

Original Research Paper

Controlled Delivery System for NPK Agrochemical Release from Chitosan Copolymer Hydrogels

Maysam S. Mutlaq and Fawzi Habeeb Jabrail

Department of Chemistry, Mosul University, Mosul 41002, Iraq

Article history

Received: 26-07-2022

Revised: 26-08-2022

Accepted: 29-08-2022

Corresponding Author:

Fawzi Habeeb Jabrail
Department of Chemistry,
Mosul University, Iraq
Email:
fawzijabrail@uomosul.edu.iq

Abstract: Chitosan (CS) the polysaccharide was copolymerized with Poly (Vinyl Alcohol) (PVA) for the preparation of CS-co-PVA hydrogel and with Carboxymethyl Cellulose (CMC) for CS-co-CMC hydrogel. The prepared hydrogels were characterized by FTIR, thermal analysis (TGA and DSC), and SEM. The hydrogels were studied for agriculture applications, where their ability to swell and take large quantities of water many times its weight was exploited for water retention when the hydrogel was mixed with agricultural soil. For almost 40 days the soil in the soil/hydrogel sample was kept wet whereas the reference sample (without hydrogel) has a maximum of 20 days wet. The next application was loading the NPK fertilizer applied as a model into the prepared hydrogels and then allowing to release of the loaded fertilizer in a controlled manner and for long time intervals. Both hydrogels CS-co-PVA and CS-co-CMC have shown a high maximum loading percentage ($L_{max}\%$) and a highly efficient loading percentage (EL%). Equivalent to the release character of both hydrogels has shown a controlled agrochemical deliver pattern.

Keywords: NPK Agrochemical Fertilizer, Chitosan, Poly (Vinyl Alcohol), Carboxymethyl Cellulose, Controlled Release, Water Retention

Introduction

Hydrogels are three-dimensional network polymers that maintain their structure by cross-linking their chains and absorbing a huge amount of water (Kabir *et al.*, 2017). Hydrogels, the Superabsorbent Polymers (SAP) have special properties, like super absorbency, biodegradability, viscoelasticity, biocompatibility, and softness (Nezhad-Mokhtari *et al.*, 2019). The hydrogels are found to respond to different stimuli, such as temperature, magnetic field, electric field, ionic strength, and biological molecules (Jabrail *et al.*, 2016). Polysaccharides blended with synthetic polymers give several advantages, like increased biocompatibility, thermal and chemical stability, hydrophilicity, and film-forming ability (Jabrail *et al.*, 2019). Where the hydrophilic groups of both natural and synthetic polymers such as -OH, -COOH, -NH₂, -SO₃H, and -CONH₂ are increasing the ability of the blend hydrogels to absorb water (Al-Ojar and Jabrail, 2019). Hydrogels are cross-linked with different categories including chemical cross-linking which led to the formation of covalent bonds between the polymer chains and gives non-reversible, permanent, and stable hydrogels (Sinha *et al.*, 2019; Ahmed, 2015).

Hydrogels can play important functions in the agriculture sector and help with irrigation water efficiency (Dehkordi, 2017). Moreover, fertilizers are inefficient to reach the target because of the excessive loss of fertilizers and only 20-30% of used fertilizer could be absorbed and the remaining percentage is lost through nitrification, volatilization, and leaching (Purnomo *et al.*, 2017). Therefore, the hydrogel-based controlled release systems are helpful and could release an optimum amount of agrochemical for a sustained period (Jabrail *et al.*, 2019). Chitosan (CS), the cationic amino polysaccharide, the deacetylated product of chitin is a biocompatible, biodegradable, and non-toxic polymer (Mallakpour and Ezhie, 2017). Poly (Vinyl Alcohol) (PVA), is a hydrophilic synthetic polymer that has a semi-crystalline structure. PVA has a good ability to blend with other polymers and form hydrogel as described properties (Jabrail and K Al-Ojar, 2019). Carboxymethyl Cellulose (CMC), the anionic water-soluble polysaccharides material is an important cellulose derivative that has linear and long chains (Jabrail and K Al-Ojar, 2019).

In the present work, two hydrogels are prepared by blending Chitosan (CS) with Poly (Vinyl Alcohol) (PVA) for the preparation of CS/PVA hydrogel and with Carboxymethyl Cellulose (CMC) for the preparation of

CS/CMC hydrogel. The prepared hydrogels were cross-linked chemically using N, N -Methylene Bisacrylamide (MBA). The hydrogels were characterized by FTIR, thermal analysis (TGA and DSC), and SEM. The degree of swelling of the prepared hydrogels was studied and their loading with NPK fertilizer was done and then allowed to release out of the hydrogel system. The water retention of agricultural soil mixed with a few amounts of the prepared hydrogels was examined.

Materials and Methods

Chitosan (CS), highly viscous from Sigma-Aldrich, Poly (Vinyl Alcohol) (PVA), from Fischer Scientific, USA, and carboxymethyl Cellulose (CMC), commercial material was supplied from local markets. The cross-linker N, N -Methylene Bisacrylamide (MBA), from BDH, UK. The NPK fertilizer model commercial material was supplied from agricultural markets. All other chemicals were analytical grade reagents and received from Fluka, Switzerland.

