PECTIN-BASED HYDROGEL FOR COPPER MICRONUTRIENT RELEASE

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SOUMYA KUMARI

(2k23/MSCCHE/41)

&

BHAVYA RUSTAGI

(2k23/MSCCHE/56)

Under the Supervision of

Prof. Sudhir G. WARKAR

Department of Applied Chemistry

DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College of Engineering)

Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India

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DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College of Engineering)

Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India

CANDIDATE'S DECLARATION

We Soumya Kumari (2k23/MSCCHE/41) and Bhavya Rustagi (2k23/MSCCHE/56) hereby certify that the work which is being presented in the dissertation entitled **"Pectin-Based Hydrogel for Copper Micronutrient Release"** in partial fulfilment of the requirements for the award of Degree of Master of Science, submitted in the Department of Applied Chemistry, Delhi Technological University is an authentic record of our own work carried out during the period from August 2024 to May 2025 under the supervision of Prof. Sudhir. G. Warkar.

We have not submitted the matter presented in the dissertation for the award of any other degree of this or any other Institute.

Soumya Kumari
(2k23/MSCCHE/41)

Bhavya Rustagi
(2k23/MSCCHE/56)

DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College of Engineering)

Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India

CERTIFICATE BY THE SUPEVRISOR

Certified that Soumya Kumari (2k23/MSCCHE/41) and Bhavya Rustagi(2k23/MSCCHE/56) has carried out their search work presented in this dissertation entitled **"Pectin-Based Hydrogel for Copper Micronutrient Release"** for the award of Master of Science from Department of Applied Chemistry, Delhi Technological University, Delhi, under my supervision. The dissertation embodies results of original work, and studies are carried out by the students themselves, and the contents of the dissertation do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/ Institution.

PLACE – DELHI

DATE -

Prof. Sudhir G. Warkar

(SUPERVISOR)

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ABSTRACT

In this study, we focus on addressing the deficiency of an essential micronutrient in soil, namely copper (Cu), using biopolymer-based superabsorbent hydrogel. The novel hydrogel based on Pectin, poly (sodium methacrylate) (PSMA) and carboxymethyl tamarind kernel gum (CMTKG) was synthesized, and ex-situ Cu loading was carried out. The hydrogels were characterized using FTIR, SEM, and TGA techniques. The swelling of Cu-loaded Pectin/PSMA/CMTKG hydrogel was studied in distilled water, 0.9 % NaCl, pH 4, 9, and 12 solutions. The highest swelling was noticed for distilled water at 235.86 g/g. Moreover, the maximum water holding capacity of the hydrogel was observed as 57%. The initial release of Cu in soil was 26.44% in 5 days, compared to 61.17% in water within 30 hr. The kinetic studies revealed that the Cu release data from followed the Korsmeyer-Peppas model. The Cu-loaded Pectin/PSMA/CMTKG hydrogel showed an increase in the germination of the number of seeds and the height of tomato plants in comparison to the control soil. Hence, the Cu-loaded Pectin/PSMA/CMTKG hydrogel exhibited a potential for controlled release of Cu in soil.

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LIST OF ABBREVIATIONS AND SYMBOLS

$CONH_2$	Amide group
NH_2	Amine group
AAS	Atomic Absorption Spectroscopy
ATR-FTIR	Attenuated Total Reflection- Fourier Transform Infrared Spectroscopy
COO^-	Carboxylate ion
COOH	Carboxylic Acid Group
CMTKG	Carboxymethyl Tamarind Kernel Gum
cm	Centimetre
Cu	Copper
$CuSO_4$	Copper Sulphate
N_2	Dinitrogen
g	Gram
OH	Hydroxyl group
Mn	Manganese
MAA	Methacrylic Acid
ml	Millilitre
mg	Milligram
MWHC	Maximum Water Holding Capacity
Λ_{max}	Maximum Wavelength
MBA	N, N’-methylene-bis(acrylamide)
KPS	Potassium per sulphate
PAM	Polyacrylamide
PSMA	Polysodium methacrylate
R^2	Regression coefficient
SEM	Scanning Electron Microscopy
NaCl	Sodium Chloride

