FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 7 No. 2, April, 2023, pp 210 - 215
DOI: https://doi.org/10.33003/fjs-2023-0702-1729

EFFECTS OF WATER, KOH, HCl AND IONIC STRENGTH ON SWELLING CAPACITY OF CARBOXYMETHYL CELLULOSE (CMC) BASED GRAFT COPOLYMER HYDROGEL

[1]S. Yahaya, [1]S. A. Zauro, [1]U. Ibrahim, [1]A. M. Tolani , *[2]I. Y. Shinkafi and [2]Y. Albashir

[1]Department of Energy and Applied Chemistry, Usmanu Danfodiyo University, Sokoto Nigeria
[2]Department of Applied Chemistry, Federal University Dutsin-ma, Katsina State Nigeria.

*Corresponding authors' email: ishinkafi@fudutsinma.edu.ng Phone: +2348136524042

ABSTRACT

Hydrogels are three-dimensional crosslinked polymers with several uses in the administration and loading of drugs as well as the capacity to hold enormous amounts of water or biological fluids. Using carboxymethyl cellulose, N,N-dimethyl acrylamide (DMA), 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS), N,N-bisacrylamide (MBA) as a crosslinker, and potassium persulate (KPS) as an initiator, the CMC-g-poly(DMA-co-AMPS) was created. FTIR spectroscopy was used to characterize the CMC-g-poly(DMA-co-AMPS). In distilled water, KOH, and HCl, the CMC-g-poly(DMA-co-AMPS)'s swelling capability was assessed. CMC-g-poly(DMA-co-AMPS has the largest swelling ratio in KOH, followed by HCl, while pure water has the lowest swelling ratio. Various salt solutions (FeCl3.6H2O, CuCl2, and NaCl) were used at predetermined times in distilled water to test the effect of ionic strength on CMC-g-poly(DMA-co-AMPS). The swelling of CMC-g-poly(DMA-co-AMPS) increased with the increase in salt solution concentration, and the ionic strength of a solution is the measure of the concentration of ions in salt solutions. In salt solutions (CuCl2, NaCl, and FeCl3.6H2O), the maximal swelling ratio of CMC-g-poly(DMA-co-AMPS) is 10.5g, 10.0g, and 9.5g, respectively.

Keywords: Hydrogel, initiator, crosslinker, swelling ratio

INTRODUCTION

Hydrogels are crosslinked polymeric three-dimensional matrices that may hold a lot of water or biological fluids. (Musa *et al.*, 2021). In many different industries, including agriculture (Raafate et *al.*, 2012), the pharmaceutical sector (Dragan *et al.*, 2014), food (Tomi'c *et al.*, 2010), personal hygiene (Murphy *et al.*, 2013), and biomedicine, hydrogels have found use. (Song *et al.*, 2018). These hydrogels are frequently utilized as biosensors (Zhao *et al.*, 2014), in sanitary products such as tampons and pads, in plant irrigation regulators (Bajpai *et al.*, 2003), in the treatment of wastewater (Ji *et al.*, 2018), and in the construction of disposable diapers and sanitary napkins. Natural polymers have drawn interest as affordable, accessible, and non-toxic materials. They can undergo chemical changes, they may be biodegradable, and they are also biocompatible. (Yahaya *et al.*, 2021).

All plants' biological functions depend on polysaccharides in one way or another. (Klemm *et al.*, 2005). The production of cellulose-based hydrogels using cellulose is appropriate for use in a variety of industries, including food additives, agriculture, civil engineering, cosmetics, and medicines. One of the most significant and sustainable sources of raw materials for environmentally friendly manufacturing is cellulose, a biorenewable substance. (Thakur and Thakur, 2014). Cellulose-based hydrogels have been created using cellulose derivatives as hydroxypropyl cellulose (HPC), methyl cellulose, and carboxymethylcellulose (CMC). (Shen *et al.*, 2016). You can create it through a physical, chemical, or radical crosslinking process. (Pourjavadi and Hosseinzadeh, 2010).The polar carboxyl group in CMC gives it chemical reactivity, no flavor, no toxicity, and water-soluble properties. (Wang *et al.*, 2013). The production of CMC-g-poly(DMA-co-AMPS) and examination of its ability to swell in water, KOH, HCl, as well as other salt solutions, are among the goals of this work.

