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Medium Effect on Swelling and Sorption Behaviour of Sodium Chloride from-and-into Poly(vinyl alcohol)-Glutaraldehyde Hydrogel at Room Temperature

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This work aims to study the swelling behaviour of poly(vinyl alcohol)-glutaraldehyde (PVA/GA) hydrogel under various acidity and NaCl concentration of medium and release behaviour of NaCl from PVA/GA hydrogels. The hydrogels were characterized by FT-IR and SEM techniques. Repeated washing was necessary to produce a residual-free PVA/GA hydrogel. The FTIR spectra demonstrated that the incorporation of NaCl into the PVA/GA hydrogel did not result in specific interactions. The swelling profile of PVA/GA at the different pH medium was due to protonation and charge screening effects, while its swelling behaviour at various salt concentrations in medium was associated with the charge screening and osmotic pressure effects. The kinetic profile of NaCl absorption and desorption from-and-into PVA/GA was presumed to be controlled by the physical properties of hydrogel such as porosity, cavity and characteristic of the hydrodynamic radii of NaCl.

Keywords: Sorption, Hydrogel, Poly(vinyl alcohol), Glutaraldehyde, Sodium chloride, Swelling.

INTRODUCTION

At the right dosage, sodium actually promotes plant growth, despite to common belief that it is hazardous to some plants. In this case, controlling the amount of sodium ions in plants and their availability in the environment becomes a very crucial issue. For instance, several results have been reported that the difference between salt tolerant and sensitive plants is due to the control of sodium up-taking and internal sodium ion (Na^+) fluxes [1]. In addition, it was also found that sodium chloride (NaCl) at low and medium concentrations could increase plant height, but did not change the number and area of *Vicia faba* (L.) bean plant leaves [2]. Petjukevičs *et al.* [3] also reported that at concentrations of 0.1 M to 1.0 M of NaCl reduced the amounts of photosynthetic pigments in leaves and inhibited the overall growth of chloroplasts of *Elodea canadensis*.

For typical plants, NaCl also plays its essential role as a micronutrient. Sodium is an essential element for plants that have the C4 dicarboxylic photosynthetic pathway [4]. Low dosage of NaCl can also stimulate plant growth, whereas the availability of 5 mM NaCl was able to increase the shoot and root biomass [5]. Therefore, the regulation of the NaCl quantity in the surrounding area of root is very crucial. One of the approaches that has received much attention to regulate the availability of nutrients around plant roots is development of controlled release materials (CRM) [6-9]. Among materials, hydrogels, which is a type of hydrophilic polymer with a 3D network structure, has a great potential to be used as CRM [10,11]. This structure promotes hydrogel to absorb and hold large amounts of water and/or other liquids while its structure still preserved [12]. This capability brings hydrogel to be widely applied in various fields, such as controlled-release fertilizer agents, drug delivery, ion exchange and superabsorbent [13-16].

Release behaviour of hydrogel is influenced by many physico-chemical properties, the nature of hydrogel precursors, medium and environment conditions [17]. For example, in case of hydrogels composed by amine groups, the swelling ratio decreased with increase of pH, which is due to the protonation of amine group at a suitable pH of the swelling medium. In addition, Gupta & Shivakumar [18] showed that chitosan-based hydrogels demonstrated the larger swelling ratio in an acidic environment (low pH) than that in an alkaline environment (high pH). This is due to the amine group in the chitosan is protonated into ammonium ion ($-NH_3^+$) and this charge in the hydrogel will develop the repulsive forces between charged of polymer molecules. Likewise, the ability of glycol chitosan-based hydrogel at a low pH (pH 4) is greater than the swelling ability at a neutral pH (pH 7) [19]. However, in case of chitosan-reinforced calcium pectinate (ChCP) gel, the swelling ratio is lower in an acidic medium than that in a neutral medium, which is possible due to dissolution of chitosan in an acidic medium [20].

The opposite phenomenon occurs in hydrogels with -COOH groups, where the swelling ability proportionally increase to pH, at least up to pH 7, owing to protonation of the -COOH moieties [21-23]. Similarly, hydrogel poly(vinyl alcohol) (PVA)/citric acid (CA) showed the increase in swelling ratio with the increase of pH of the swelling medium. The COOH groups in the hydrogel matrix are slowly protonated to $-COO^-$ as the pH of the medium increases over the pK_a value of hydrogel, resulting in a negative net surface charge for the material [22]. The ionization of the hydrogel also increases the electrostatic repulsion force between the negative charges of the carboxylate group, leading to an increase in swelling [21].

Ionic strength has also been reported affecting the swelling capacity of hydrogels. In case of amine-based hydrogels, the increase in ionic strength causes a significant decrease in swelling ability, however, when the ionic strength was less than 0.001 M the effect was diminishes [18]. The effect of ionic strength on swelling ability is related to the charge distribution on the surface of the gel network. The increase in the concentration of anions in the swelling medium causes a stronger charge screening effect, which results in imperfect electrostatic repulsion between the anions and reduce the osmotic pressure difference between the polymer network and the external solution and consequently reducing the swelling capacity. When the ionic strength of medium is less than 0.001 M, it has no effect on the surface charge of the polymer chains and eventually on the swelling ability [24].