Preparation of (CS-co-PVA) and (CS-co-CMC) Hydrogels

The chitosan solution was prepared by dissolving 1.0 g of chitosan in 100 mL of (2%w/v) acetic acid in dist. water. 10 mL PVA solution of (1.0%w/v) was heated at 65°C in a 250 mL three-necked round flask using mental with magnetic stirring. The flask was connected to the nitrogen line and passed on an alkaline pyrogallol solution free of oxygen. 5.0 mL of (10.0%w/v) the initiator Ammonium Persulfate (APS) was added, followed by the stepwise addition of 20 mL of (1.0%w/v) Chitosan (CS) at 65°C with stirring and under N₂ gas environment. 5.0 mL of (2%w/v) of the cross-linker MBA was added after stop heating and flows of N₂ gas, but kept stirring for an extra 15.0 min. The formed hydrogel was filtered, washed, and dried in an oven at 50°C.

Similarly, the aforesaid procedure was used except 10.0 mL of (1.0% w/v) CMC solution was added instead of PVA solution. The CMC solution was prepared by adding the solid CMC stepwise and carefully to its water solution with vigorous stirring to prevent accumulation and heated at 60°C instead of 65°C. The precipitate hydrogel was filtered, washed, and dried in an oven at 50°C.

Degree of Swelling (DS)

The Degree of Swelling (DS) of the prepared hydrogels was measured. 100 mg of dry hydrogel were immersed in 20 mL of the following solutions to achieve the best swelling, Distilled Water D.W; River Water R.W; buffer solution of PH4, and buffer solution of PH9. Whereas, the temperature of the swelling media was changed between 10, 25, and 50°C for better swelling. The hydrogel microspheres

were weighted after removal of the outside drops of solution each 6 for 24 h and the following equation was used:

$$\text{Degree of Swelling (DS)} g / g = W_t - W_0 / W_0 \quad (1)$$

W_t = The weight of the swell sample after (t) time and
 W_0 = The weight of the dry sample

Water-Retention Percentage of Soil/Hydrogel Mixture

The agricultural soil was dried and 200.0 g was kept in a ventilated paper cup, 1.0 g of studied hydrogel was put into 1 cm depth of the soil surface. Thereafter, 100 mL of river water R.W was added slowly which represents the minimum rainfall level recorded in most arid and semi-arid regions (Wu and Liu, 2008). A reference sample was prepared including all used materials except the hydrogel. Both cups were maintained in the same place under the same conditions at 20°C and 25% humidity. Both samples were weighted daily until no change in their weight and the water-retention percentage was calculated as follows:

$$\text{Water retention (\%)} = W_t / W_0 \times 100 \quad (2)$$

W_t = The decrease in sample weight at (t) time and
 W_0 = The initial sample weight

Loading of NPK Fertilizer on Hydrogel

The calibration curve of the NPK fertilizer model was done at λ_{\max} 299 nm. Where UV-Visible spectrophotometer type UV-Visible JASCO V-630, Japan was used for measuring the absorbance of different concentrations of NPK fertilizer prepared and measured at fixed λ_{\max} . In addition, NPK fertilizer was prepared in three concentrations, 50, 100, and 200%w/v and the temperature of the loading solution was changed between 10, 25, and 50°C. Finally, the time depends for loading was 6, 12 h, and 24 h. All the aforesaid variable conditions are for best loading percentages. The type of loading solution used was that solution that gave the maximum degree of swelling of the hydrogel. Two values were calculated as follows:

$$L_{\max} \% = \frac{\text{Amount of agrochemical loaded on hydrogel}}{\text{amount of hydrogel taken for loading}} \times 100 \quad (3)$$

$$EL \% = \frac{\text{Amount of agrochemical loaded on hydrogel}}{\text{amount of agrochemical taken for loading}} \times 100 \quad (4)$$

where, $L_{\max} \%$ is the maximum loading percentage and $EL \%$ is the efficiency of loading percentage.

Controlled Agrochemical Release of NPK Fertilizer

The loaded hydrogels were allowed for release and studied their cumulated release percentage $R_{cum} \%$,

where 100 mg of NPK loaded hydrogel microspheres have been immersed in a 20 mL release solution selected according to the best solution of swelling. The degree of the temperature of the release medium was fixed at 10, 25, and 50°C for reaching a more controlled release. The concentration of the released NPK has measured at fixed time intervals of 3 for 24 h, where 3 mL was taken from the release solution each 3 h and replaced with 3 mL of native solvent. UV spectrophotometer was used for absorbance measurement and applied on calibration curve for determining the concentration of released NPK at (t) time. The cumulative release percentage was calculated according to the following equation:

$$\text{Cumulative release}(\% R_{Cum}) = W_t / W_o \times 100 \quad (5)$$

W_t = The amount of NPK released at the time (t) and
 W_o = The total amount of NPK released finally

Results and Discussion

Irrigation and providing nutritional elements to plants are considered one of the most important issues in agriculture. Hydrogels are polymers that can save water and then release it inside agricultural soil for long time intervals. Moreover, the hydrogels can be loaded with agrochemicals and then released into the soil to the plants in a controlled way. The prepared hydrogels chitosan-co-Poly(Vinyl Alcohol) (CS-co-PVA) and chitosan-co-carboxymethyl cellulose (CS-co-CMC), were used for water retention inside the soil/hydrogel mixture, and in addition, both hydrogels were loaded with NPK fertilizer as a model and then examined for their release.

