Asian Journal of Chemistry; Vol. 33, No. 5 (2021), 1019-1024

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23124

Synthesis and Characterization of Poly(acrylamide) Hydrogels as pH and Salt Sensitive Material

MADHUSUDANA THIPPESWAMY[1], MAMATHA GANJEENAHALLI PUTTAGIDDAPPA[2,*], DEMAPPA THIPPAIAH[3] and NAYAK DEVAPPA SATYANARAYAN[1]

[1]Department of Pharmaceutical Chemistry, Kuvempu University, P.G. Centre, Kadur-577548, India
[2]Department of Chemistry, Davangere University, Shivagangotri, Davangere-577002, India
[3]Department of Polymer Science, University of Mysore, Sir M.V.P.G. Centre, Mandya-571402, India

*Corresponding author: E-mail: mamatha_gp2005@rediffmail.com; vmskt5@gmail.com

Received: 11 January 2021; *Accepted*: 19 February 2021; *Published online*: 16 April 2021; AJC-20320

This work reports the synthesis of poly(acrylamide) hydrogel and its characterization. Hydrogel will be synthesized by a chemical cross-linking method using sodium metabisulfite and potassium persulphate as initiators with crosslinker methylenebisacrylamide. The synthesized hydrogels were examined by FT-IR, SEM and TGA to determine chemical interactions in the polymer network. Moreover, the swelling study explains that hydrogels swelling capacity and it depends on the concentration of the crosslinking agent. The pH, temperature and salt solutions will impact on swelling properties. In acid and base solutions, the swelling ratio order is as follows HCl < CH_3COOH < $HClO_4$ < NaOH and the swelling ratio order in salt solutions is as follows: NaCl > $CaCl_2$ > $AlCl_3$.

Keywords: Hydrogel, Swelling, pH, Crosslinking agent, Acrylamide.

INTRODUCTION

In current years, there has been significant attention to smart, super absorbent and swellable hydrogels. These hydrogels are 3D polymer networks by physical or chemical crosslinking and it expands in biological fluids or water without dissolving as a consequence of physical or chemical cross-linking [1,2].

Hydrogels are applied in pharmaceuticals [3], agriculture [4], food additives [5], drug delivery systems, hygienic products, sealing, artificial snow [6,7], coal dewatering [8], biomedical applications [9,10], barrier materials to regulate biological adhesions [11], tissue engineering and wound dressing [12], diagnostics [13], regenerative medicines [14,15], separation of cells or biomolecules [16] and biosensors [17].

Smart or stimuli-sensitive hydrogels are undergo huge changes in the swelling response by changing environmental conditions, such as pH [18,19], temperature [20], light [21], pressure [22], electric field [23,24], antigens [25,26] and carbohydrates [27]. Among them, pH-sensitive hydrogels are developed in the evolution of new drug delivery systems, these hydrogels changes their properties by respond to the pH of the solution [28]. These gels are good candidates for drug delivery based on pH conditions [29,30]. Hydrogels can absorb large amounts of water without being dissolved. This is often thanks to their physical and chemical network of hydrophilic polymeric chains with -OH, -CONH-, $-CONH_2$ and -COOH groups [31-34].

Drug delivery systems in medicine can be developed by utilizing the swelling behaviour of hydrogel [32,33]. Free radical polymerization is a leading process for the polymerization of water dissolved monomers and to develop hydrogels [32,35]. Free radical polymerization is a dynamic and generally used method and leads to the swift production of the gel even under moderate condition using lesser molecular weight monomers with the existence of a crosslinker can be used to produce hydrogels for bio-applications [36].

In this work, a hydrogel using acrylamide as a monomer and methylene bisacrylamide as the crosslinker by free radical polymerization is synthesized. The swelling study, FT-IR, SEM and TGA were performed to evaluate the swelling and structural characteristics of the obtained gel. The synthesized gel could also be used as pH and salt-sensitive super absorbent materials and drug delivery applications.

EXPERIMENTAL

Acrylamide (AAM), potassium persulphate (PPS), methylenebisacrylamide (MBA), sodium hydroxide, hydrochloric acid, acetic acid and perchloric acid were obtained from SDFCL, Mumbai, India. Sodium metabisulfite (SMBS) obtained from Avra Synthesis Pvt. Ltd., Hyderabad, India. Aluminum chloride, calcium chloride and sodium chloride were purchased from Merck, Mumbai, India. Distilled water was used throughout the experiment.