The hydrogels materials that has good compatibility for agricultural applications are poly(vinyl alcohol) (PVA) and glutaraldehyde (GA). PVA is a water soluble, biocompatible and degradable polymer with good physical properties [25] and has pH sensitive nature, so that it offers great potential applications [26]. Meanwhile, glutaraldehyde (GA) is a crosslinker, with high water solubility and relatively inexpensive. The aldehyde group in glutaraldehyde, in particular, can easily react with the hydroxyl group in PVA to form acetal bridge through a crosslinking reaction [27,28].

The study of the influence of the medium on the swelling ability and the release behaviour of hydrogel is an interesting and challenging, especially related to the application of agricultural materials. This study carefully examines the influence of pH and medium salt concentration on the swelling ratio and the absorption and desorption patterns of NaCl from PVA-GA in aqueous media. In addition, the investigation of residual acid leaching in preparation stage of hydrogel has also great concern in this study.

EXPERIMENTAL

The materials used in this study were fully hydrolyzed poly(vinyl alcohol) (*m.w.* 60000 g/mol), glutaraldehyde (ρ = 1.055-1.065 g/cm^3 at 20 ºC), methanol 96% (ρ = 0.791-0.793 g/cm^3 at 20 ºC), sulfuric acid 97% (ρ = 1.474-1.480 g/cm^3); acetic acid (ρ = 1.050 g/cm^3), hydrochloric acid, sodium chloride and deionized water. All chemicals were in high purity grade and purchased from Merck, Germany.

The equipment used for characterization were Fourier transform infrared spectrophotometer (Shimadzu, Japan), atomic absorption spectroscopy (GBC Scientific Equipment, Australia), mini scanning electron microscopy tabletop TM3030 (Hitachi, Japan), conductometer (Mettler toledo series LE703/UK), pH meter (Mettler toledo, UK) and Bitec-300 incubator (Shimadzu, Japan).

Synthesis of PVA/GA hydrogels and its residual leaching: The hydrogel was synthesized using the solution mixing method at the same volume ratio composition of the PVA and the GA crosslinker solutions. The mixture was stirred at temperature of 55 ºC for approximately 5 min (until homogeneous mixture was obtained). The mixture was then casted by pouring it into an acrylic mold and stored in an incubator at 25 ± 0.1 ºC for 24 h. Here after, the wet hydrogel was removed from the mold and dried at room temperature until the mass of hydrogel remained constant. The possible entrapped residual of impurities was then washed using deionized water repeatedly, in order to determine the residue (mostly proton) leaching rate from the hydrogel. In particular, the time dependent residue release profile was determined by measuring the change in conductivity and pH of the leached liquid (medium) as function of time (every 30 s). The dried hydrogel was washed repeatedly using deionized water until the pH and conductivity of medium remained constant.

Characterization of PVA/GA hydrogels: The interaction of PVA and GA crosslinker in the hydrogels was characterized by FT-IR spectroscopy. The hydrogel series were PVA, PVA/GA, PVA/GA-NaCl (0.5 M) and PVA/GA-NaCl (1.0 M). Each sample consisted of three pieces of hydrogel, crushed and mixed with KBr powder, then compacted under high pressure to form transparent KBr pellet. The measurement was carried out in the wavenumber range from 4000-400 cm^{-1}. The surface morphology of hydrogels series was examined by scanning electron microscopy technique.

Performance of PVA/GA hydrogels

Determination of swelling ratio: Swelling ratio (SR) of PVA/GA hydrogels was determined using gravimetric method. In this work, the effects of pH and NaCl concentration of medium on the swelling ratio of PVA/GA hydrogels were also examined. In the first part, the SR of PVA/GA was analyzed in distilled water at various acidity conditions (*i.e.* pH 5, 6, 7 and 8). Secondly, the SR of PVA/GA hydrogels was measured in a medium at pH 7 and various NaCl concentrations (0.0 M, 0.25 M, 0.50 M, 0.75 M and 1.0 M). In particular, 10 pieces of dried PVA/GA hydrogels were weighed and then immersed into 100 mL media. At certain time, the hydrogels were separated from the media, drained for 3 min, weighed again. The swelling ratio value (%SR) of the hydrogel was calculated using eqn. 1:

$$\text{Swelling ratio (SR, \%)} = \frac{W_s - W_0}{W_0} \times 100 \qquad (1)$$

Determination of salt absorption: The absorption profile of 0.5 M and 1.0 M NaCl solutions into the PVA/GA hydrogels were investigated. The loading or impregnation of NaCl into hydrogel was carried out by immersing 40 pieces of dried PVA/GA hydrogel in 500 mL of NaCl 0.5 M solution, stirred at ± 200 rpm for 48 h at room temperature. The hydrogels were then squeezed, dried and stored in an incubator at 25 ± 0.1 ºC. To determine the amount of loaded NaCl from the media, sampling was carried out by pipetting 20 mL of liquid from media at time interval of 0 (before the immersion process), 5, 10, 25, 40 and 60 min. To keep the volume of media constant (at 500 mL), immediately after sampling, 20 mL of distilled water was added into the media. The quantity of sodium ions in the sample was measured with atomic absorption spectroscopy (AAS). The same procedure was carried out for NaCl 1.0 M, separately and the hydrogels loaded with NaCl at different concentration were then denoted as PVA/GA-NaCl (0.5 M) and PVA/GA-NaCl (1.0 M).

Determination of release behaviour: The release profile of NaCl from the NaCl loaded hydrogels was carried out by immersing the hydrogel into media with various acidity conditions (pH 5, 6, 7 and 8) at room temperature. In this stage, 9 pieces of PVA/GA-NaCl (0.5 M) were immersed into 500 mL aqueous media of pH 5, with a stirring speed of ± 200 rpm at room temperature. To determine the amount of NaCl released into the media, sampling was carried out by pipetting 20 mL of liquid media at time interval of 0 (before the immersion process), 5, 10, 25, 40 and 60 min. To keep the volume of the media at 500 mL, immediately after sampling, 20 mL of distilled water was added into the media. The same procedures were conducted for the PVA/GA-NaCl (0.5 M and 1.0 M) in media with pH of 6, 7 and 8. The quantity of sodium ions in the sample was then measured using AAS.

RESULTS AND DISCUSSION

Preparation and characterization of PVA/GA hydrogels

Kinetic studies of residual leaching from hydrogel: Since the hydrogel synthesis was conducted in acidic condition, there is a potential of residual protons remaining in the hydrogels, Therefore, the washing procedure was applied to ensure the complete removal of hydrogen ions from the hydrogel. It was found that after repeated washing the residual hydrogen ions was completely removed indicated by insignificant change in the pH of media (pH 7). The residual leaching profile of H^+ ions from the hydrogel into the media in term of pH and conductivity is shown in Fig. 1.

Fig. 1a-b showed that during the first washing process the pH of solution became highly acidic and at the same time the conductivity significantly increased as a function of time. The second stage (Fig. 1c,d) demonstrated the similar trend, even though the pH media was higher compared to the pH values at the first washing, in contrast, the conductivity was lower than that of first stage. This result indicates a gradual decrease in the quantity of residual ions proportional to the washing repetition. The decrease in conductivity corresponds to the leached ions during the washing process. This process was stopped when the pH medium reached 7, which was also confirmed by the conductivity value. The washed hydrogel was used for further investigation in this study.

Regarding to ions, desorption kinetics of the synthesized hydrogel (Fig. 1), an increase in conductivity and decrease in pH at the shorter time interval was clearly observed, then gradually sloped and come to the plateau at the later time period. The relation between conductivity (after corrected for κ_0) and leaching time (Fig. 1b and 1d) can be expressed as second order of desorption kinetics (eqn. 2):