Characterization of Hydrogels

FTIR Analysis

FTIR spectroscopy was used for the characterization of the functional groups of the prepared hydrogel. The absorption frequencies of the CS-co-PVA hydrogel, Fig. 1a and Table 1, appear the important functional groups of the hydrogel. Where the band at 3239 cm^{-1} represents the $\nu(\text{O-H})_{\text{str}}$ of PVA and CS and the bands at (3361 and 1529) cm^{-1} are belongs to the $\nu(\text{N-H})_{\text{str}}$ of CS and MBA. The bands at (1632 and 1320) cm^{-1} are belongs to asymmetric and symmetric bands respectively of $\nu(\text{C} = \text{O})_{\text{str}}$ which belongs to CS and MBA.

The FTIR spectrum of CS-co-CMC hydrogel, Fig. 1b and Table 1, has shown absorption bands at 3239 cm^{-1} which represent $\nu(\text{O-H})_{\text{str}}$ of CS and CMC. The absorption band at (1531 and 3410) cm^{-1} belongs to $\nu(\text{N-H})_{\text{str}}$ of CS and MBA, whereas those at (1634 and 1319) cm^{-1} belong to $\nu(\text{C} = \text{O})_{\text{str}}$ the asymmetric and symmetric bands respectively of CMC and MBA.

Thermal Analysis of the Hydrogels

Thermal analysis TGA and DSC were measured for the prepared hydrogels, where the sample CS-co-PVA hydrogel has shown thermally stable hydrogel, Fig. 2(a and b), Table 2, with high Initial Decomposition Temperature (IDT) and Final Decomposition Temperature (FDT). Similarly, the maximum decomposition temperature (T_{max}) and crystalline decomposition Temperature (T_{cr}) were high, Fig. 2a, Table 2 and give stability to the hydrogel. The DSC thermogram of the CS-co-PVA hydrogel, Fig. 2b and Table 2, has shown endothermic behavior of the hydrogel where the heat of the fusion (ΔH_f) was +386.7 J/g at 204.2°C with a glass transition temperature (T_g) of 71.3°C. All the aforesaid data indicate that the hydrogel is generally stable thermally.

Table 1: FTIR characteristic frequencies of the most important functional groups of the hydrogels

CS-co-PVA		CS-co-CMC	
ν/cm^{-1}	Functional group	ν/cm^{-1}	Functional group
3239	-OH	3239	-OH
1529	= N-H	1531	= N-H
1632	-C = O	1634	-C = O
2905	-CH ₂ -	2925	-CH ₂ -
1023	-C-O-C-	1030	-C-O-C-
1072	-C-O-	1058	-C-O-
1430	-C-OH	1425	-C-OH
980	-C = C-	897	-C = C-

Table 2: Thermal analysis of TGA and DSC of the hydrogels

Sample	TGA weight loss (%)					DSC (W/g)	
	IDT °C	FDT °C	T_{max} °C	T_{cr} °C	T_g °C	ΔH_f (J/g)	
CS-co-PVA	3.5	64.0	36.5	74.2	71.3	+386.7
	71.3°C	734.0°C	425.0°C	800.0°C		204.2°C
CS-co-CMC	2.5	94.0	50.0	95.0	96.3	+489.6	-3825.0
	96.3°C	715.0°C	405.0°C	608.0°C		209.8°C	540.9°C

The TGA analysis of CS-co-CMC, Fig. 3a and Table 2 has shown also hydrogel with thermal properties of high stability due to the presence of CMC semi-crystalline polysaccharide. Similarly, the DSC analysis of CS-co-CMC hydrogel has shown, Fig. 3b, and Table 2, high T_g and ΔH_f with exothermic behavior of +489.6 J/g at 209.8°C and endothermic behavior of -3825 J/g at 540.9°C, where chitosan gives exothermic behavior due to its morphological structure, whereas CMC shows endothermic behavior due to its semi-crystalline structure

SEM Analysis

SEM images of the prepared hydrogels were studied and their morphological surface with corrugated and homogeneous materials has been cleared for CS-co-PVA hydrogel. Where the SEM images, Fig. 4(a and b) with different magnifications have shown elastic form with a homogenous compact surface with folds. Moreover, the SEM images of CS-co-CMC hydrogel, Fig. 5(a and b) have shown less homogenous components with protrusions and a less compact surface means the presence of CMC polysaccharide with its semi-crystalline structure has less capability to react with homogeneously with chitosan morphological form.

Measurement of the Degree of Swelling

The Degree of Swelling (DS) of the prepared hydrogels was measured using Eq. 1. Where the DS was measured in different swelling solutions like R.W, D.W, PH4, and PH9 and their degree of temperature was changed between 10, 25, and 50°C and then select the favorable degree of temperature to reach the maximum degree of swelling.

The DS of CS-co-PVA hydrogel was shown clearly in Fig. 6, where it reached its maximum in D.W and at 50°C and gradually decreased in R.W then PH 9 and it is very low in PH 4, which means the hydrogel components have ionized functional groups that carry charges which affected by the charges of the ions present in the swelling

solution like R.W (contain salts) or PH 9 or PH 4 which force hydrogel chains to close and cause a decrease in swelling of the hydrogel (Djumaev and Tashmukhamedova, 2020; Mazuki *et al.*, 2020).