Preparation of poly(acrylamide) hydrogels: From the free radical mechanism, poly(acrylamide) hydrogel was synthesized. Primarily free radical initiator pair of potassium persulphate and sodium metabisulfite was transferred into a beaker containing water. Then add acrylamide and stir for 10 min at room temperature, finally add crosslinker methylenebisacrylamide and reaction carried out on a water bath till gel was formed. Prepared hydrogel washed with water to remove unreacted materials, then cut into suitable size and dry at 50 ºC in the oven. Similarly, hydrogel formulations were prepared using the same method as given in Table-1.

TABLE-1
SYNTHESIS SCHEMES OF HYDROGELS

Formulation code	Water (mL)	Acrylamide (mg)	Initiator		MBA (mg)
			SMBS (mg)	PPS (mg)	
AAMH1	10	600	32	45	06
AAMH2	10	600	32	45	11
AAMH3	10	600	32	45	16
AAMH4	10	600	32	45	21

FT-IR analysis: FT-IR analysis of acrylamide, methylenebisacrylamide and synthesized hydrogel were administered using FT-IR spectrometer (Perkin-Elmer FT-IR C94012) in the 4000-400 cm^{-1} range.

Morphology analysis: The surface morphology of the acrylamide, methylenebisacrylamide and synthesized hydrogel samples was observed using scanning electron microscopy, Zeiss, LS15.

Thermal analysis: Thermal stability of hydrogel was performed using Perkin-Elmer STA 600 thermogravimetric analyzer. TGA was performed with a specified amount of sample by increase the heating rate to 20 ºC.

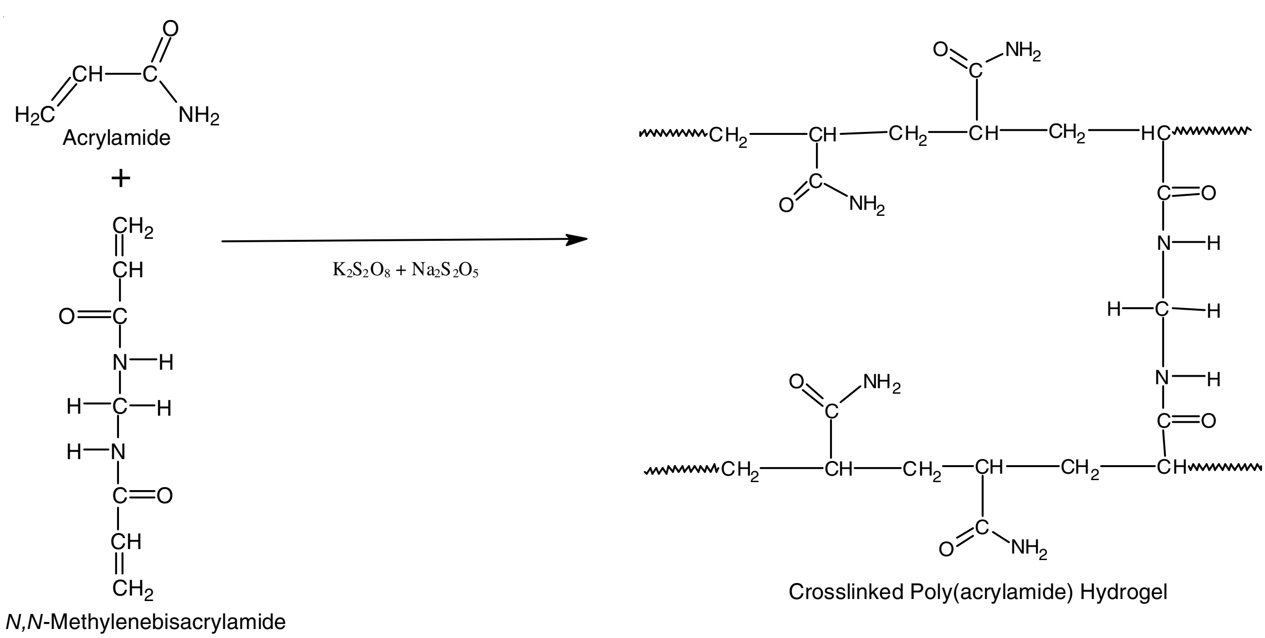
Swelling study: The swelling study was conducted by the gravimetric method using dried hydrogels in water, acids (HCl, CH_3COOH, $HClO_4$), base (NaOH), salts ($AlCl_3$, $CaCl_2$, NaCl) and pH solutions. The dried pre-weighed hydrogel was placed in water, acid, base, salt and pH solutions to investigate swelling ratio at specific intervals. The swelled hydrogel was taken out from the solution and wiped with filter paper for removing excess water, followed by weight measurement, then by using eqn. 1 swelling ratio was calculated:

$$\text{Swelling ratio (\%)} = \frac{W_b - W_a}{W_a} \times 100 \quad (1)$$

where, W_a = Weight of dried hydrogel and W_b = Weight of swelled hydrogel.

