

Preparation and Swelling Study of CMC Hydrogel as Potential Superabsorbent

Nur Fitrah Che Nan, Norhazlin Zainuddin* and Mansor Ahmad

Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia

ABSTRACT

Carboxymethylcellulose (CMC) is a water-soluble polymer, which is widely used in various fields such as food additives, textiles, pharmaceuticals and cosmetics. In this study, hydrogel was prepared from CMC by using calcium chloride as a crosslinking agent. Optimization of the reaction was done through investigation of four different parameters which had different percentage of CMC (w/v), percentage of calcium chloride (w/v), reaction time and temperature. The gel content and swelling properties of the CMC hydrogel were studied. The highest gel content was 85.33% at 7% of CMC (w/v) with 2% of calcium chloride (w/v) in 24 hours reaction time at room temperature. The gel content increased with the increasing concentration of CMC and CaCl₂. This was due to the higher number of functional groups of COO⁻ that were available in more concentrated CMC which could crosslink with CaCl₂ to give higher gel content. Increasing the percentage of CaCl₂ will increase the electrostatic attraction between anionic charges of polymer chains and multivalent cation (Ca²⁺) that leads to increase in ionic crosslinking of CMC. The swelling properties of CMC hydrogel showed that the optimum degree of swelling was 45.33 (g/g). The swelling capacity of the hydrogel in water decreased with the increase of the gel content of CMC hydrogel. This could be due to the increase in the degree of crosslinking of the CMC hydrogel.

Keywords: Calcium chloride, carboxymethylcellulose, hydrogel, polymer, superabsorbent

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E-mail addresses:

norhazlin@upm.edu.my (Norhazlin Zainuddin)

nurfitrahchenan@yahoo.com (Nur Fitrah Che Nan)

mansorahmad@upm.edu.my (Mansor Ahmad)

* Corresponding author

INTRODUCTION

Polysaccharides play crucial roles in life processes of all plants. Furthermore, polysaccharides can form glycoconjugates with proteins and lipids resulting in biological macromolecules in the cell wall and cell wall membranes, which play important roles in many physiological

and biochemical processes. The main polysaccharides of primary walls are cellulose, hemicellulose, and pectin.

Cellulose is the most inexhaustible natural polymer on earth and rich with hydroxyl groups which can easily form hydrogen bonding. It is characterized by its hydrophilicity, chirality, and biodegradability which is formed from repeated connection of *D*-glucose building blocks (Klemm, et al., 2005). Cellulose is suitable in the making of cellulose-based hydrogel and can be applied in various fields such as food additives, agriculture, civil engineering, cosmetic and pharmaceuticals. Cellulose is biorenewable material that represents one of the largest and renewable sources of environmentally friendly raw materials (Thakur & Thakur, 2014). Cellulose is the main component that provides the strength in plants. Other than cellulose, starches and chitin are also part of natural polymers that can be obtained from plants and animals. Both of cellulose and starches are made from sugars and are known as polysaccharides.

Cellulose derivatives such as hydroxypropyl cellulose (HPC), methyl cellulose, and carboxymethylcellulose (CMC) have been used to make cellulose based hydrogel (Shen, Shamshina, Berton, & Rogers, 2016). It can be made through physical, chemical and radical crosslinking (Pourjavadi and Hosseinzadeh, 2010). In this study, we concentrated on carboxymethylcellulose (CMC) since it has great properties that can be applied in various applications especially in hydrogel form.

Carboxymethylcellulose (CMC) known as a polyelectrolyte cellulose derivative that contains carboxyl and hydroxyl groups (Benhalima, Ferfera-Harrar, & Lerari, 2017). This polymer chain is composed of anhydroglucopyranose units joined together by 1,4-glycosidic bonds. Moreover, CMC is regarded as anionic carboxymethyl ether which is prepared by reacting alkali cellulose with sodium monochloroacetate. The polar carboxyl group makes CMC chemically reactive, tasteless, nontoxic, and have water soluble characteristics (Wang et al., 2013). CMC is an important material in industries especially as stabilizing and bonding agent.