SO_4^{2-}	Sulfate ion
SO_3H	Sulfonic group
SR	Swelling Ratio
TKG	Tamarind Kernel Gum
TGA	Thermal Gravimetric Analysis
UV-vis	Ultraviolet-Visible spectroscopy
H_2O	Water
Zn	Zinc

CHAPTER 1

INTRODUCTION AND LITERARY SURVEY

1.1. Introduction

For ages, agriculture has been working to reduce poverty and improve the nutritional requirements of the rural masses in India. It is the sector where a 1% growth is two to three times more effective in countering poverty than any other non-agricultural sector. [1] The agricultural sector, as the largest user of water resources, is the most vulnerable to the effects of drought, which are occurring more often and are longer-lasting. On average, 63% of water supplied to agricultural areas is lost as a result of evaporation and runoff [1]. In a world where water demand is increasing day by day, we cannot afford to lose water, therefore, it is essential to adopt methods that gradually release water in times of deficiency but at the same time reduce water loss. One such additive that can help counter both these issues is hydrogels, first reported in the 1960s by Wichterle and Lim. They are defined as three-dimensional, hydrophilic polymer networks swollen with water. The application of hydrogels is not limited to agriculture but it also has numerous functions in the field of medicine, cosmetics, and the food industry[2]. Particularly, the smart polymer hydrogel finds extensive use in agriculture application. They have a crosslinked three-dimensional network, which is generally derived from water-soluble acrylic or methacrylic monomers. One such example is poly (sodium methacrylate) (PSMA) hydrogels. These smart hydrogels are capable of imbibing and retaining water up to 200 g to 2 kg of fluids without dissolving [3]. The ability of hydrogels to hold an amount of water many times greater than their mass allows them to release moisture to the plant gradually. In addition, these hydrogels are used as a depot of mineral fertilizers and pesticides (herbicides, insecticides, fungicides) with the possibility of their prolonged release [4]. Hydrogels also help in the improvement of soil structure and its physical properties, such as permeability, infiltration rate, aeration, and drainage[1]. Superabsorbent hydrogel can also use to release micronutrients, under regulated conditions in soil, so that the plant has access to the nutrients for a longer period[5].

Copper (Cu) is one such essential micronutrient for plants. A micronutrient is defined as an element essential for all plants, where the requirement is small, usually measured in milligrams per kilogram of soil or biomass or in grams per hectare. Although required in lesser quantities than macronutrients, micronutrients are essential for plant growth as their deficiency leads to a lowering the productivity [6]. Cu is an essential redox-active transition metal that is involved in many physiological processes in plants because it can exist in multiple oxidation states. Cu ions act as cofactors in many enzymes such as Cu/Zn superoxide dismutase (SOD), cytochrome c oxidase, amino oxidase, lactase, plastocyanin and polyphenol oxidase [7]. Cu plays important roles in photosynthetic and respiratory electron transport chains, cell wall metabolism, and oxidative stress protection [8]. Recently biopolymers such as carboxymethyl tamarind kernel Gum, pectin and cellulose-based hydrogel are gaining attention in the agricultural field.

Carboxymethyl Tamarind Kernel Gum (CMTKG) is a polysaccharide obtained from carboxymethyl functionalization of tamarind kernel polysaccharide (TKP)[9]. TKP is obtained from *Tamarindus indica,* also known as Indian date, composed of glucose, xylose, and galactose units in the ratio 3:2:1 [10]. The carboxymethylation leads to lower biodegradability than TKP, which enhances the swell capacity, hydrophilicity, steadiness, high drug loading capacity, and release kinetics. These are some of the reasons why CMTKG-based hydrogels have been used in agriculture, enzyme immobilization, and controlled drug delivery [10,11].

Pectin is another polysaccharide, found in several plants, generally in citrus fruits, principally in the lemon. It is composed of various units of poly (1→4) α D-galacturonic acid found in other cell wall components such as cellulose, hemicellulose, and lignin [12,13]. Pectin has exceptional gelling properties compared to other biopolymers such as cellulose, collagen, chitosan, and agarose. Moreover, it provides the advantage of controllable gelation and interactions through its adjustability by modifying its degree of methoxylation and acetylation [14]. These are some of the reasons why pectin hydrogels are being studied for their application in agriculture, drug delivery, and food technologyClick or tap here to enter text.[12,15,16]. To the best of our knowledge, CMTKG has not been combined with pectin and PSMA and also used first time for agricultural purpose.