RESULTS AND DISCUSSION

Poly(acrylamide) hydrogels was synthesized successfully from acrylamide monomer using sodium metabisulfite and potassium persulphate as free-radical initiators. The free-radical polymerization method is used to prepare hydrogels. The free radicals generated from sodium metabisulfite and potassium persulphate solution. Then hydroxyl free radicals will generate by abstract protons from the water molecules and these radicals further abstract protons from acrylamide and methylenebisacrylamide to initiate polymerization [37,38]. In this polymerization, methylenebisacrylamide is presented as a crosslinker in the system. The mechanism of the reaction is shown in **Scheme-I**.



Scheme-I: Synthesis of poly(acrylamide) hydrogel

FT-IR studies: FT-IR spectra of acrylamide, methylenebisacrylamide and synthesized hydrogel are shown in Fig. 1. The spectra of the acrylamide monomer (Fig. 1a) show the absorption band around 3349 cm^{-1} is due to the NH stretching frequency of the amide group. The peak at 1664 cm^{-1} is attributed due to C=O stretching, while the absorption band around 1134 cm^{-1} is due to the C-N stretching. In the spectra of methylenebisacrylamide (Fig. 1b), the peak at 3309 cm^{-1} is attributed due to the NH stretching and the absorption band around 1664 cm^{-1} is due to C=O stretching. The C-N stretching give rise to a band at 1121 cm^{-1} and a band at 2958 cm^{-1} is assigned for C-H stretching vibrations [39,40]. In the spectra of hydrogel (Fig. 1c), the absorption peak at 3308 cm^{-1} for the NH stretching is also observed. The absorption peaks around 2957 cm^{-1} for C-H stretching, at 1663 cm^{-1} for C=O stretching and at 1119 cm^{-1} for C-N stretching were also observed.

Morphology studies: The surface morphology play important role in swelling and control release behaviour. Hence, it is important to explore these properties [41]. SEM images show the morphology of dried hydrogel. The lower mechanical strength hydrogels have a higher swelling rate [42]. According to the SEM images, pure acrylamide and methylenebisacrylamide show a crystal surface (Fig. 2a-b). However, the addition of methylenebisacrylamide increases to acrylamide hydrogel provides a very smooth and uniform surface structure (Fig. 2c-f).

Thermal study: The thermal behaviour of the synthesized hydrogel was investigated by TGA and the result is shown in Fig. 3. The initial weight loss was attributed to the evaporation of moisture content present in the hydrogel. Poly(acrylamide) hydrogel was thermally unstable and degradation starts at 159 ºC with mass loss of 5.4%, the second degradation at 294 ºC with mass loss of 5% and more amount of weight loss occurred at 394 ºC with mass loss of 8% due to breakage of the polymer chain in the hydrogel [43].

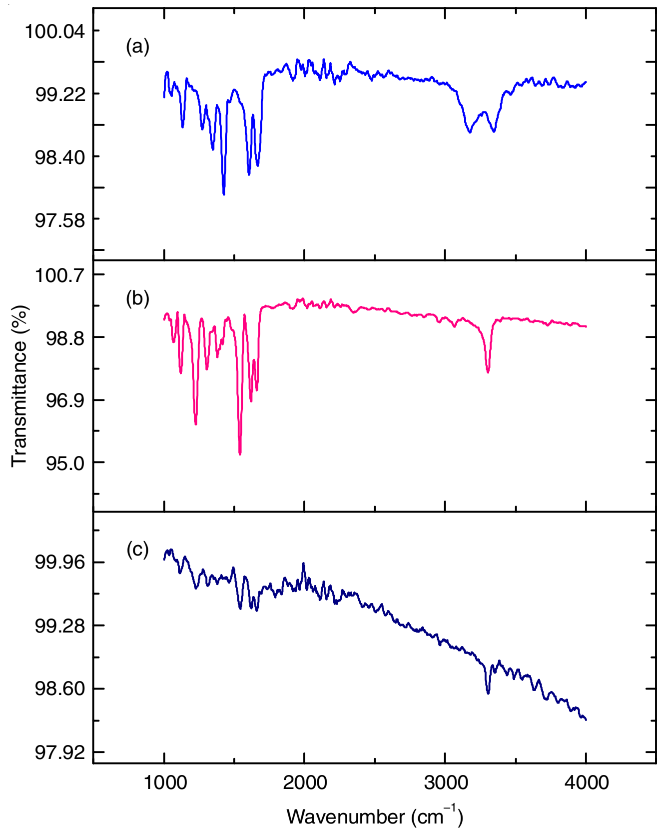


Fig. 1. FT-IR spectra of (a) acrylamide, (b) methylenebisacrylamide and (c) hydrogel