Whereas the DS of CS-co-CMC, Fig. 7 has shown high in both R.W at 25°C and D.W at 50°C, while very low DS in PH9 and PH4 at 25°C. In general, both hydrogels consist of CS and both are cross-linked chemically with MBA, only the accompanied polysaccharide is different, where PVA behave different than CMC which has many hydroxyl and carboxyl groups and their ions are more affected by the swelling solution. Therefore, the DS of CS-co-CMC hydrogel is high in R.W, Fig. 7, but its curve is non-uniform and becomes high only after 24hrs, while its DS in D.W is high and behaves uniformly due to no ions there in its swelling solution.

Measurement of Water-Retention of Soil/Hydrogel Mixture

The water-retention percentages of both prepared hydrogels mixed with agricultural soil were studied and Fig. 8 has shown the hydrogels when mixed with agricultural soil with 0.5%w/w and irrigated with river water R.W could retain water for a long time inside the agricultural soil and release the water from the hydrogel as the soil become dry.

The Water-Retention % (WR%) was calculated by Eq. 2. However, Fig. 8 has shown the behavior of the soil/hydrogel mixture of both prepared hydrogels and also shows the reference sample where no hydrogel was present. The CS-co-PVA hydrogel mixture has shown Fig. 8, 38 days of water retention before the sample becomes dry, while the CS-co-CMC hydrogel mixture has shown 40 days of water retention before the sample becomes dry. Whereas, the reference sample has become dry after 20 days under the same environmental conditions.