MATERIALS AND METHODS

Materials

Hydrochloric acid, potassium hydroxide, carboxymethyl cellulose, N'N-methylene-bis-acrylamide, 2-acrylamido-2-methyl-1-propane, sulphuric acid, sodium chloride, iron (III) chloride, cupper (II) chloride, dimethylacetamide, distilled water, weighing balance, microwave, magnetic stirrer and FTIR machine. All glassware is analytical grade and rinsed in distilled water.

Methods

Preparation Of Cmc-Graft-Poly [(N,N-Dimethylacrylamide)-Co- (2-Acrylamido-2-Methyl-1-Propane Sulfonic Acid)] Cmc-G-Poly (Dma-Co-Amps)

The CMC-*g*-poly(DMA-*co*-AMPS) was prepared by a slight modification of procedure of Zauro and Vishalakshi 2018. A known amount (0.05-0.125 g) of CMC was added to distilled water (15 mL) and stirred overnight at room temperature. Then 2 mL of KPS was added to CMC solution and stirred for 10 minutes. This was followed by the simultaneous addition of DMA (0.2 mL) and AMPS (1.0 g) under stirring. MBA solution (2 mL) was added to the reaction mixture and continuously stirred for 5-6 hours. The reaction mixture was then subjected to microwave (MW) irradiation at 50 watt for 5 minutes using alternate heating and cooling. The reaction product was allowed to cool. The gel produced was separated and placed in acetone for 4 hours. It was then washed with distilled water and dried in an oven at 50^0C till constant weight.

Swelling Studies in Distilled Water, HCl AND KOH

The swelling behaviour of the CMC-g-poly(DMA-co-AMPS) hydrogels in distilled water was studied by the weight measurements. Amount of water in milligrams absorbed per gram of the hydrogels were measured as follows: A known amount (g) of the grafted polymers samples were immersed in excess of the swelling media at room temperature and at different time intervals, the materials were removed and the surface water was drained (wiped away) using tissue paper and reweighed (Shukla *et al.*, 2012). This process is continued until constant weight was obtained. The same procedure was used for swelling of CMC-g-poly(DMA-co-AMPS) using HCl and KOH respectively. The data were reported as the

mean of three different measurements. The swelling ratio (SR) in mg/g and swelling equilibrium (S_{eq}) in mg/g were calculated using the following equations:

$$SR = \frac{(W_t - W_o)}{W_o} \quad (1)$$

$$S_{eq} = \frac{(W_e - W_O)}{W_O} \quad (2)$$

Where W_0, W_t and W_e are the weight of the gel at time t=0, time=t and at equilibrium respectively (Atta *et al.*, 2016).

Preparation of Salt Solutions

For NaCl

(0.1M of NaCl)

NaCl (0.0585 g) was dissolved in 100 cm^3 of distilled water in 100 cm^3 volumetric flask and made up to the mark.

(0.2M of NaCl)

NaCl (0.117 g) was dissolved in 100 cm^3 of distilled water in 100 cm^3 volumetric flask and made up to the mark.

(0.3M of NaCl)

NaCl (0.1755 g) was dissolved in 100 cm^3 of distilled water in 100 cm^3 volumetric flask and made up to the mark.

(0.4M of NaCl)

NaCl (0.234 g) was dissolved in 100 cm^3 of distilled water in 100 cm^3 volumetric flask and made up to the mark.

For $CuCl_2$

(0.1M of $CuCl_2$)

$CuCl_2$ (1.35 g) was dissolved in 100 cm^3 of distilled water in 100 cm^3 volumetric flask and made up to the mark.

(0.2M of $CuCl_2$)

$CuCl_2$ (2.7 g) was dissolved in 100 cm^3 of distilled water in 100 cm^3 volumetric flask and made up to the mark.

(0.3M of $CuCl_2$)

$CuCl_2$ (4.05 g) was dissolved in 100 cm^3 of distilled water in 100 cm^3 volumetric flask and made up to the mark.

(0.4M of $CuCl_2$)

$CuCl_2$ (5.4g) was dissolved in 100cm^3 of distilled water in 100cm^3 volumetric flask and made up to the mark.

For $Fecl_3.6H_2O$

(0.1M of $Fecl_3.6H_2O$)

$Fecl_3.6H_2O$ (2.705g) was dissolved in 100cm^3 of distilled water in 100cm^3 volumetric flask and made up to the mark.