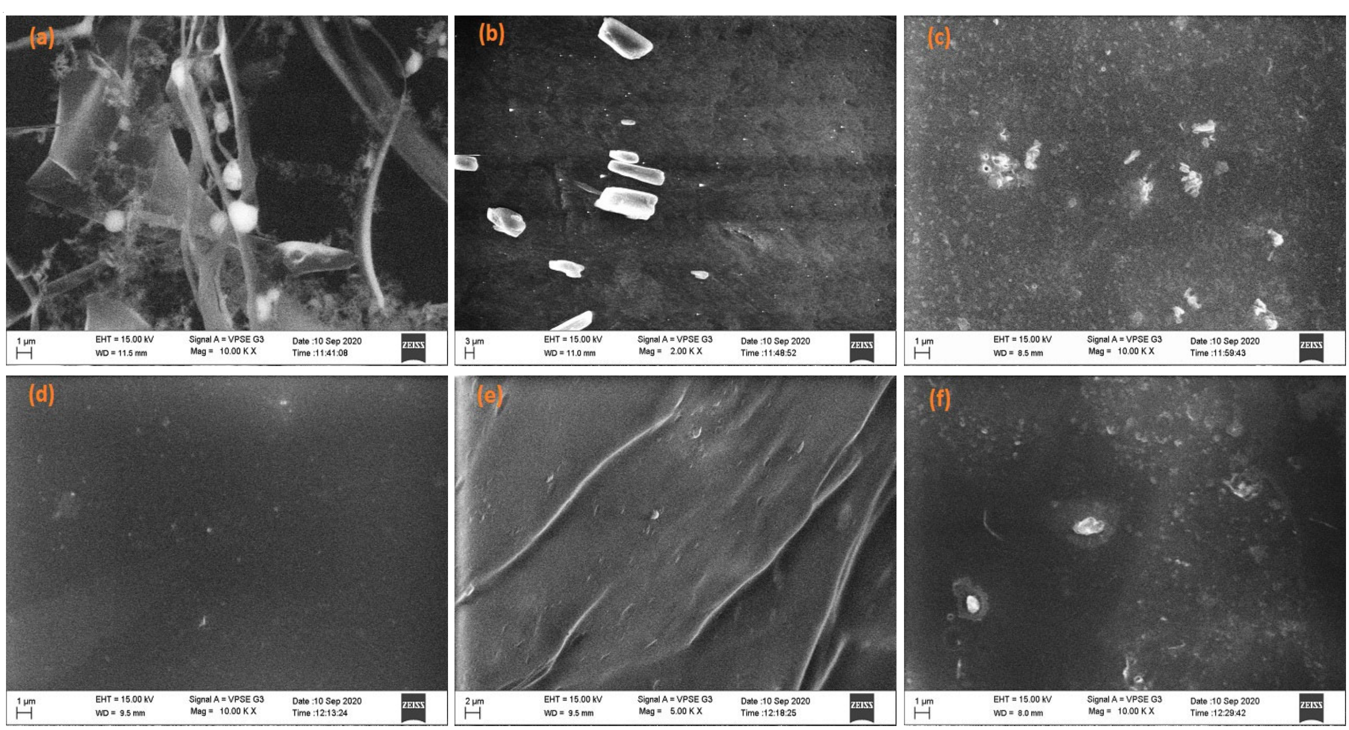


Fig. 2. SEM images of (a) acrylamide, (b) methylenebisacrylamide, (c) AAMH1, (d) AAMH2, (e) AAMH3 and (f) AAMH4

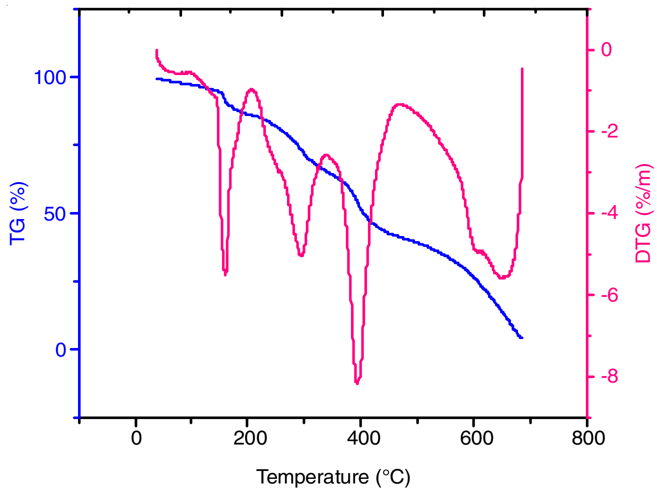


Fig. 3. Thermogravimetric graph of hydrogel

Swelling study: The swelling study is most important to figure out its applications. Here we investigated using water, acid, base, salt and pH solutions. Fig. 4 shows the images of dried and swollen hydrogel.