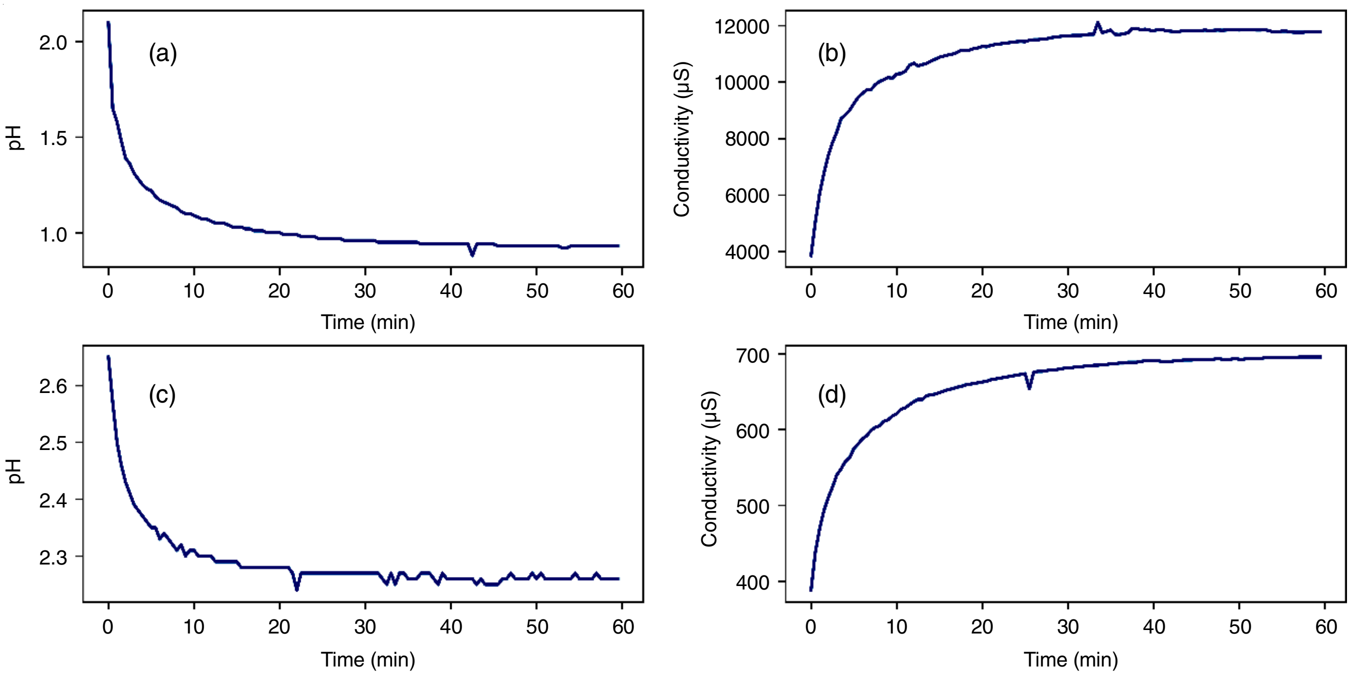

Fig. 1. pH (a,c) and conductivity (b,d) of leaching liquid at the first and the second leaching, respectively

$$\kappa_t = \kappa_\infty \left(1 - \frac{1}{\kappa_\infty kt}\right) \qquad (2)$$

where κ_t is the conductivity at time t; κ_∞ is the conductivity at time ∞ (equivalent to initial number of solute); k is the rate constant for desorption kinetics, with the value for each parameter at first and second leaching are presented in Table-1.

TABLE-1
PARAMETERS VALUES OF SECOND ORDER DESORPTION KINETICS

Parameters	First leaching	Second leaching
k ($mS^2\ cm^{-2}\ s^{-1}$)	$(4.07 \pm (3.94 \times 10^{-8})) \times 10^{-5}$	$(8.02 \pm (1.31 \times 10^{-6})) \times 10^{-4}$
k_∞ ($mS\ cm^{-1}$)	8454.9990 ± 256.9092	328.8318 ± 0.43023
R^2	0.9955	0.9967

Thus, the second order kinetic model produced the desorption rate constant with good precision value (R^2) and with such a small standard deviation. This means that the leaching of impurities from the hydrogel into the media follows the second order kinetics, both in the first and in the second leaching processes.

FT-IR spectral studies: The typical functionalities and its interaction in PVA, PVA/GA, PVA/GA-NaCl (0.5 M) and PVA/GA-NaCl (1.0 M) hydrogels are shown in Fig. 2. The absorption peaks at 3400, 2900, 1656.7, 1438.8 and 1100 cm^{-1} indicate the O-H stretching, C-H sp^3 stretching, C=O stretching, $-CH_2$ bending and C-O stretching, respectively [29,30]. In comparison to the PVA spectrum, the FTIR spectrum of PVA/GA showed a decrease in the intensity of the absorption peak at 3400 cm^{-1}. Also, there was a decrease in the intensity at the wavenumber of 1100 cm^{-1}, which corresponds to the conversion of C-O to C-O-C functional group due to the cross-linking reaction and the formation of acetal bridge. Impregnation of NaCl from the solution with concentration of either 0.5 M or 1.0 M into the PVA/GA hydrogel matrix did not change the absorption peak or formation of a new peak, but only modified the absorption intensity. This phenomenon may indicate that the interaction between NaCl and hydrogel matrix did not change the hydrogel structure, that possibly predominated by hydrogen bonding and van der Waals interaction.

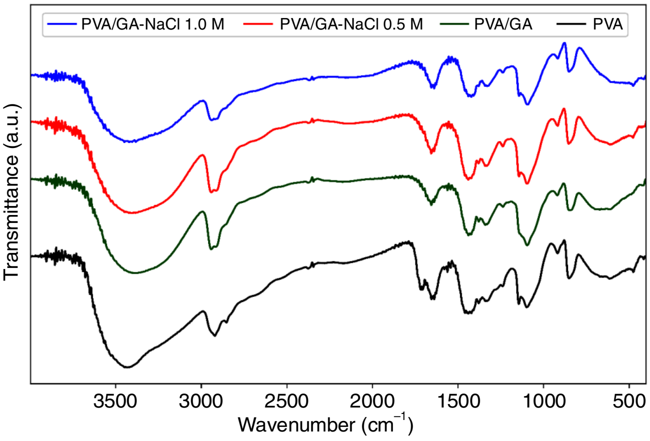

Fig. 2. FT-IR spectra of PVA, PVA/GA, PVA/GA-NaCl (0.5 M) and PVA/GA-NaCl (1.0 M)