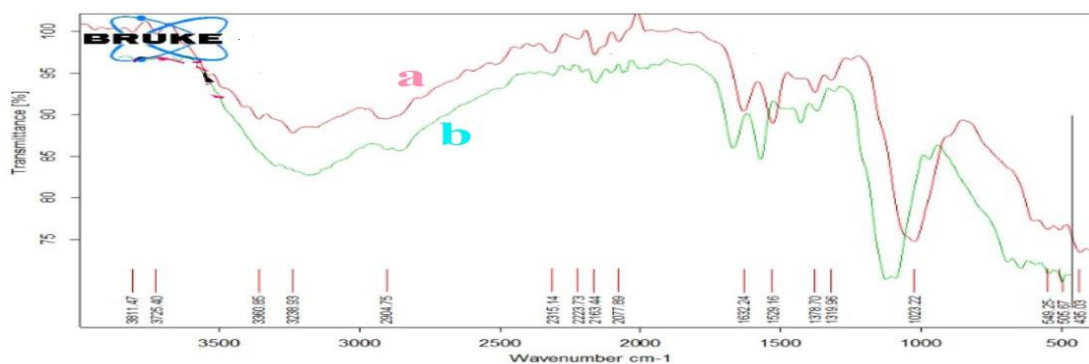


Fig. 1: FTIR spectrum of (a) CS-co-PVA and (b) CS-co-CMC hydrogel

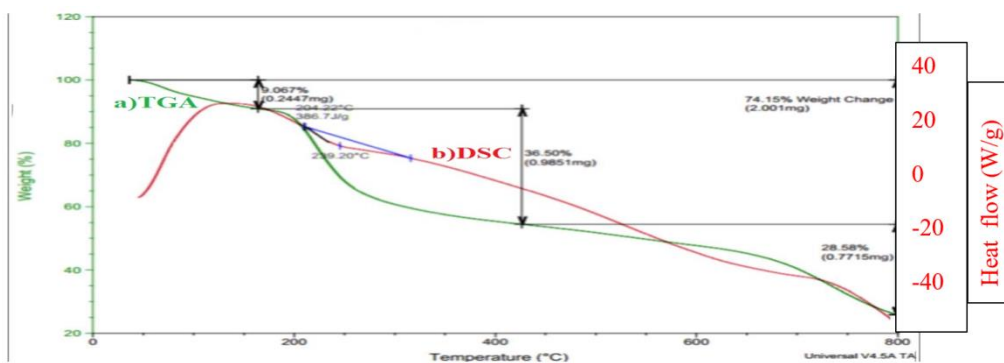


Fig. 2: Thermal analysis thermograms as a- TGA and b- DSC of CS-co-PVA hydrogel

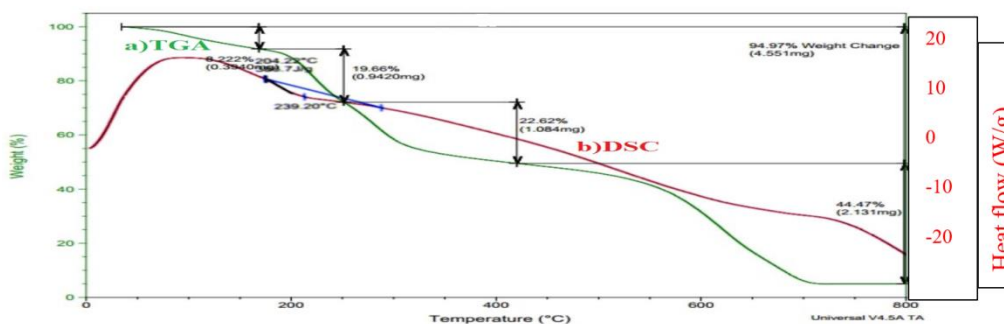


Fig. 3: Thermal analysis thermograms as a- TGA and b- DSC of CS-co-CMC hydrogel

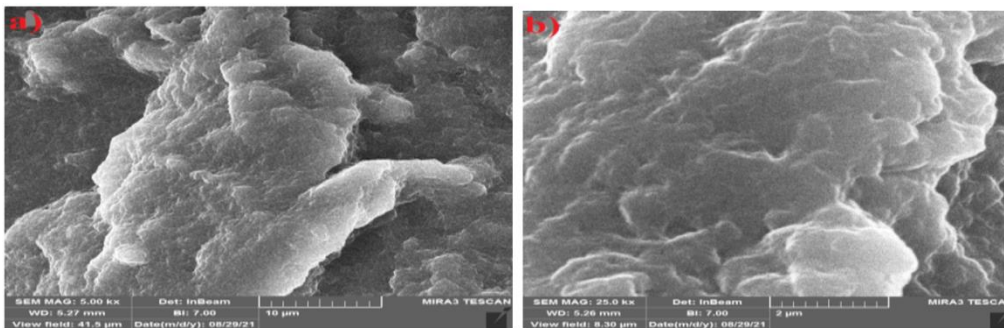


Fig. 4: SEM images of CS-co-PVA hydrogel with (a) 5.0 kx, and (b)25.0 kx magnifications

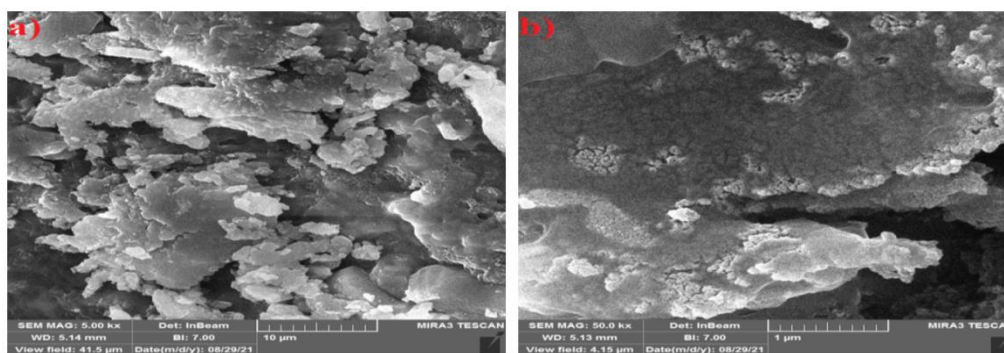


Fig. 5: SEM images of CS-co-CMC hydrogel with (a) 5.0 kx, and (b) 50.0 kx magnifications

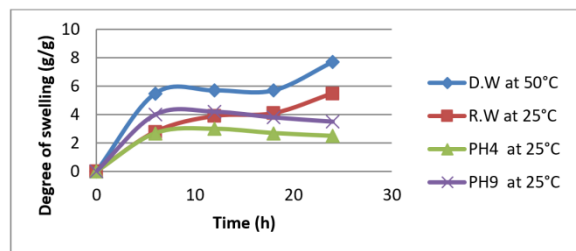


Fig. 6: Degree of swelling of CS-co-PVA hydrogel in different swelling mediums done at favorable temperature

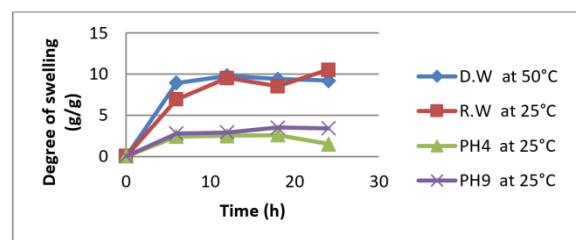


Fig. 7: Degree of swelling of CS-co-CMC hydrogel in different swelling mediums done at favorable temperature

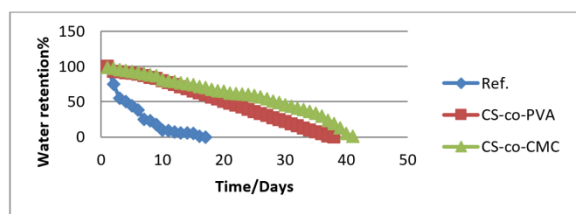


Fig. 8: Water-retention percentage of soil-hydrogel mixture with time (day) at 20°C and 25% humidity using CS-co-PVA and CS-co-CMC hydrogels

Measurement of NPK Loading Inside Hydrogel Microspheres

The prepared hydrogels were loaded with NPK fertilizer used as a model which was then prepared for release in agricultural soil. The system CS-co-PVA hydrogel has been loaded with different concentrations of NPK. The loading medium used was the solution where the hydrogel gets maximum DS, therefore, D.W was used for the preparation of different concentrations of NPK as 50, 100, and 200% w/v. In addition, the loading solution was fixed at 50°C where the DS of the hydrogel reached its maximum. Moreover, the time of loading was fixed at 6, 12, and 24 h to reach maximum loading. The calibration curve of NPK was used for the determination of the NPK concentration loaded in hydrogel microspheres. Equation (3 and 4) are used for the calculation of maximum loading percentage $L_{max}\%$ and efficiency of loading percentage EL% respectively.