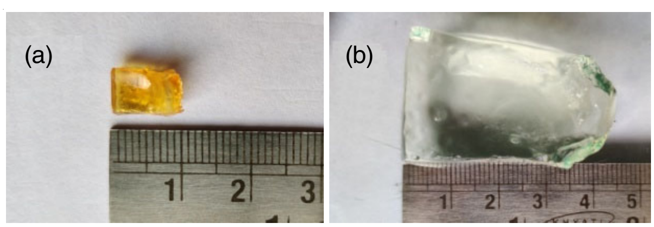


Fig. 4. Digital camera photographs of (a) dried and (b) swollen hydrogel

Swelling study in water: The swelling ratio of the synthesized hydrogels was studied at 37 ºC in water and results shown in Fig. 5. When the less amount of crosslinking agent usage leads to a high swelling ratio due to less crosslinking points and availability of free space between crosslinking points, which helps the gels to hold more amount of solvent molecules. Similarly, more crosslinking agent usage will lead to less swelling ratio due to more crosslinking points and less space [44]. Hence, more amount of crosslinker promotes tight-packed polymer networks, which avoid flexibility and decreases the space in a polymer network and the swelling rate decreased. Hence, we used AAMH1 hydrogel for further study due to its maximum swelling capacity.

Swelling study in acid and base solutions: The swelling study was investigated in HCl, CH_3COOH, $HClO_4$ and NaOH solutions at room temperature. The results are summarized in Figs. 6-9. Hydrogels swelling ability will explain the interaction between functional groups and osmotic pressure [45]. Under acid solutions like HCl, CH_3COOH and $HClO_4$, the amide group of acrylamide hydrogel is mainly controlled the swelling capacity. It will get protonated (NH_3^+) and electrostatic repulsion occurs with osmotic pressure results shows swelling. However, in an acidic solution like HCl the screening effect of chloride counter-ion guard the ammonium cation charges and avoid a dynamic repulsion in HCl solution. Hence, swelling was decreased in HCl solution compared to CH_3COOH and $HClO_4$ solution. Under basic condition like NaOH solution, the $-CONH_2$ and -CONH- groups are deprotonated and electrostatic repulsion occurs. The existence of sodium ions will lead to high osmotic swelling pressure and help to increase swelling even in a very low concentration of NaOH solution. The swelling percentage in acid and base solution is in the order: HCl < CH_3COOH < $HClO_4$ < NaOH [46,47].