Morphological studies: Fig. 3 demonstrated the SEM images in the surface and cross-section of hydrogel with magnification of 3000x where the PVA/GA hydrogels demonstrated the large pores at the bulk and small pores on the surface. It appeared that although the surface was looked smooth, the bulk was actually very porous, as represented by the cross-sectional images. Meanwhile, the SEM images of the PVA/GA-NaCl (0.5 M) and the PVA/GA-NaCl (1.0 M) hydrogels indicated that the hydrogel surface had been covered by NaCl crystals. The covering material on the surface of the PVA/GA-NaCl (1.0 M) hydrogel was thicker than that on the surface of the 0.5 M hydrogel. Meanwhile, at the inner part of both hydrogels, it was appeared that PVA/GA-NaCl (0.5 M) was more porous than PVA/GA-NaCl (1.0 M), indicating that at higher concentration of NaCl solution, salt more excessively penetrated into the hydrogel matrix.

Optimized parameters for agricultural applications

Effect of pH medium on swelling ratio of PVA/GA: The correlation between the swelling ratio of PVA/GA hydrogel and the pH of medium was investigated by evaluating the gel weight increase upon immersion in media with varying acidity levels. The result is illustrated as the swelling ratio in relation to the pH of medium. Fig. 4 showed that the swelling ratio of PVA/GA was influenced by the pH of the environment, where at immersion time up to 7 days, the swelling ratio experienced an increase up to pH 7 due to water absorption in hydrogel matrix and then, it decreased at pH 8. These results can be explained as at low pH aqueous media (pH 5), hydrogen ions protonated the carboxylate anions in the bulk of hydrogel, reducing the repulsion between the carboxylate anions. The increase in number of –COOH group in the hydrogel also increase the number of hydrogen bonds, which could increase the degree of crosslinking, thereby, increase the rigidity of hydrogel structure and decrease the ability of hydrogel to absorb water. At higher pH, the –COOH group will be deprotonated, resulting in the enhanced repulsion between negative charges and, therefore an enhancement in the swelling capacity of hydrogel is observed [31,32]. This explanation is applicable until the pH of the solution was around 7 as shown in Fig. 4. The phenomenon of the decrease in the swelling ability of PVA/GA above pH 7 can be explained by involving the framework of the non-proton cation effect, namely as the ionic strength effect [26,33]. Non-proton cations in the solution derived from the substance then was utilized to increase the pH of the solution. The non-protonic cations may neutralize the charge on the acetate, thus reduce the repulsion between anions, increase hydrogel rigidity, shrink the hydrogel network and consequently reduce swelling ability of hydrogel [29].

Effect of NaCl concentration in medium on swelling ratio of PVA/GA: The swelling ratio (%SR) value of hydrogel immersed in NaCl solution at various concentration is shown in Fig. 5. Increasing the concentration of NaCl at the same acidity level (pH = 7) decreased the swelling capacity of the PVA/GA, where the swelling ratio for NaCl solution media at concentrations of 0.00, 0.25, 0.50, 0.75 and 1.00 M were 177.83%, 154.20%, 144.46%, 134.23% and 125.85%, respectively. It