Hydrogels which are physically or chemically crosslinked with hydrophilic polymer networks are capable of absorbing large amount of water and retain significant amount of water in their structures. Hydrogels do not dissolve and can swell in the water. The rate of absorption of hydrogels in the water is influenced by the presence of functional groups such as alcohols, carboxyls, sulphonic acid on the polymer backbone (Dafader et al., 2011). Many physical forms of formulating hydrogel can be obtained due to the ability of the semi-flexible polymer. For example slabs, membranes, beads, microgels (microspheres), and nanogels (nanoparticles). Other than that, once the hydrogels had been dried using freeze-dried or supercritically dried, hydrogels will become aerogels or cryogels respectively (Shen et al., 2016).

By definition, superabsorbent can be considered as a three-dimensional network structure that can absorb a large amount of water without dissolving it in the water due to particular amounts of hydrophilic groups (Wang et al., 2013). Superabsorbent mostly

comes from polymer that are highly crosslinked and able to swell when they are immersed in aqueous solutions. In terms of the crosslinking, either through chemical or physical crosslinking, solubilization can be avoided as water can invade without breaking the vigorous interaction that binds the polymer chains.

In this study, calcium chloride was used as a crosslinker via ionic crosslinking. Many researchers investigated the potential of CMC in various applications especially in the making of CMC hydrogel that acts as superabsorbent. However, the making of superabsorbent from CMC using divalent salts as crosslinker has not been studied widely. It has been reported previously that cellulose hydrogel is capable in response to external stimuli such as solvents, temperature, pH, ionic force, electric field, light irradiation, and salt concentration (Sanna, 2013). In this study, optimization and swelling studies of CMC hydrogel were investigated and the reaction of four different parameters with different percentage of CMC (w/v), percentage of calcium chloride (w/v), reaction time and temperature were studied as it can be used as potential superabsorbent in the future.

MATERIALS AND METHODS

Carboxymethylcellulose sodium salt (CMC) and calcium chloride were purchased from R&M Chemical. All the other chemicals used were of analytical grade. Distilled and deionized water were used throughout the experiment.

Preparation of CMC Hydrogel

The preparation of CMC hydrogel in calcium chloride solution which acts as a crosslinker was carried out according to the method published by (Chia et al., 2015). (1-7%) of CMC (w/v) was dissolved in (1-6%) of calcium chloride (w/v). The paste-like solution of CMC-CaCl₂ was then transferred into petri dish and it was expected to crosslink for 24h reaction time at room temperature. The optimization of CMC hydrogel was determined by percentage of gel content and degree of swelling.

Determination of Gel Content

The CMC hydrogel was immersed in deionized water for 72 hours at room temperature. After 72 hours, the hydrogel was dried in an oven at 60°C until constant weight was obtained. The percentage of gel content was calculated using the following formula:

$$\text{Percentage of gel content (\%)} = \frac{(W_i - W_o)}{W_i} \times 100 \quad (1)$$

where W_i = initial weight of the sample, and W_o = weight of the sample after immersion and drying process.

Determination of Degree of Swelling

The degree of swelling of CMC hydrogel was calculated after removal of the surface water until equilibrium swelling value was obtained. The degree of swelling was determined by following equation:

$$\text{Degree of swelling} = \frac{(W_t - W_o)}{W_i} \times 100 \tag{2}$$

where W_t and W_o are the weight of the swollen hydrogel at time t and the weight of dry samples. All experiments were carried out in triplicate or quadruplicate. Where appropriate, data were presented as means \pm standard deviation.

RESULTS AND DISCUSSION

Effect of Concentration of CMC on CMC Hydrogel

Figure 1(a) shows the gel content of CMC hydrogels. To isolate the effect of percentage of CMC, all other parameters were fixed. Percentage of calcium chloride was kept at 1% (w/v), and the experiment was conducted for 24 hours of reaction time at room temperature. In this study, the percentage of CMC was varied from 1 to 9% (w/v). The gel content increased from 4% to 7%. At higher concentration of CMC, the distance between CMC molecules became closer and consequently allowed the Ca^{2+} ions to crosslink the CMC molecules. However, the gel content started to decrease at 8% of CMC concentration. This may be due to incomplete dissolution of CMC powder in the salt solution. Interactions between $-\text{OH}$ groups of the polymer (CMC) and the metal ions (Ca^{2+}) contributed to the stability and the water insolubility of these polymer aggregated (Patil et al., 2010). CMC was found to be at the optimum condition at 7% w/v with 50.83% gel content.