The $L_{max}\%$ of NPK fertilizer in CS-co-PVA hydrogel has been measured and Fig. 9a has shown $L_{max}\%$ at three-time intervals (6, 12, and 24) h using D.W as loading solution and its temperature fixed at 50°C. Where 98% is the maximum loading of CS-co-PVA hydrogel with NPK after 24 h. Moreover, the EL% calculated for CS-co-PVA hydrogel, Fig. 9b has shown at different concentrations of 50, 100, and 200% w/v of NPK in D.W, that at 100% w/v NPK concentration, the hydrogel reached its maximum efficiency loading percentage.

Similarly, the $L_{max}\%$ of NPK fertilizer in CS-co-CMC hydrogel been measured and Fig. 10a has been shown the hydrogel reached its maximum loading almost at all tested time intervals where its 80.95% at 6 h and 84.4% at 12 h and reached 89.64% at 24 h. The used loading solution was R.W where the hydrogel reached it is maximum swelling and the solution was kept at a temperature of 25°C which is more suitable for swelling and loading. The efficiency loading percentage EL%, Fig. 10b, reached its maximum when the concentration of NPK was 100% w/v.

Measurement of NPK Release from Hydrogel Microspheres

The loaded microspheres of the studied hydrogels have been allowed to release their loaded NPK and Eq. 5 has been used for the calculation of cumulated release percentage $R_{cum}\%$, depending on the calibration curve of the NPK fertilizer. The releasing process was studied depending on two variables, the time and the temperature of the releasing medium. The release of NPK was measured each 3 h until the concentration of NPK become zero or almost after 24 h. The degrees of temperature of the release medium was fixed at 10, 25, and 50°C to get a more controlled release of NPK.

The $R_{cum}\%$ of NPK fertilizer from CS-co-PVA hydrogel was studied in different release solutions mediums, D.W, R.W, PH4, and PH9 and the best-controlled release was found, Fig. 11, in PH9 and at 25°C where the chains of the hydrogel are swell under the aforesaid conditions to the point enough to release in a controlled manner.

The $R_{cum}\%$ of NPK fertilizer from CS-co-CMC hydrogel was studied also in different release solutions mediums, D.W, R.W, PH 4, and PH 9. The best release medium was found, Fig. 12, for best-controlled release also is PH9 and at 25°C which is the best release medium to make the loaded NPK leave the core of hydrogel microspheres in a controlled manner means the salts in the R.W controlled the swelling of the hydrogel.

Studies of the Hydrogels after Releasing FTIR Studies

FTIR spectroscopy was used for the characterization of the hydrogels after the release of their loaded NPK fertilizer.

The important functional groups of the studied hydrogels with their wave numbers were listed in Table 3. The hydrogel CS-co-PVA after the release of NPK fertilizer its FTIR spectrum has an absorption band at 3200 cm^{-1} representing $\nu(\text{O-H})_{\text{str}}$ of PVA and CS polymers. In addition, the band at 1518 cm^{-1} belongs to $\nu(\text{N-H})_{\text{str}}$ of CS and the cross-linker MBA. The band at 1610 cm^{-1} which belongs to $\nu(\text{C=O})_{\text{str}}$ is also for the polysaccharide CS and cross-linker MBA means the main functional groups of CS-co-PVA hydrogel, Table 3, are still present after the release process.

The FTIR characteristic bands of CS-co-CMC hydrogel after the release of its loaded NPK fertilizer have shown in Table 3, the absorption band at 1650 cm^{-1} which belongs to $\nu(\text{C=O})_{\text{str}}$ of CMC polysaccharide and the cross-linker MBA. The band at 3274 cm^{-1} of $\nu(\text{O-H})_{\text{str}}$ is of CS and CMC polysaccharides. In addition, the band at 1520 cm^{-1} which belongs to $\nu(\text{N-H})_{\text{str}}$ is of the amine group of CS polysaccharides.

The above FTIR characterization has concluded that the hydrogels are coherent materials after release.

SEM Analysis

The SEM images of the hydrogels after the release of their loaded NPK fertilizer were studied. The SEM images of CS-co-PVA hydrogel, Fig. 13(a and b) have shown the surface morphology of the hydrogel which seems a paste of coherent materials containing holes spread among them and cracks formed after the release of NPK.

Moreover, the SEM images of CS-co-CMC hydrogel after the release of its NPK fertilizer, Fig. 14(a and b) have shown that cracked hydrogel materials with the folded surface have a paste nature with round microspheres spread as clusters and holes are interspersed the hydrogel body.