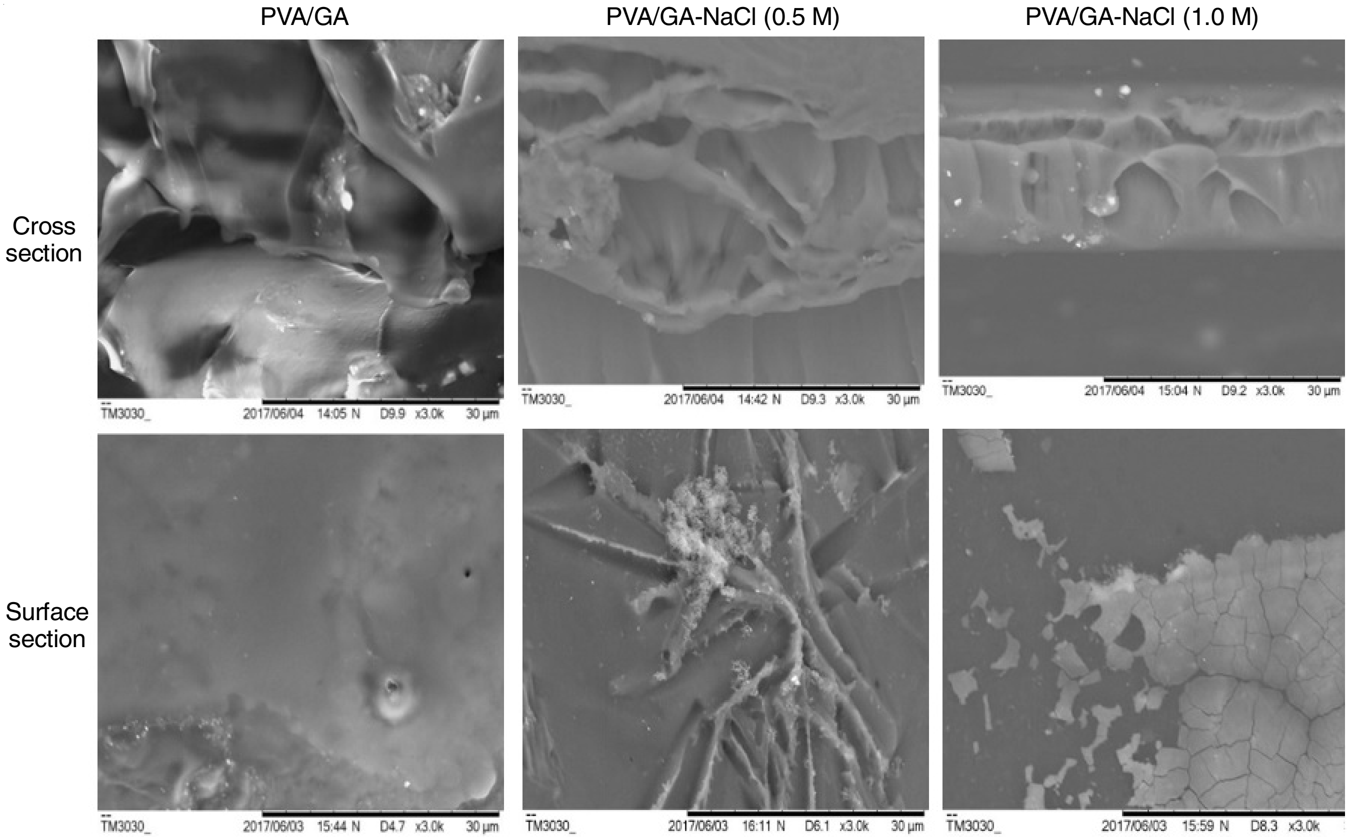

Fig. 3. Surface and cross section SEM images of PVA/GA, PVA/GA-NaCl (0.5 M) and PVA/GA-NaCl (1.0 M)

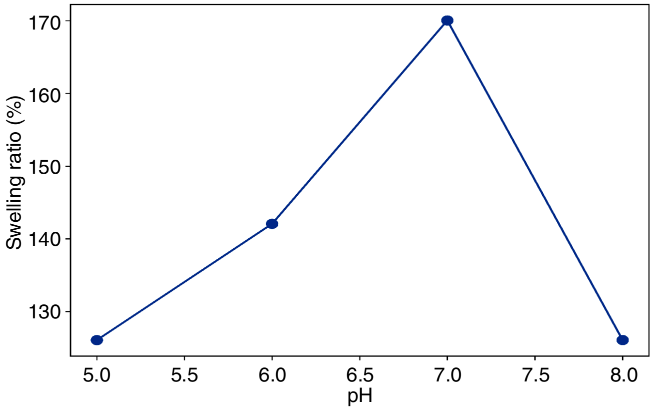

Fig. 4. Swelling ratio of PVA/GA in aqueous media

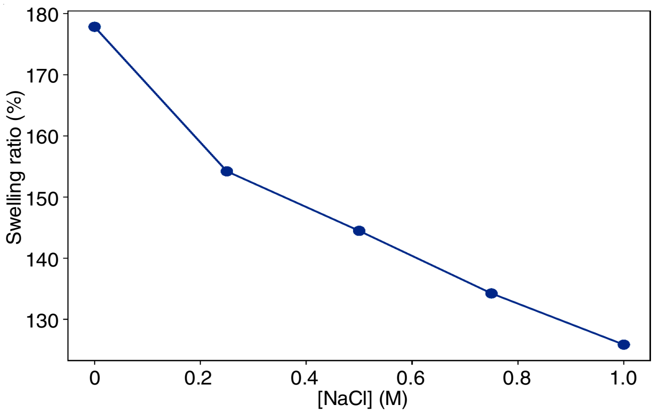

Fig. 5. The swelling ratio PVA/GA at various concentration of NaCl solution at pH 7

can be inferred that the swelling ratio of PVA/GA in distilled water (without NaCl) was the highest and the swelling ratio of hydrogel in 1.0 M NaCl solution media was the lowest. These results are in agreement with the results reported by Zhao *et al.* [34] for the swelling ratio of poly(aspartic acid) super absorbents resin in NaCl solution. This phenomenon could be explained using at least two theoretical frameworks, namely the shielding (charge screening effect) and osmotic pressure effects [29,33,35,36]. The swelling capacity of the hydrogel is reduced since the carboxylate anions are shielded from the non-protonic cations in the salt solution which migrate into the gel, reducing the network size and preventing total electrostatic repulsion between them.