(0.2M of $Fecl_3.6H_2O$)

$Fecl_3.6H_2O$ (5.41g) was dissolved in 100cm^3 of distilled water in 100cm^3 volumetric flask and made up to the mark.

(0.3M of $Fecl_3.6H_2O$)

$Fecl_3.6H_2O$ (8.115g) was dissolved in 100cm^3 of distilled water in 100cm^3 volumetric flask and made up to the mark.

(0.4M of $Fecl_3.6H_2O$)

$Fecl_3.6H_2O$ (10.82g) was dissolved in 100cm^3 of distilled water in 100cm^3 volumetric flask and made up to the mark.

Fourier Transforms Infrared Spectroscopy (FTIR)

The spectra of the monomer and the synthesized hydrogel were recorded on a CARRY 630 FTIR Agilent. All spectra (32 scans at 8.0 cm−1 resolution) were recorded at 25ºC and the spectra were at range of 4000–650 cm^{-1}.

RESULTS AND DISCUSSIONS

Preparation of Carboxymethyl cellulose-*graft*-poly[(N,N-dimethylacrylamide)-*co*-(2-acrylamido-2-methyl-1-propane sulfonic acid)].

The hydrogels were prepared by crosslinked copolymerization of AMPS, DMA and MBA in water in the presence of CMC. During the polymerization reaction, the bi-functional MBA copolymerizes with AMPS and DMA to form a network, While CMC takes part in the free-radical polymerization reaction by forming macro-radicals.

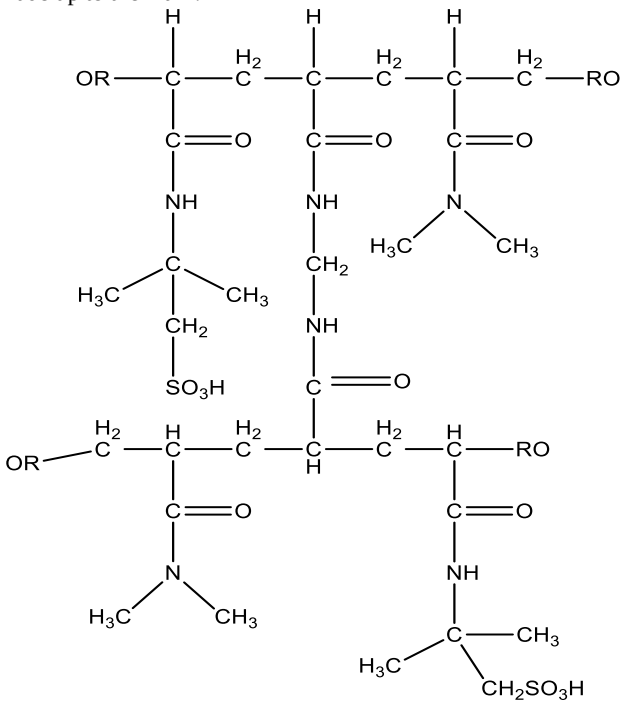

Figure 1: Scheme for the formation of CMC-*g*-poly(DMA-co-AMPS)

