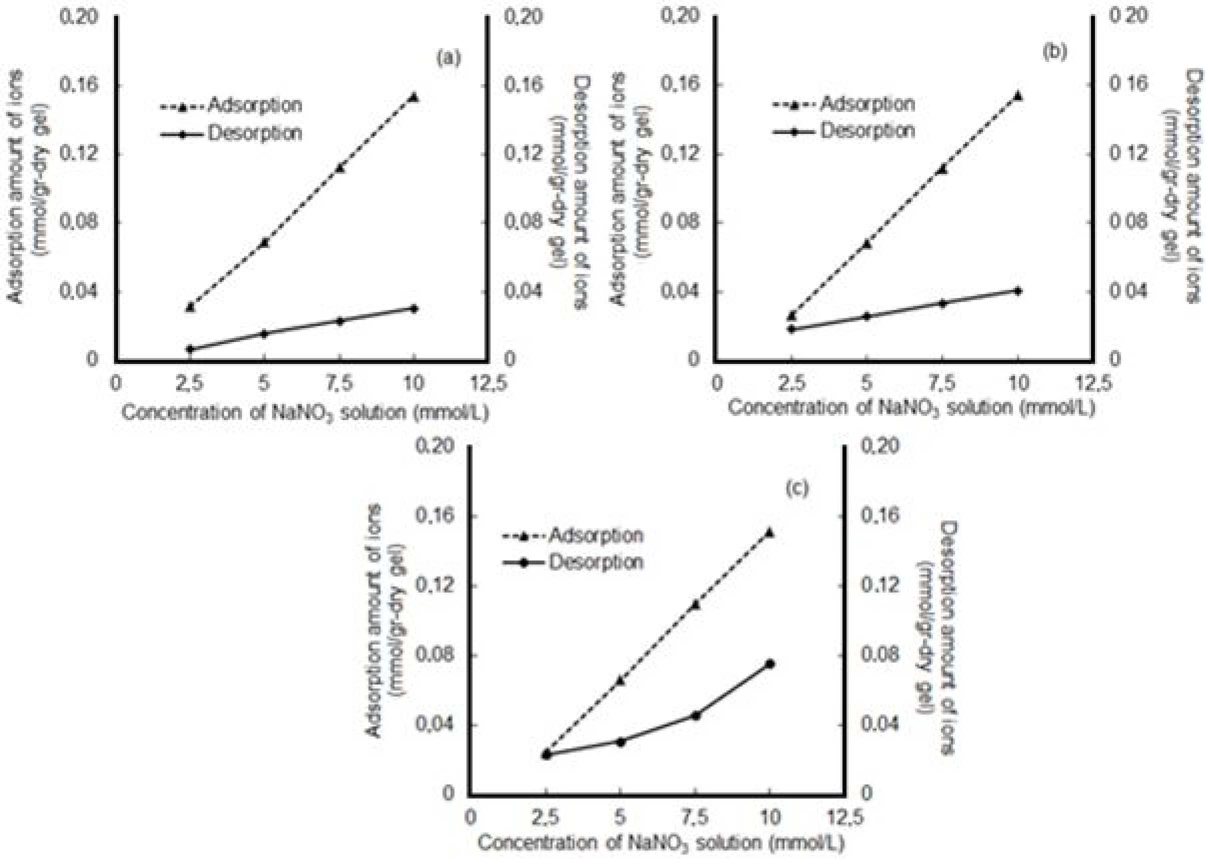

Fig 6. Adsorption and desorption of ions on NIPAM-*co*-DMAAPS gel in various $NaNO_3$ solution concentrations at temperature (a) 10, (b) 30, and (c) 50 °C

CONCLUSION

The effects of sodium nitrate solution concentration and temperature on the adsorption and desorption of ion on NIPAM-*co*-DMAAPS gel were investigated. Moreover, the relationship between adsorption and desorption of Na^+ and NO_3^- ions on the copolymer gel was also elucidated. It was found that the higher temperature and concentration of the solution increased the amount of swelling degree of the gel. The higher concentration of $NaNO_3$ solution increased the amount of ion adsorbed ono the copolymer, however the higher temperature the amount of ion adsorbed by the copolymer gel slightly decreased at fixed solution concentration. The higher temperature and concentration of the solution used, the amount of ion desorbed from the gel also increased. Based on the relationship between the adsorption and desorption properties, it was found that the number of ions adsorbed decreased slightly with increasing temperature. However, the desorption ability increased with increasing temperature.

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