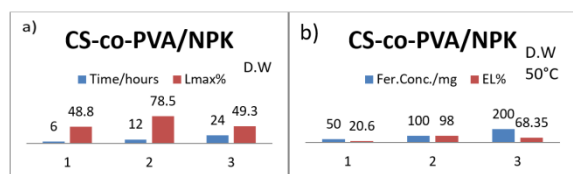


Fig. 9: Loading of NPK fertilizer in CS-co-PVA hydrogel showing (a) $L_{\text{max}}\%$ at different time intervals and (b) $EL\%$ at different NPK concentrations

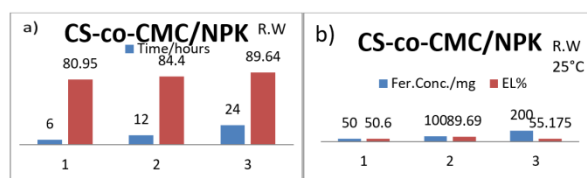


Fig. 10: Loading of NPK fertilizer in CS-co-CMC hydrogel showing (a) $L_{\text{max}}\%$ at different time intervals, and (b) $EL\%$ at different NPK concentrations

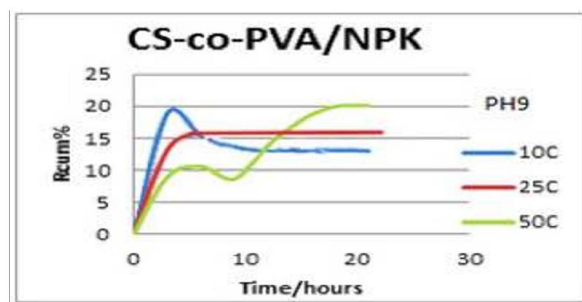


Fig. 11: $R_{\text{cum}}\%$ of NPK from CS-co-PVA hydrogel with time (hr) at different temperatures

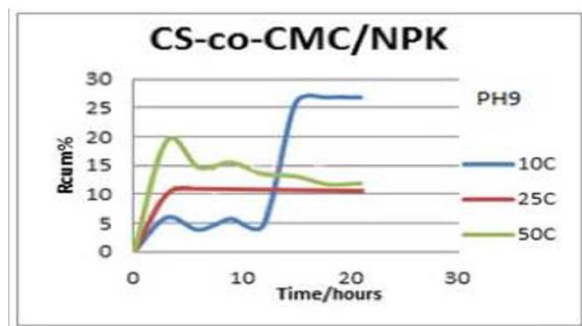


Fig. 12: $R_{\text{cum}}\%$ of NPK from CS-co-CMC hydrogel with time (hr) at different temperatures

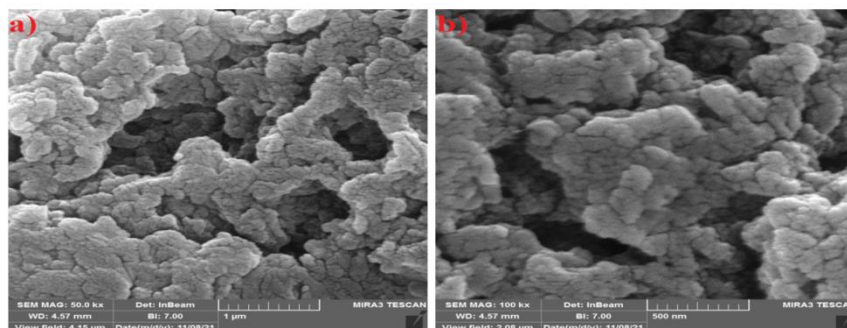


Fig. 13: SEM images of CS-co-PVA hydrogel with (a) 50 kx, and (b) 100 kx magnifications

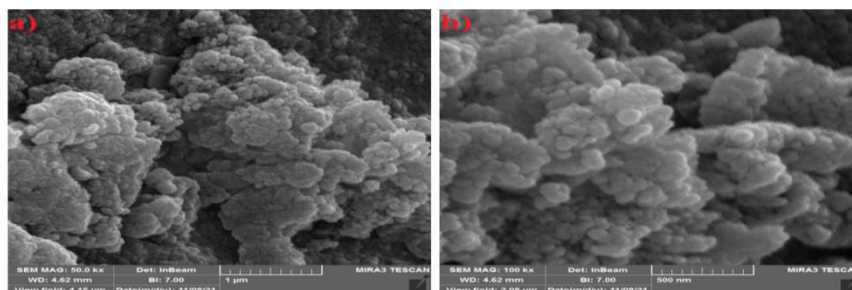


Fig. 14: SEM images of CS-co-CMC hydrogel with (a) 50.0 kx, and (b) 100.0 kx magnifications

Table 3: FTIR characteristic frequencies of the most important functional groups of the hydrogels after release of NPK fertilizer

Main functional groups	Hydrogel sample after release	
	CS-co-PVA hydrogel Wave number (cm ⁻¹)	CS-co-CMC hydrogel
v(C = O)	1610	1650
v(O-H)	3200	3274
v(C-H)	3031	2851; 2921
v(C-OH)	1379	1369
v(C-O)	1069	1095
v(C-O-C)	1010	1019
v(N-H)	1518	1520

Conclusion

Two hydrogels were prepared mainly from Chitosan (CS) copolymerized with Poly (Vinyl Alcohol) (PVA) and with Carboxymethyl Cellulose (CMC) and cross-linked chemically with MBA. The prepared hydrogels were examined in the field of agriculture for water retention where imbibe water and reach their maximum swelling. The swell hydrogels can release the absorbed water in a controlled manner and for a long time, which is useful for irrigation of arid and semi-arid regions. Both hydrogels CS-co-PVA and CS-co-CMC have shown a good ability for water retention in comparison with the reference sample. The second application of hydrogels in agricultural matters was loading of the hydrogels with agrochemicals and as a model, the NPK fertilizer was used. Both prepared hydrogels have shown good $L_{max}\%$ with efficient loading percentage EL% and are then allowed to release their loaded agrochemical in a suitable solution and at a desirable temperature. The release patterns have shown a controlled release character, which starts with a burst release curve and is followed by a controlled release manner for 24 h.