Fourier Transform Infrared Spectroscopy

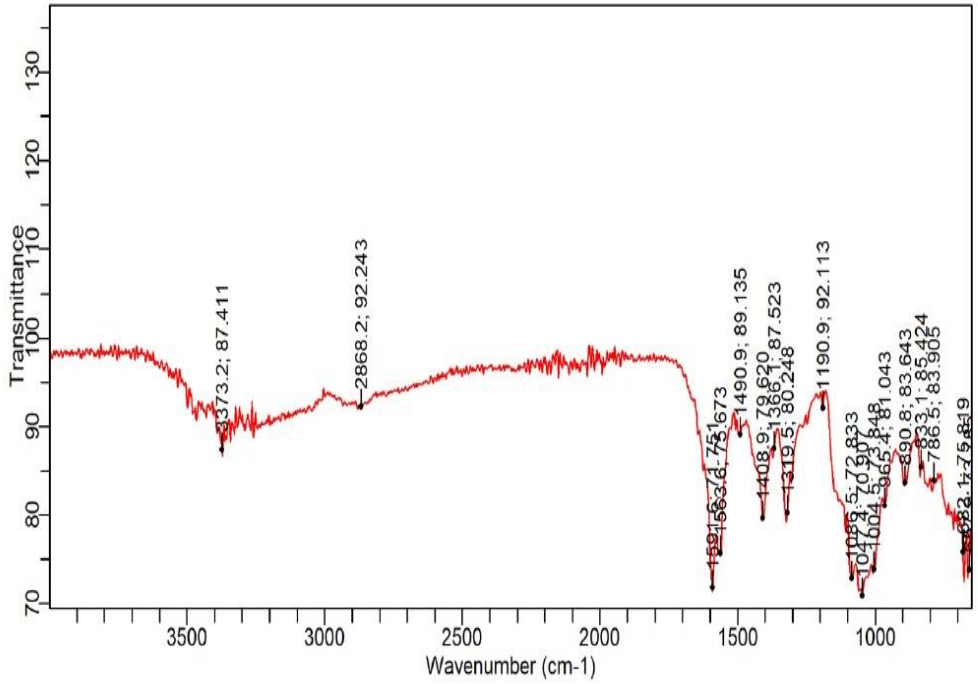

Figure 2: FTIR spectra of CMC

The IR spectra of CMC has shown the peaks of various compounds such as 3326.6 cm^{-1} OH for Alkanol, aldehyde and carboxylic acid, 1612.1cm^{-1} C=C for aromatic and alkenes, 1556.2 C=N for amine and amides, 1144.3cm^{-1} S=O for sulfones, 2922.2 cm^{-1} C-H for alkanes, 1073.5 cm^{-1} Si-O for organosilicone compounds, 1144.3 cm^{-1} S=O, C-F for Sulphur and Fluoride compounds, 1509.6cm^{-1} NO_3 for nitro compounds, etc. (Zietler *et al.,* 2007).

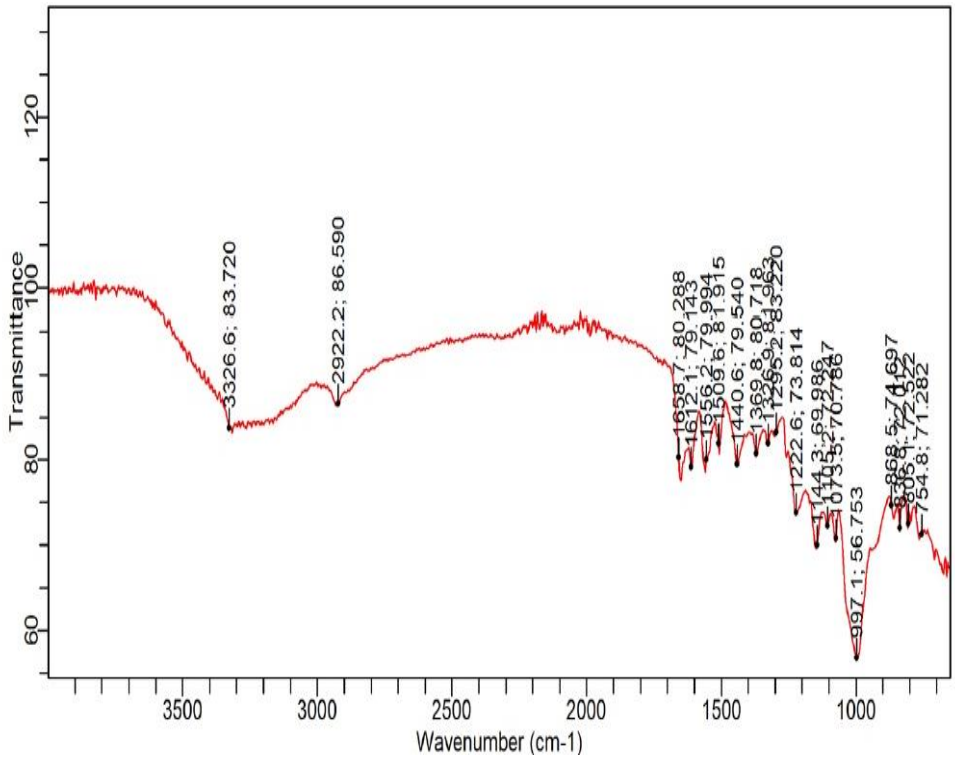

Figure 3: FTIR spectra of CMC-*g*-poly(DMA-co-AMPS)

The peak at 1591, 1563, cm^{-1} related to the N-H stretching. The peak at 1490, 1366, 1319, cm^{-1} which are attributed to asymmetric stretching vibration of C-N stretching, The peak at 1086,1047,1004 cm^{-1} is assigned to C-O bond stretching, The peaks at 965, 890, 833, 786, and 682 cm^{-1} assigned to C-O and S-O stretching of the -SO_3H respectively. The additional characteristics bands of 1658,1612, cm^{-1} for C=O stretching of COO^- of the CMC were observed in the spectra of CMC-*g*-poly(DMA-co-AMPS).