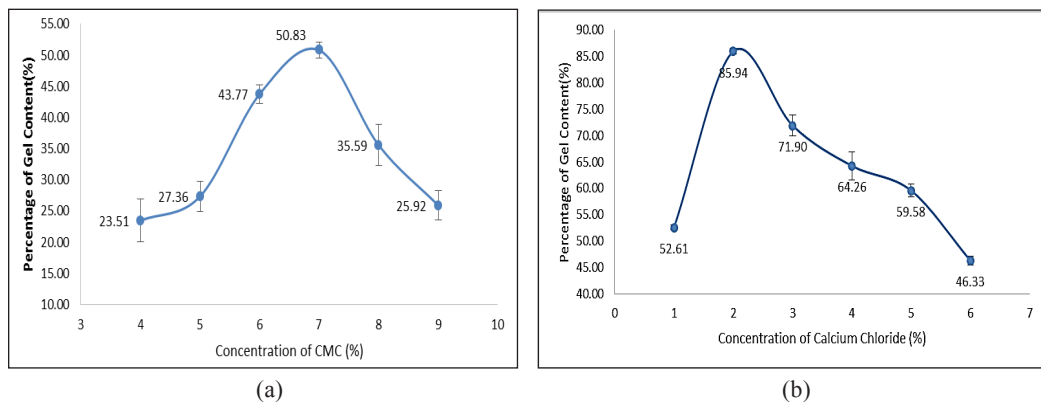


Figure 1. Percentage of gel content: (a) Effect of concentration of CMC; and (b) Effect of concentration of calcium chloride

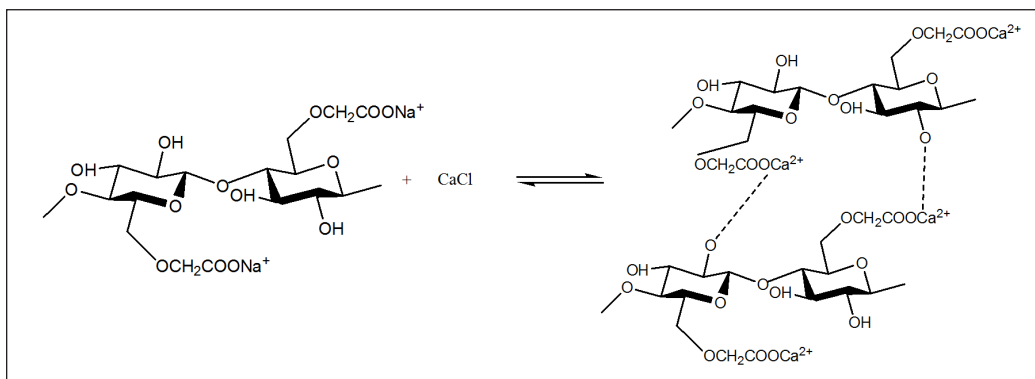
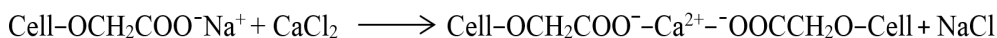


Figure 2. Reaction between carboxymethylcellulose and calcium chloride

Effect of Percentage of Calcium Chloride on CMC Hydrogel

Figure 1(b) shows that the percentage of gel content rapidly increased when less than 2% of CaCl_2 were used and gradually decreased when more than 2% were used. The reduction was slightly rapid when the concentration of CaCl_2 was between 2%-3% where the percentage dropped from 85.94% to 71.90%. Increasing the electrostatic attraction between anionic charges of polymer chains and multivalent cation (Ca^{2+}) lead to the increase of ionic crosslinking of polymer (Sultana et al., 2012). Figure 2 shows the reaction between carboxymethylcellulose and calcium chloride. Ionic strength of salt had a remarkable effect on the cross-linking of CMC but at 3% CaCl_2 , ionic strength showed a reversible result. At high concentrations of salt, the CMC chains lose their flexibility. Thus, the hydrodynamic size of the molecule diminished, producing an agglomeration of polymer chains. The presence of high concentration of calcium ion prevented the full hydration of the CMC in water, thus, reducing the dissolution of CMC in the water. (Khaled & Abdelbaki, 2012). Equation 1.1 shows the reaction between CMC and CaCl_2 to form CMC hydrogel.