Acknowledgment

The authors are thankful to the University of Mosul, Iraq, for providing the facilities to carry out this study. The first author would like to thank Fawzi Habeeb Jabrail for guiding this study.

Author's Contributions

Maysam S. Mutlaq: Contributed in collection of literatures and for caring out the experimental work.

Fawzi H. Jabrail: Contributed in analyzing, discussing and interpreting the idea, besides checking the final review of the draft.

Ethics

Both authors have read and agreed to the published version of the manuscript. There are no ethical issues associated with this research. The article is original and contains unpublished materials.

References

- Ahmed, E. M. (2015). Hydrogel: Preparation, characterization and applications: A review. *Journal of Advanced Research*, 6(2), 105-121.
<https://doi.org/10.1016/j.jare.2013.07.006>
- AL-Ojar, R. K., & Jabrail, F. H. (2019). Release behavior of bovine serum albumin loaded on hydrogels of natural polymer blend poly (vinyl alcohol) and analyze their compositions. *American Journal of Polymer Science and Technology*, 5(2), 40-54.
- Dehkordi, D. K. (2017). Effect of superabsorbent polymer on salt and drought resistance of Eucalyptus globulus. *Applied Ecology and Environmental Research*, 15(4), 1791-1802.
<https://www.cabdirect.org/cabdirect/abstract/20183164161>

- Djumaev, A., & Tashmukhamedova, S. (2020). Physical and chemical properties of PVA-CMC based hydrogel carrier loaded with the herbal hemostatic agent for application as wound dressings. *National Journal of Physiology, Pharmacy and Pharmacology*, 10(10), 905-905.
<https://www.njppp.com/fulltext/28-1596674883.pdf>
- Jabrail, F. H., & K Al-Ojar, R. (2019). Studies on preparation and characterization of blend polymers for hydrogels synthesis and use for protein release. *Rafidain Journal of Science*, 28(2), 211-227.
https://rsci.mosuljournals.com/article_159975.html
- Jabrail, F. H., Ahmad, A. Z., & Gupta, K. C. (2016). Synthesis and characterization of pH-responsive polyvinyl alcohol hydrogels with chitosan and polyacrylonitrile. *Journal of Polymer Materials*, 33(3), 539.
- Jabrail, F. H., Jamil, W. M., Elsabee M. Z., & Gupta, K. C. (2019). Controlled Release Behaviors of Tribenuron Methyl Herbicide and Potassium Nitrate Fertilizer from Natural polymer blended poly(vinyl alcohol) hydrogel microspheres. *American Journal of Applied Sciences*, 16(5), 162-181.
<https://thescipub.com/abstract/ajassp.2019.162.181>
- Kabir, M. H., Ahmed, K., & Furukawa, H. (2017). A low-cost sensor-based agriculture monitoring system using polymeric hydrogel. *Journal of the Electrochemical Society*, 164(5), B3107.
<https://iopscience.iop.org/article/10.1149/2.0171705jes/meta>
- Mallakpour, S., & Ezhieh, A. N. (2017). Preparation and characterization of chitosan-poly (vinyl alcohol) nanocomposite films embedded with functionalized multi-walled carbon nanotube. *Carbohydrate Polymers*, 166, 377-386.
<https://doi.org/10.1016/j.carbpol.2017.02.086>
- Mazuki, N. F., Majeed, A. A., Nagao, Y., & Samsudin, A. S. (2020). Studies on ionics conduction properties of modification CMC-PVA based polymer blend electrolytes via impedance approach. *Polymer Testing*, 81, 106234.
<https://doi.org/10.1016/j.polymertesting.2019.106234>
- Nezhad-Mokhtari, P., Ghorbani, M., Roshangar, L., & Rad, J. S. (2019). A review of the construction of hydrogel scaffolds by various chemical techniques for tissue engineering. *European Polymer Journal*, 117, 64-76.
<https://doi.org/10.1016/j.eurpolymj.2019.05.004>
- Purnomo, C. W., Indarti, S., Wulandari, C., Hinode, H., & Nakasaki, K. (2017). Slow-release fertilizer production from poultry manure. *Chemical Engineering Transactions*, 56, 1531-1536.
- Sinha, A., Kalambate, P. K., Mugo, S. M., Kamau, P., Chen, J., & Jain, R. (2019). Polymer hydrogel interfaces in electrochemical sensing strategies: A review. *TrAC Trends in Analytical Chemistry*, 118, 488-501.
<https://doi.org/10.1016/j.trac.2019.06.014>
- Wu, L., & Liu, M. (2008). Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled release and water retention. *Polymers for Advanced Technologies*, 19(7), 785-792.
<https://doi.org/10.1002/pat.1034>