Swelling Studies in Distilled Water, KOH and HCl

The swelling capacity of CMC-g-poly(DMA-co-AMPS) in distilled water is the ability of a CMC-g-poly(DMA-co-AMPS) to swell and retain a significant fraction of water within its structure but will not dissolve in water. As shown in the figure 4 below, the CMC-g-poly(DMA-co-AMPS) increase in size at different time interval, when it get to a certain period of time the CMC-g-poly(DMA-co-AMPS) stop swelling due to less spaces available for the free water to enter the hydrogel network. The higher the time the more the CMC-g-poly(DMA-co-AMPS) increase till it reached equilibrium.

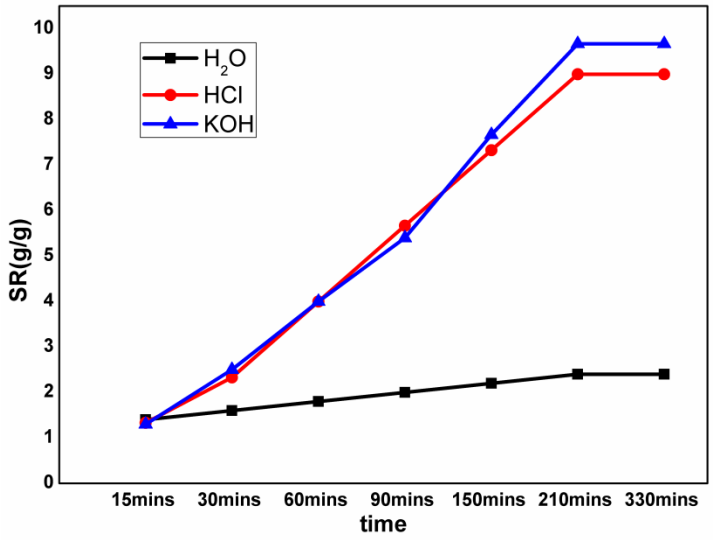

Figure 4: Effect of contact time on the Swelling ratio CMC-g-poly(DMA-co-AMPS) in distilled water, KOH and HCl

The swelling capacity of the gel in potassium hydroxide (KOH) is higher than that of Hydrochloric acid (HCl) and that of Hydrochloric acid is higher than that of water. However, due to the higher swelling capacity in KOH it shows that it's mostly used in hygiene. The ionic hydrogel is sensitive to ambient pH in acidic conditions, according to equilibrium swelling tests (Yahaya *et al.*, 2021).

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 (Deghiedy, 2004).

Swelling Studies in Different Salt Solutions

Effect of ionic strength of CMC-g-poly(DMA-co-AMPS) was determined using various salt solutions ($FeCl_3.6H_2O$, $CuCl_2$ and NaCl) at preoptimized time in distilled water. Salt solution of different ionic strength (0.1M, 0.2M, 0.3M, and 0.4M) was prepared. As shown in the figure 5, the swelling of CMC-g-poly(DMA-co-AMPS) increased with the increase in the concentration of the salt solution. Initially when the CMC-g-poly(DMA-co-AMPS) was immersed in the salt solution it did not show any swelling behaviour but after certain time interval a definite difference in the selling behaviour of the CMC-g-poly(DMA-co-AMPS) in each salt solution was observed.