Absorption of NaCl by PVA/GA hydrogels: In order to determine the quantity of loaded NaCl in PVA/GA hydrogels, the washed hydrogel was immersed into salt solution with an estimated concentration of 0.5 M and 1.0 M, where after being verified with AAS gave the real concentration values of 0.64 M and 1.18 M, correspond to 0.5 M and 1.0 M PVA/GA-NaCl hydrogels, respectively. The immersion of these hydrogels into salt solutions was carried out for 60 min. Then, the remaining salt in the media was carefully determined. Fig. 6 demonstrated the swelling ratio (%) of NaCl loaded PVA/GA hydrogels as a function of immersion time. As shown in Fig. 6, it was observed that the salt content of the two media decreased sharply during the first 10 min of immersion, and then remained relatively unchanged until 60 min. Moreover, it was also observed that the residual salt content in the medium was consistently lower when the initial concentration was 0.64 M NaCl compared to 1.18 M NaCl.

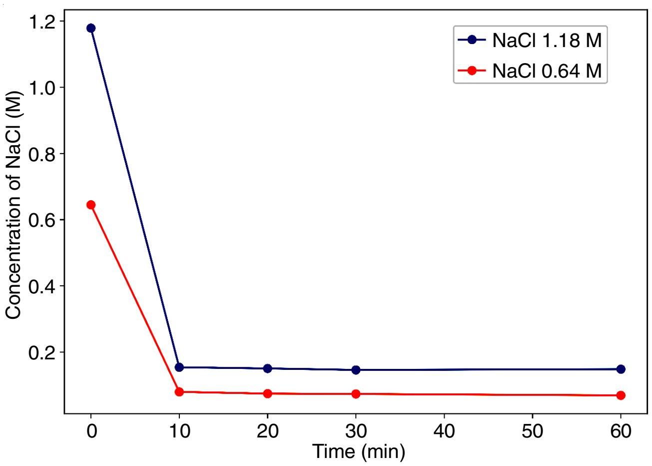

Fig. 6. Remaining amount of NaCl in media after the hydrogels immersed in NaCl solutions

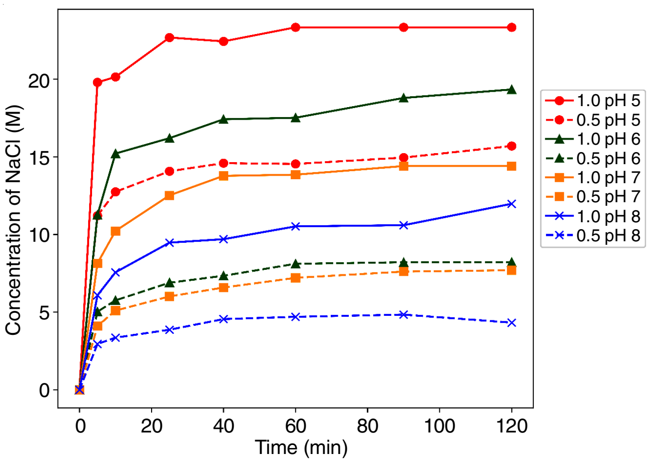

Fig. 7. Release profile of NaCl from PVA/GA-NaCl (0.5 M) and PVA/GA-NaCl (1.0 M) into aqueous medium at different pH

The amount of salt that remains in the hydrogels after 0-10 min cannot be measured in this experiment, but it is plausible to believe that the hydrogels are saturated with salt at that point. It was also observed that the salt amount remaining constant after time interval of approximately 10 min, indicating that the absorption of salt into the gel tends to follow zero-order kinetics (from the beginning of immersion to time when the gel was saturated with salt). In this case, the absorption kinetics is presumably to be influenced by the physical state of hydrogel, such as the pore diameter and cavity area of the gel and the amount of salt in the medium, suggesting that the absorption of the salt by the gel predominantly controlled by diffusion process. This means that the chemical conditions of the bulk and the media have no effect on the absorption kinetics. To achieve this condition, the cavity in the hydrogel must first be covered by cations so that charge shielding occurs perhaps in the first layer and the sodium cations and their counter ions in the media were completely hydrated, thus neglecting the effect of electrostatic interaction. The hydrated cations and the counter ions entered the inner cavity of the gel diffusively. The diameter of the hydrate is influenced by the environmental factors, particularly ionic strength. Consequently, the diffusion rate of hydrate must be defined by the diffusion coefficient, which is dependent upon the hydrodynamic radius [37,38].

Effect of NaCl quantity in PVA/GA and pH of medium on release profile of NaCl from PVA/GA: Fig. 7 shown that in general the amounts of desorbed ions from the PVA/GA tend to increase with the decrease in pH at the same initial concentration of NaCl (when loading into the hydrogel matrix). It was also observed that at the same level of acidity, the amounts of desorbed ions from PVA/GA-NaCl (1.0 M) was higher than that from PVA/GA-NaCl (0.5 M) within the same release period. Thus, both ion concentrations in the PVA/GA and the acidity of the medium significantly affected the desorption capacity of the hydrogel.