Equation 1.1

Effect of Reaction Time on CMC Hydrogel

In this investigation, the reaction time of cross-linking was varied from 12 hours to 96 hours. 7% CMC (w/v) was dissolved in 2% of CaCl_2 (w/v) at different reaction time. It was found that, 24 hours was the optimum condition for the highest gel content. Figure 3(a) shows that after 24 hours, the gel content reduced and reached to half of its optimum value at 96 hours reaction time. There was a weak electrostatic attraction between CMC molecule and Ca^{2+} ion. The longer the CMC was in contact with calcium chloride solution, the stronger the physical appearance of the gel formed, as more crosslinks were formed (Patil et al.,

2010). However, after 24 hours, the reduction of the gel content of CMC hydrogel was observed. This could be due to the presence of NaCl in the hydrogel. As the Ca^{2+} ions attached to the polymer chains and formed crosslinkages, the Na^+ ion from $-\text{CH}_2\text{COONa}$ combined with Cl^- ions to form NaCl. The presence of NaCl will weaken the electrostatic attraction between the charges on the polymer chains. Therefore, the longer reaction time may trigger reversible reaction in CMC hydrogel (Qiao et al., 2012).

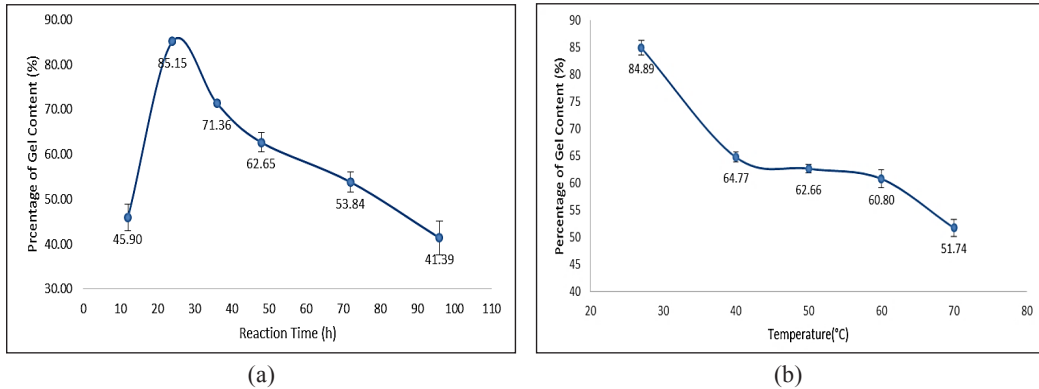


Figure 3. Percentage of gel content at different: (a) reaction time; and (b) reaction temperature

Effect of Temperature on CMC Hydrogel

Figure 3(a) shows the percentage of gel contents of CMC hydrogel formed at room temperature to 70°C. The trend of the graph depicts that, the higher the reaction temperature, the lower the gel content. The highest percentage of gel content obtained was at room temperature with 84.89% gel content. The gel content reduced to 64.77% when the temperature increased to 40°C. As ionic interaction is a physical crosslinking then it could be a reversible reaction. At high temperature with low concentration of calcium chloride it triggered the reversible reaction thus lowering the gel content. Similar finding was reported by Nie et al. (2004) where they stated that hydrogel structure formed through salt crosslinking with CMC was stable at low temperature and easily decomposed at high temperature.

Degree of Swelling

The swelling capacity of the hydrogel is inversely proportional to gel content for all parameters studied using deionized water (Figure 4). The swelling emulated the degree of crosslinking of CMC hydrogel. The swelling behavior is influenced by hydrophilicity of the carboxylic group in the structure of the hydrogels (Jamingan et al., 2015). As cross-linked density of CMC hydrogel increased, the swelling capacity of CMC hydrogel was reduced as a result of the limited space available for the free water to enter into the

hydrogel network. Therefore, the lowest degree of swelling was found in all parameters at the highest gel content of CMC hydrogel which due to the limited space available for the water. Furthermore, swelling process can occur in three particular steps: (a) diffusion of water molecules through the matrix, (b) relaxation of polymer chains via hydration, and (c) expansion of polymer network upon relaxation. This process occurred when CMC hydrogel was immersed in deionized water, the hydrophilic polymeric chains created an osmotic pressure within the hydrogel leading to the swelling of the hydrogel matrix (Abd El-salam Deghiedy, 2004).