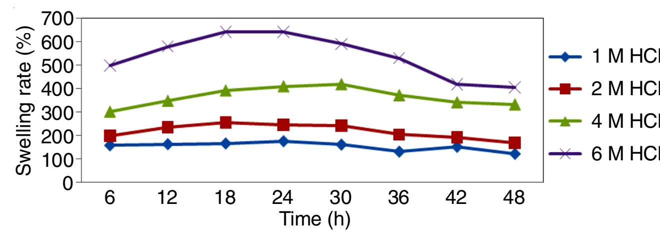


Fig. 6. Swelling ratio in HCl solutions

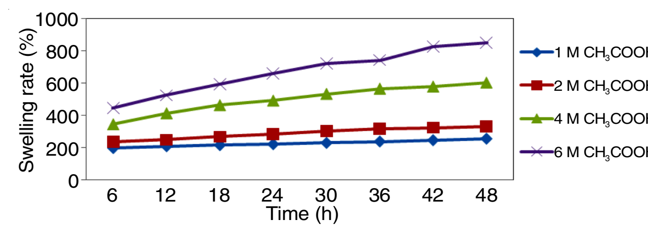


Fig. 7. Swelling ratio in CH_3COOH solutions

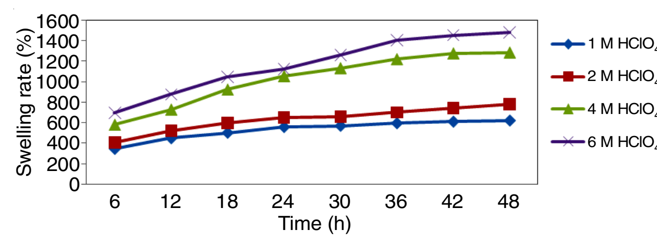


Fig. 8. Swelling ratio in $HClO_4$ solutions

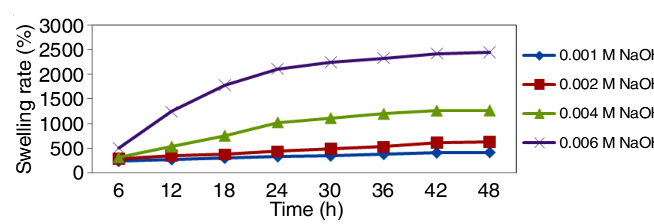


Fig. 9. Swelling ratio in NaOH solutions

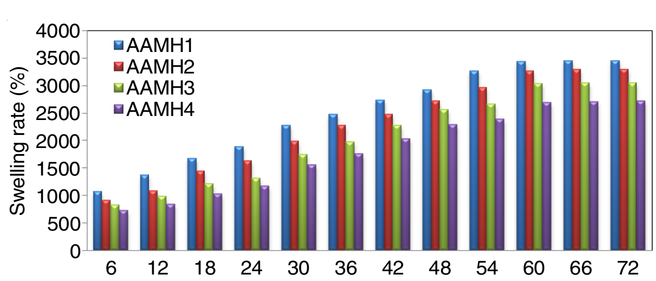


Fig. 5. Swelling ratio in water

Swelling study in pH solutions: The swelling study was investigated at 37 ºC in pH 1 to 12 solutions. The swelling ratio depend on the pH of the solution [37]. Fig. 10 shows the pH response of the poly(acrylamide) hydrogel at 37 ºC. The stock solutions HCl (pH 1.0) and NaOH (pH 12.0) were diluted with deionized water to prepare pH solutions and no additional ions were added to the medium for setting the pH of the solutions due to the hydrogel is more influenced by ionic strength. The swelling ratio increased when pH increased from 1 to 12 and when the temperature increases swelling also increases, it was evident from the data given [45]. However, up to pH 4.0, we observed very little swelling due to the screening effect of Cl^- counter-ion. From pH 5 to 12, the swelling increases due to amide groups are deprotonated and the presence of osmotic pressure of Na^+ ions. The result shows when pH increase the swelling ratio also increases [46].

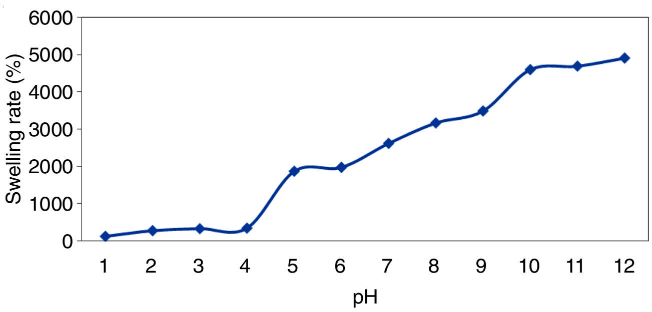


Fig. 10. Swelling ratio of hydrogel in 1 to 12 pH solutions at 37 °C

Swelling study in salt solutions: Fig. 11 shows the swelling ratio of poly(acrylamide) cross-linked hydrogel in salt solutions (0.15 M NaCl, $CaCl_2$ and $AlCl_3$). The swelling ratio in water (Fig. 5) is more compared to the salt solutions due to the presence of the additional ions and leads to the osmotic pressure between the hydrogel network and external solution with screening effect. The swelling percentage decrease when increase the charge of the metal cation ($Na^+ > Ca^{2+} > Al^{3+}$) [37,45]. In crosslinked hydrogel, the screening effect of chloride counterion and complex formation between ionic groups leads to crosslinking density increases and swelling capacity decreases.

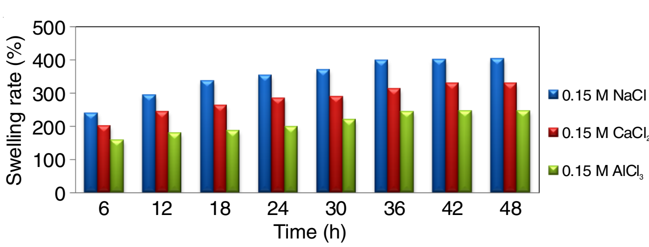


Fig. 11. Swelling ratio in salt solutions

Conclusion

In this investigation, the poly(acrylamide) hydrogels were synthesized by using both potassium persulphate and sodium metabisulfite as a free radical generator for polymerization. Different hydrogels were synthesized by increasing the amount of crosslinker. The increasing amount of crosslinker will affect the characterization and swelling study. Furthermore, the swelling ratio changes based on the composition of the hydrogel, ionic strength, temperature and pH. Synthesized hydrogels exhibit good swelling nature in water, pH, acid, base and salt solutions. The composition of hydrogel and the surrounding environment will affect the swelling capacity. The swelling response of the hydrogel may be considered a good material for the design of controlled release fertilizers in agricultural applications and biomedical drug delivery systems.