In term of sodium ion and its counter ion, the quantity of NaCl in PVA/GA-NaCl (1.0 M) is higher than that in PVA/GA-NaCl (0.5 M), consequently the PVA/GA-NaCl (1.0 M) potentially enables to desorbed more salt into media. The high concentration gradient observed in 1.0 M PVA/GA-NaCl solution compared to 0.5 M PVA/GA-NaCl solution suggests that the 1.0 M solution has a higher sodium ion desorption capability than the 0.5 M solution. Macroscopically, the desorption of NaCl was stopped when the chemical potential of ions in the solid phase (hydrogel) and liquid phase (media) is equal, causing the accumulated ions concentration in the media to be greater when PVA/GA-NaCl (1.0 M) used as source of desorbed ions.

At the initial phase of desorption, as shown in Fig. 7, there was a sharp increase in the NaCl concentration in the medium. According to the fact that an increase in NaCl concentration indicates the rate of desorption, it was of great interest to analyze the factors that might influence the rate of NaCl desorption. For several reasons, it can be suggested that the chemical factors became negligible compared to the physical factors. Firstly, when the amount of salt in hydrogel was quite high, the electrostatic interactions between the carboxylate anions in the hydrogel may be completely shielded, so that the desorption process tended to be more diffusive in nature. Secondly, the possibility of ion exchange can be ruled out by considering the fact that the desorption at low pH occurred faster than that at higher pH and the possibility of protons replacing sodium ions is difficult to accept since the affinity of carboxylate ions to sodium ions is higher than to protons.

However, the suitable reason to explain this phenomenon is the ionic strength (I). Neglecting the influence of water on ionic strength, it is evident that the ions from acid in the medium, together with the desorbed NaCl from PVA/GA, are the primary contributors to the ionic strength of medium. When considering the release profile of PVA/GA-NaCl (1.0 M) as standard, it becomes evident that variations in either pH or the initial concentration of NaCl will lead to changes in the release profile. Fig. 7 also indicated that the desorption behaviour in the composite hydrogels at the initial period were different in term of curve slope at the same pH medium. Meanwhile, the slope of desorption curve at lower pH was steeper than that at higher pH for the composite hydrogels. If pH is the only factor that affect the rate of desorption, then the steepness desorption curve of NaCl from the composite hydrogel should be alike at the same pH value. It was also observed that the PVA/GA-NaCl

(1.0 M) desorption curve was steeper than that of PVA/GA-NaCl (0.5 M), indicating faster released NaCl. This result indicated that there was another contribution to ionic strength, namely the increase of the desorbed salt ions amount. It can be suggested that the steepness of the curves was affected by the ionic strength, which consisted of contribution from pH and dissolved salts concentration, therefore these two factors must be included in the explanation of the desorption phenomenon.

As the desorption process is entirely controlled by diffusion, the ionic strength should directly influence the diffusion coefficient. Several researchers have reported the relationship between the hydrodynamic diameter of polyelectrolytes and ionic strength of the medium and corelates the hydrodynamic diameter with ionic strength [37,38]. Sodium ions and its counter ions desorbed from the hydrogel into medium are in the hydrated form, which have a certain hydrodynamic radius. Initially, during desorption, the ionic strength is primarily influenced by pH, which affects the hydrodynamic radius, leading to the shrinkage of hydrated ions, thereby reducing their diameter and enhancing their diffusivity. This is evidenced by the increased desorption rate as pH decreases (and ionic strength increases). The introduction of salt into the medium, in addition, increases the ionic strength, more affecting the hydrated ions and eventually increases the rate of desorption. This provided the reason that at initial period the system with highest salt concentration and lowest pH induces the steepest slope and the highest desorbed salt.

Conclusion

The synthesized poly(vinyl alcohol)-glutaraldehyde (PVA/GA) hydrogel exhibited a granular gel morphology, characterized by large internal holes and smaller surface pores; the incorporation of NaCl did not alter the structure of the synthesized hydrogel. Pre-washing the gel, prior to sodium ion loading, was crucial to eliminate any unabsorbed ions from the hydrogels. The impurity leaching from the gel constitutes the second order kinetics model, at least for the first and the second leaching processes. The swelling ratio of PVA/GA hydrogels in aqueous media (without salt) increased with increasing pH of the medium up to pH 7, then decreased at pH 8. At the same acidity level, swelling ratio of PVA/GA hydrogels in aqueous media decreased with increasing concentration of NaCl. The maximum saturation level of NaCl absorption into the hydrogel was nearly attained at 10 min in both 0.5 M and 1.0 M NaCl solutions, with 1.0 M NaCl concentration exhibiting a higher absorption rate. Desorption of NaCl from composite hydrogels was gradually increased with the decrease in pH of media, where the NaCl impregnated hydrogel the higher concentration exhibited the higher release rate.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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