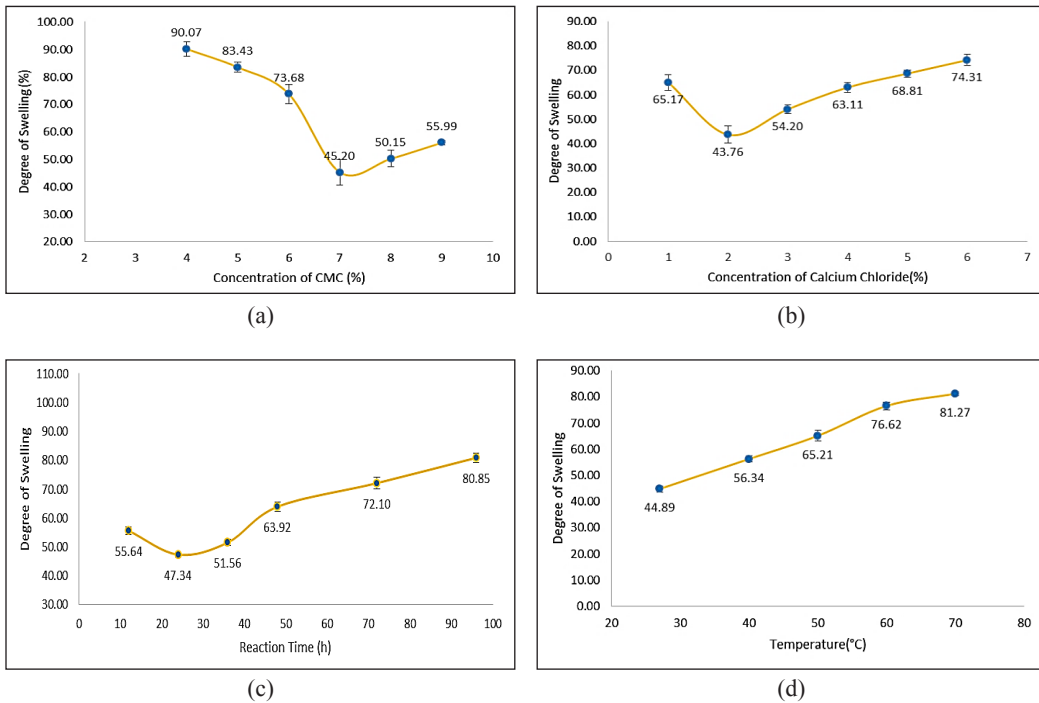


Figure 4. Degree of swelling of CMC hydrogel at different parameters: (a) concentration of CMC; (b) concentration of calcium chloride; (c) reaction time; and (d) temperature