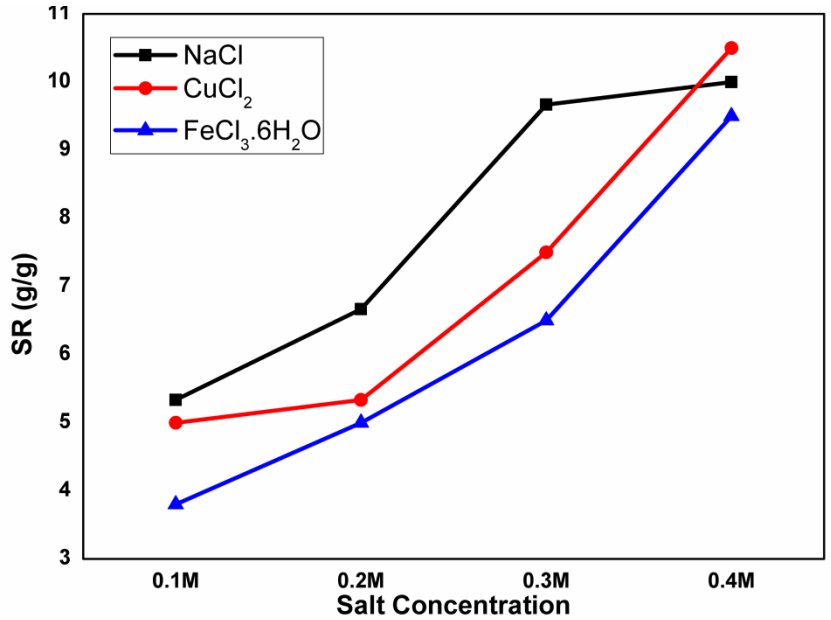

Figure 5: Effect of salts solution on the Swelling ratio CMC-g-poly(DMA-co-AMPS)

The ionic strength of a solution is the measure of the concentration of ions in salt solutions. The decrease of the swelling capacity of the hydrogels is due to the loss of the osmotic pressure of the hydrogel, initially hydrogel showed swelling behavior in each salt solution but after certain time interval a definite difference in swelling behavior of hydrogel in different salts was observed. It could be due to the fact that as the ionic charge increased. This ultimately led to decreasing trend in swelling behavior of the hydrogel and increase in ionic strength of the cations was due to reverse osmosis process (Griffith, 2000).

From figure 5 above; NaCl, $CuCl_2$ and $FeCl_3.6H_20$ salt solution which have their ionic charge as Na^+, Cu^{2+} and Fe^{3+} respectively. Since increase in ionic strength is decrease in swelling behaviour, that is the higher the ionic charge the lower the swelling behaviour which is in this order (Na^+> Cu^{2+} > Fe^{3+}). Therefore, NaCl have the highest swelling behaviour, then the $CuCl_2$ have the second highest swelling behaviour and the $FeCl_3.6H_20$ have the lowest swelling behaviour.

Other factor that affects the swelling behaviour is the ionic crosslinking. Ionic crosslinking causes decrease in swelling capacity. The increase in ionic character of the salt results is the proportionate increase in the crosslinking of subsequent and decrease in swelling (Dahou*et al.*, 2010).

CONCLUSION

Successful production of the hydrogel composed of CMC-g-poly(DMA-co-AMPS). With passing time, the CMC-g-poly(DMA-co-AMPS) in the distilled water began to swell, but at a certain point, the swelling ceased. This is due to the enlargement of the CMC-g-poly(DMA-co-AMPS) network reaching equilibrium because it could no longer absorb water. The hydrogel swells more in the KOH solution than in the HCl solution as well. Additionally, the concentration of the salt solution rose along with the swelling of CMC-g-poly(DMA-co-AMPS). In the salt solution, the CMC-g-poly(DMA-co-AMPS) swelled to a size that was more than twice as large as before, and this swelling increased with salt concentration.

REFERENCES

Abd El-salam D. N. M. (2004). Synthesis and characterization of superabsorbent hydrogels based on natural polymers using ionizing radiations. (Master Thesis). Al-Azhar University, Cairo, Egypt.

Atta, S., Khaliq, S., Islam, A., Javeria, I., Jamil, T., Athar, M. M., Shafiq, M. I. and Ghaffar, A. (2015). Injectable biopolymerbased hydrogels for drug delivery applications. *International Journal of Biological Macromolecules*,**80:** 240-245

Bajpai, A.; Giri, A. (2003), Water sorption behaviour of highly swelling (carboxy methylcellulose-g-polyacrylamide) hydrogels and release of potassium nitrate as agrochemical. *Carbohydr. Polym*., 53, 271–279.

Dahou, W., Ghemati, D., Oudia, A. and Aliouche, D. (2010). Biochemistry. *England Journal* **48:** 187.

Dragan, E.S. Design and applications of interpenetrating polymer network hydrogels. *A review. Chem. Eng.* J.2014, 243, 572–590.