CONFLICT OF INTEREST

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

REFERENCES

1. N.A. Peppas and A.R. Khare, *Adv. Drug Deliv. Rev.*, **11**, 1 (1993); https://doi.org/10.1016/0169-409X(93)90025-Y
2. R. Niladri and S. Nabanita, PVP-Based Hydrogels: Synthesis, Properties and Peppas Applications, Nova Science Publishers, New York, p. 1 (2012).
3. N. Kashyap, N. Kumar and M. Kumar, *Crit. Rev. Ther. Drug Carrier Syst.*, **22**, 107 (2005); https://doi.org/10.1615/CritRevTherDrugCarrierSyst.v22.i2.10
4. E. Karada, D. Saraydin, Y. Caldiran and O. Güven. *Polym Adv Technol.*, **11(2)**, 59 (2000); https://doi.org/10.1002/(SICI)1099-1581(200002)11:2<59::AID-PAT937>3.0.CO;2-Z
5. X. Chen, B.D. Martin, T.K. Neubauer, R.J. Linhardt, J.S. Dordick and D.G. Rethwisch, *Carbohydr. Polym.*, **28**, 15 (1995); https://doi.org/10.1016/0144-8617(95)00082-8
6. A. Singh, P.K. Sharma, V.K. Garg and G. Garg, *Int. J. Pharm. Sci. Rev. Res.*, **4**, 97 (2010).
7. M. Hamidi, A. Azadi and P. Rafiei, *Adv. Drug Deliv. Rev.*, **60**, 1638 (2008); https://doi.org/10.1016/j.addr.2008.08.002
8. G.P.T. Dzinomwa, C.J. Wood and D.J.T. Hill, *Polym. Adv. Technol.*, 8, 767 (1997); https://doi.org/10.1002/(SICI)1099-1581(199712)8:12<767::AID-PAT717>3.0.CO;2-G
9. S. Kaihara, S. Matsumura and J.P. Fisher, *Eur. J. Pharm. Biopharm.*, **68**, 67 (2008); https://doi.org/10.1016/j.ejpb.2007.05.019
10. D.F. Stamatialis, B.J. Papenburg, M. Girones, S. Saiful, S.N.M. Bettahalli, S. Schmitmeier and M. Wessling, *J. Membr. Sci.*, **308**, 1 (2008); https://doi.org/10.1016/j.memsci.2007.09.059
11. D. Roy, J.N. Cambre and B.S. Sumerlin, *Prog. Polym. Sci.*, **35**, 278 (2010); https://doi.org/10.1016/j.progpolymsci.2009.10.008
12. P. Sikareepaisan, U. Ruktanonchai and P. Supaphol, *Carbohydr. Polym.*, **83**, 1457 (2011); https://doi.org/10.1016/j.carbpol.2010.09.048
13. H.J. Van der Linden, S. Herber, W. Olthuis and P. Bergveld, *Analyst*, **128**, 325 (2003); https://doi.org/10.1039/b210140h
14. L. Zhang, K. Li, W. Xiao, L. Zheng, Y. Xiao, H. Fan and X. Zhang, *Carbohydr. Polym.*, **84**, 118 (2011); https://doi.org/10.1016/j.carbpol.2010.11.009
15. J.M. Saul and D.F. Williams, Hydrogels in regenerative medicine, Elsevier: Amsterdam, The Netherlands, p. 279 (2013).
16. F. Wang, Z. Li, M. Khan, K. Tamama, P. Kuppusamy, W.R. Wagner, C.K. Sen and J. Guan, *Acta Biomater.*, **6**, 1978 (2010); https://doi.org/10.1016/j.actbio.2009.12.011
17. P. Krsko, T.E. McCann, T.T. Thach, T.L. Laabs, H.M. Geller and M.R. Libera, *Biomaterials*, **30**, 721 (2009); https://doi.org/10.1016/j.biomaterials.2008.10.011
18. Y. Chu, P.P. Varanasi, M.J. McGlade and S. Varanasi, *J. Appl. Polym. Sci.*, **58**, 2161 (1995); https://doi.org/10.1002/app.1995.070581203
19. B.A. Firestone and R.A. Siegel, *J. Biomater. Sci. Polym. Ed.*, **5**, 433 (1994); https://doi.org/10.1163/156856294X00130