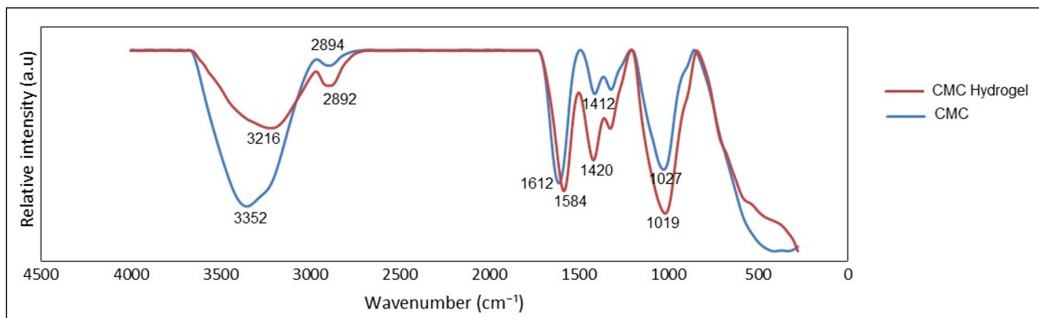


Figure 5. IR spectra for a) CMC and b) CMC hydrogel

Figure 5 shows the IR spectra for CMC and CMC hydrogel. In comparison to CMC, the absorbance region of O-H bonds for CMC hydrogel shifted to lower wavenumber. The difference occurs due to the engagement of hydroxyl and carboxylate groups of CMC to calcium ion forming chelating structure and subsequent decrease in hydrogen bonding between hydroxyl functional groups that promote shifting to lower wavenumber. In addition, the asymmetric stretching vibration of carboxylate ion at 1612 cm^{-1} deviates to lower wavenumber at 1584 cm^{-1} . This could be due to substitution of calcium ion for sodium ion in CMC to form CMC hydrogel. The replacement of sodium ion contribute to the change of charge density, the radius and the atomic weight (Daemi & Barikani, 2012). Hence, the absorbance was expected to shift to lower wavenumber. The formation of COO^- group will give resonance effect between two C-O bond that caused the carbonyl absorbance to vanish and replaced by two bands between $1610\text{-}1550\text{ cm}^{-1}$ and $1400\text{-}300\text{ cm}^{-1}$ due to anti-symmetrical and symmetrical vibration of -COO^- structure.

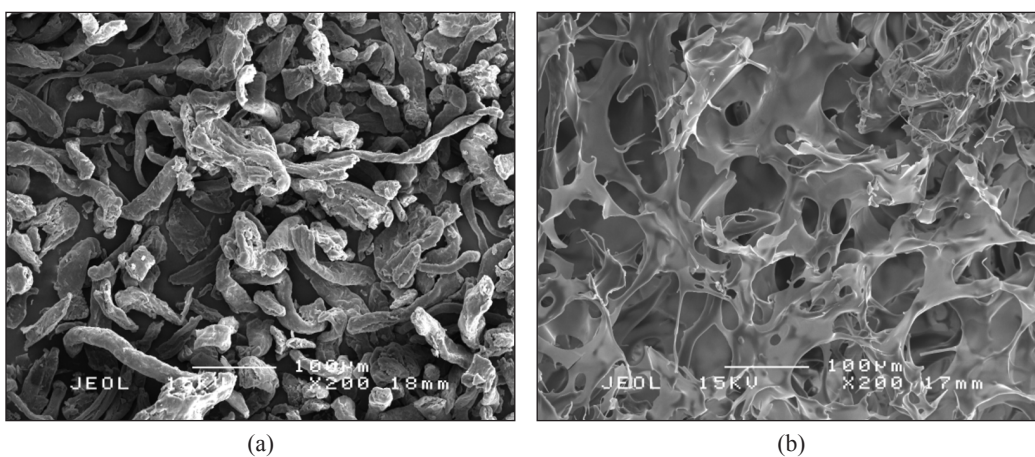


Figure 6. SEM micrograph of: (a) CMC and (b) CMC hydrogel at $200\times$

Figure 6 shows a $200\times$ magnification morphology of CMC and CMC hydrogels, respectively. CMC exhibited irregular granular surfaces and long ‘thread’ in structure while CMC hydrogel confirmed the macroporous structure of the crosslinked hydrogels which has three dimensional networks with empty pores. The presence of these pores in CMC hydrogel proved that a better matrix-water interaction and easier water absorption can be achieved through large surface area of the pore.

CONCLUSION

Several natural polymers have been effectively utilized as potential superabsorbent hydrogel based on natural resources. These polymers can replace and avoid excessive use of petroleum based polymer. In this study, we investigated the potential of CMC hydrogel as superabsorbent. The highest percentage of gel content obtained was 85.33% and the degree of swelling was 45.29 g/g. Overall, CMC hydrogel was obtained by ionic crosslinking and addition of calcium chloride has a significant effect on crosslinking of CMC. Optimum conditions of formation of CMC hydrogel obtained were 7% (w/v) of CMC, 2% (w/v) CaCl₂, 24h reaction time at room temperature. High percentage of gel content gives low degree of swelling due to less spaces available for the free water to enter the hydrogel network.