Griffith, L. G., (2000). Polymeric biomaterials. *Acta Mater* **48:** 263-277.

Jamingan, Z., Ahmad, M. B., Hashim, K., and 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.

Ji, H.; Song, X.; Shi, Z.; Tang, C.; Xiong, L.; Zhao, W.; Zhao, C. (2018) Reinforced-Concrete Structured Hydrogel Microspheres with Ultrahigh Mechanical Strength, Restricted Water Uptake, and Superior Adsorption Capacity. ACS Sustain. *Chem. Eng.*, 6, 5950–5958.

Klemm, D., Heublein, B., Fink, H. P., and Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *AngewandteChemie International Edition* **44:** 3358–3393.

Murphy, S.V.; Skardal, A.; Atala, A. (2013), Evaluation of hydrogels for bio-printing applications. *J. Biomed. Mater. Res. Part A*, 101A, 272–284.

Musa, Y., Musa, H., Suleiman, M., Yahaya, S. And Yahuza, Z. A (2021) Polyacrylamide Hydrogels for Application in Oral Drug Delivery, *Nigerian Journal of Scientific Research, 20(4), 390-396.*

Pourjavadi, A. and Hosseinzadeh, H. (2010). Synthesis and properties of partially hydrolyzed acrylonitrileco- acrylamide superabsorbent hydrogel. *Bulletin of the Korean Chemical Society***31(11):** 3163–3172.

Raafat, A.I.; Eid, M.; El-Arnaouty, M.B. (2012), *Radiation synthesis of superabsorbent CMC based hydrogels for agriculture applications. Nucl. Instrum. Methods Phys*. Res. Sect. B Beam Interact. Mater. Atoms,

Shen, X., Shamshina, J. L., Berton, P. and Rogers R. D. (2016). Hydrogels based on cellulose and chitin: fabrication, properties, and applications. *Green Chemistry* **18(1):** 53–75.

Shukla, N. B., Rattan, S. and Madras, G. (2012). Swelling and dye-adsorption characteristics of amphoteric superadsorbent polymer. *Industrial and Engineering Chemistry Research*,**51:** 14941-14948.

Song, X.; Wang, K.; Tang, C. Q.; Yang, W. W.; Zhao, W. F.; Zhao, C. S. (2018). Design of arrageenan-Based Heparin-Mimetic Gel Beads as Self-Anticoagulant Hemoperfusion adsorbents. Biomacromolecules, 19, 1966–1978.

Thakur, V. K. and Thakur, M. K. (2014). processing and characterization of natural cellulose fibers/thermoset polymer composites. *Carbohydrate Polymers***109:** 102–117.

Tomi´c, S. L.;Mi´ci´c, M. M.; Dobi´c, S. N.; Filipovi´c, J. M.; Suljovruji´c, E. H. (2010). Smart poly(2-hydroxyethyl methacrylate/itaconic acid) hydrogels for biomedical application. *Radiat. Phys. Chem.*, 79, 643–649.

Wang, Y., Shi, X., Wang, W. and 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.

Yahaya, S. Adiya, Z. I. S. G. Adamu, S. S. Bature, H. B. Ibrahim, I. B. (*2021*). Swelling Behaviour of Starch-g-Acrylic Acid Hydrogel and its Potential Application in Removal of

Rhodamine B and Alkali Blue Dyes, *Nigerian Journal Of Technological Development, VOL. 18(2), 98-104.*

Yahaya, S. Isah A. M., Adiya, Z. I. S. G. Zauro S. A., Shinkafi I. Y., and Darma S. M. (*2021*). Preparation of Starch-g-Acrylamide Hydrogel, Swelling behaviour and its Potential Application in Removal of Rhodamine B and Alkali Blue Dyes, *KASU Journal Of Chemical Sciences, VOL. 1(1), 82-91*.

Zeitler J. A, Taday P. F, Newnham D. A, Pepper M., Gordon K. C, Rades T. (2007). "Terahertz pulsed spectroscopy and imaging in the pharmaceutical setting--a review". The Journal of Pharmacy and Pharmacology. **59** (2): 209–23.

Zhao, W.; Glavas, L.; Odelius, K.; Edlund, U.; Albertsson, A. C.(2014).A robust pathway to electrically conductive hemicellulose hydrogels with high and controllable swelling behavior. *Polymer*, 55, 2967–2976.