20. R. Yoshida, K. Uchida, Y. Kaneko, K. Sakai, A. Kikuchi, Y. Sakurai and T. Okano, *Nature*, **374**, 240 (1995); https://doi.org/10.1038/374240a0
21. A. Mamada, T. Tanaka, D. Kungwatchakun and M. Irie, *Macromolecules*, **23**, 1517 (1990); https://doi.org/10.1021/ma00207a046
22. X. Zhong, Y.X. Wang and S.C. Wang, *Chem. Eng. Sci.*, **51**, 3235 (1996); https://doi.org/10.1016/0009-2509(95)00344-4
23. T. Shiga, Y. Hirose, A. Okada and T. Kurauchi, *J. Appl. Polym. Sci.*, **46**, 635 (1992); https://doi.org/10.1002/app.1992.070460410
24. Y. Osada, H. Okuzaki and H. Hori, *Nature*, **355**, 242 (1992); https://doi.org/10.1038/355242a0
25. T. Miyata, N. Asami and T. Uragami, *Nature*, **399**, 766 (1999); https://doi.org/10.1038/21619
26. M.A. Dabbagh, E. Moghimipour, A. Ameri and A. Sayfoddin, *Iran. J. Pharm. Res.*, **7**, 21 (2008).
27. A.A. Obaidat and K. Park, *Biomaterials*, **18**, 801 (1997); https://doi.org/10.1016/S0142-9612(96)00198-6
28. N.A. Peppas, P. Buresa, W. Leobandunga and H. Ichikawa, *Eur. J. Pharm. Biopharm.*, **50**, 27 (2000); https://doi.org/10.1016/S0939-6411(00)00090-4
29. J. Kost and R. Langer, *Adv. Drug Deliv. Rev.*, **46**, 125 (2001); https://doi.org/10.1016/S0169-409X(00)00136-8
30. Y. Qiu and K. Park, *Adv. Drug Deliv. Rev.*, **53**, 321 (2001); https://doi.org/10.1016/S0169-409X(01)00203-4
31. B. Tasdelen, N. Kayaman-Apohan, O. Güven and B.M. Baysal, *Radiat. Phys. Chem.*, **69**, 303 (2004); https://doi.org/10.1016/j.radphyschem.2003.07.004
32. S.Y. Tang, P. Shridharan and M. Sivakumar, *Ultrason. Sonochem.*, **20**, 485 (2013); https://doi.org/10.1016/j.ultsonch.2012.04.005
33. V. Jokanovic, B. Colovic, M.D. Sikiric and V. Trajkovic, *Ultrason. Sonochem.*, **20**, 535 (2013); https://doi.org/10.1016/j.ultsonch.2012.08.015
34. Shelly, H. Setia, A. Thakur and R.K. Wanchoo, *J. Polym. Mater.*, **29**, 401 (2012).
35. P. Cass, W. Knower, E. Pereeia, N. Holmes and T. Hughes, *Ultrason. Sonochem.*, **17**, 326 (2010); https://doi.org/10.1016/j.ultsonch.2009.08.008
36. K. Varaprasad, G.M. Raghavendra, T. Jayaramudu, M.M. Yallapu and R. Sadiku, *Mater. Sci. Eng. C*, **79**, 958 (2017); https://doi.org/10.1016/j.msec.2017.05.096
37. G. Mahdavinia, A. Pourjavadi, H. Hosseinzadeh and M. Zohuriaan, *Eur. Polym. J.*, **40**, 1399 (2004); https://doi.org/10.1016/j.eurpolymj.2004.01.039
38. J.R. Ebdon, T.N. Huckerby and T.C. Hunter, *Polymer*, **35**, 250 (1994); https://doi.org/10.1016/0032-3861(94)90687-4
39. B.V. Reddy and R.B. Rao, *Indian J. Pure Appl. Phys.*, **46**, 611 (2008).
40. A. Avsar, Y. Gokbulut, B. Ay and S. Serin, *Des. Monomers Polym.*, **20**, 434 (2017); https://doi.org/10.1080/15685551.2017.1332138
41. J. Chen, M. Liu, H. Liu and L. Ma, *Mater. Sci. Eng. C*, **29**, 2116 (2009); https://doi.org/10.1016/j.msec.2009.04.008
42. F.A. Aouada, B.S. Chiou, W.J. Orts and L.H. Mattoso, *Polym. Eng. Sci.*, **49**, 2467 (2009); https://doi.org/10.1002/pen.21505
43. R. Ebrahimi and M. Salavaty, *e-Polymers*, **18**, 187 (2018); https://doi.org/10.1515/epoly-2017-0123
44. J. Wu, J. Lin, G. Li and C. Wei, *Polym. Int.*, **50**, 1050 (2001); https://doi.org/10.1002/pi.728
45. S. Nesrinne and A. Djamel, *Arab. J. Chem.*, **10**, 539 (2017); https://doi.org/10.1016/j.arabjc.2013.11.027
46. A. Pourjavadi and G.R. Mahdavinia, *Turk. J. Chem.*, **30**, 595 (2006).
47. L.R. Shivakumara and T. Demappa, *Turk. J. Pharm. Sci.*, **16**, 252 (2019); https://doi.org/10.4274/tjps.galenos.2018.92408