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REFERENCES

- Abd El-salam Deghiedy, N. M. (2004). *Synthesis and characterization of superabsorbent hydrogels based on natural polymers using ionizing radiations*. (Master Thesis). Al-Azhar University, Cairo, Egypt.
- Benhalima, T., Ferfera-Harrar, H., & Lerari, D. (2017). Optimization of carboxymethyl cellulose hydrogels beads generated by an anionic surfactant micelle templating for cationic dye uptake: Swelling, sorption and reusability studies. *International Journal of Biological Macromolecules*, 105, 1025–1042.
- Chia, P. X., Tan, L. J., May, C., Huang, Y., Wei, E., & Chan, C. (2015). Hydrogel beads from sugar cane bagasse and palm kernel cake, and the viability of encapsulated *Lactobacillus acidophilus*. *e-Polymers*, 15(6), 411–418.
- Daemi, H., & Barikani, M. (2012). Synthesis and characterization of Calcium Alginate nanoparticles, Sodium Homopolymannuronate Salt and its Calcium Nanoparticles. *Scientia Iranica*, 19(6), 2023–2028.
- Dafader, N. C., Adnan, M. N., Haque, M. E., Huq, D., & Akhtar, F. (2011). Study on the properties of copolymer hydrogel obtained from Acrylamide/2-Hydroxyethyl Methacrylate (HEMA) by the application of gamma radiation. *African Journal of Pure and Applied Chemistry*, 5(5), 111–118.
- Jamingan, Z., Ahmad, M. B., Hashim, K., & Zainuddin, N. (2015). Sago starch based hydrogel prepared using electron beam irradiation technique for controlled release application. *Malaysian Journal of Analytical Sciences*, 19(3), 503–512.
- Khaled, B., & Abdelbaki, B. (2012). Rheological and electrokinetic properties of carboxymethylcellulose-water dispersions in the presence of salts. *International Journal of Physical Sciences*, 7(11), 1790–1798.

- Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, 44, 3358–3393.
- Nie, H., Liu, M., Zhan, F., & Guo, M. (2004). Factors on the preparation of carboxymethylcellulose hydrogel and its degradation behavior in soil. *Carbohydrate Polymers*, 58(2), 185–189.
- Patil, J. S., Kamalapur, M. V., Marapur, S. C., & Kadam, D. V. (2010). Ionotropic gelation and polyelectrolyte complexation: The novel techniques to design hydrogel particulate sustained, modulated drug delivery system: A review. *Digest Journal of Nanomaterials and Biostructures*, 5(1), 241–248.
- Pourjavadi, A., & Hosseinzadeh, H. (2010). Synthesis and properties of partially hydrolyzed acrylonitrile-co-acrylamide superabsorbent hydrogel. *Bulletin of the Korean Chemical Society*, 31(11), 3163–3172.
- Qiao, C., Cao, X., & Wang, F. (2012). Swelling behavior study of physically cross linked gelatin hydrogels. *Polymers and Polymer Composites*, 20, 53-58.
- Sanna, S. R. (2013). *Synthesis and Characterization of New Polymeric Materials for Advanced Applications*. (Doctoral dissertation). University of Sassari, Sassari, Italy.
- Shen, X., Shamshina, J. L., Berton, P., & Rogers, R. D. (2016). Hydrogels based on cellulose and chitin: fabrication, properties, and applications. *Green Chemistry*, 18(1), 53–75.
- Sultana, S., Islam, M. R., Dafader, N. C., Haque, M. E., Nagasawa, N., & Tamada, M. (2012). Effect of mono- and divalent salts on the properties of carboxymethyl cellulose hydrogel under irradiation technique. *International Journal of Chemical Sciences*, 10(2), 627–634.
- Thakur, V. K., & Thakur, M. K. (2014). processing and characterization of natural cellulose fibers/thermoset polymer composites. *Carbohydrate Polymers*, 109, 102–117.
- Wang, Y., Shi, X., Wang, W., & Wang, A. (2013). Synthesis, characterization, and swelling behaviors of a pH-responsive CMC-g-poly(AA-co-AMPS) superabsorbent hydrogel. *Turkish Journal of Chemistry*, 37(1), 149–159.