Thus, this study aimed at the synthesis of Pectin/PSMA/CMTKG hydrogels with different concentrations of initiator (KPS) and crosslinker (MBA) for the controlled release of Cu. The Cu loading into the hydrogel was performed through an ex-situ technique. The hydrogel was characterized using ATR-FTIR, SEM, and TGA techniques. The swelling tests were performed in distilled water, 0.9 % NaCl, pH 4, 9, and 12 solutions. The Cu release analysis was carried out in distilled water and soil. A degradation test was conducted to determine the biodegradability of the synthesized hydrogel. The kinetic analysis of Cu released data is studied using different kinetic models. The Cu-loaded Pectin/PSMA/CMTKG hydrogel was also examined for the growth study of the tomato plant.

1.2. Literature Survey

Table 1.1 summarizes recent studies on various hydrogels developed for micronutrient delivery. The reported studies demonstrate the potential of biopolymer-based hydrogels in achieving controlled and sustained micronutrient release through pH-responsive swelling, diffusion-controlled mechanisms, or degradation-assisted pathways. These studies provide a clearer perspective on the design and optimisation of smart hydrogel matrices for effective agricultural nutrient delivery applications.

Table 1.1. Reported literatures on hydrogel-based micronutrient release

Hydrogel	Synthesis Method	Micronutrient	Key Finding	Ref.
Zinc-loaded CMTKG/Xanthan Gum/poly (sodium methacrylate)	Free radical mechanism	Zn	Improved water retention and sesame plant growth by slow Zn release.	[5]
Zinc-loaded CMTKG/Sodium acrylate	Free radical mechanism	Zn	Steady release of Zn via Fickian diffusion, enhancing its suitability for agriculture.	[16]
Boron-loaded Guar gum/Acrylic Acid	Grafting	Boron	Controlled boron release in soil, releasing 38% B in 30 days with a half-life of 96 days	[17]
Boron-loaded CMTKG/Sodium acrylate	Free radical mechanism	Boron	Controlled boron release, showing high water absorption and soil utility.	[18]
Alginate/Carboxymethyl cellulose/eggshell bio-composites	Ionic cross-linking method	Cu	Delivers micronutrient to the plants with minimal losses into the environment.	[19]
Alginate/Carboxymethyl cellulose/Starch	Ionic cross-linking method	Cu, Mn, and Zn	Improved winter wheat growth via micronutrient enrichment	[20]
Nanoporous sodium carboxymethyl cellulose	Ionic cross-linking method	Cu	Hydrogel having controllable Cu release useful for agricultural applications	[21]

CHAPTER 2

MATERIAL AND SYNTHESIS

2.1. Materials

Carboxymethyl tamarind kernel gum was gifted by Hindustan Gum and Chemicals Ltd., Haryana, India. Pectin (sd-fine chem Limited, Mumbai, India), NaOH (sd-fine chem Limited, Mumbai, India), N, N'-methylene-bis(acrylamide) (CDH, New Delhi, India), Copper sulphate pentahydrate (Qualigens, Mumbai, India), Methacrylic acid (Merck, Germany), Potassium persulfate (Fisher Scientific, Mumbai, India) were used as obtained.

2.2. Fabrication of Pectin/PSMA/CMTKG hydrogel

The novel superabsorbent hydrogels were synthesized using CMTKG, Pectin, and MAA through a free radical mechanism using varying amounts of KPS as an initiator and MBA as a crosslinker, as detailed in Table 2.1. Firstly, a fixed volume of MAA was added to a beaker containing distilled water, and NaOH was added till the pH became neutral, leading to the formation of PSMA. Thereafter, the fixed amount of CMTKG and Pectin was added to this beaker and stirred for an hr at 700 rpm. To this, the fixed amount of KPS and MBA was added and stirred for another hour. Finally, the mixture was transferred into the test tube and kept in a water bath at 60°C for 2 hr. Then, the test tube was taken out from the water bath, broken, and the hydrogel was extracted. The hydrogel was cut into discs of equal size and oven-dried at 60°C for 48 hr for further analysis, as displayed in Fig. 2.1[15].

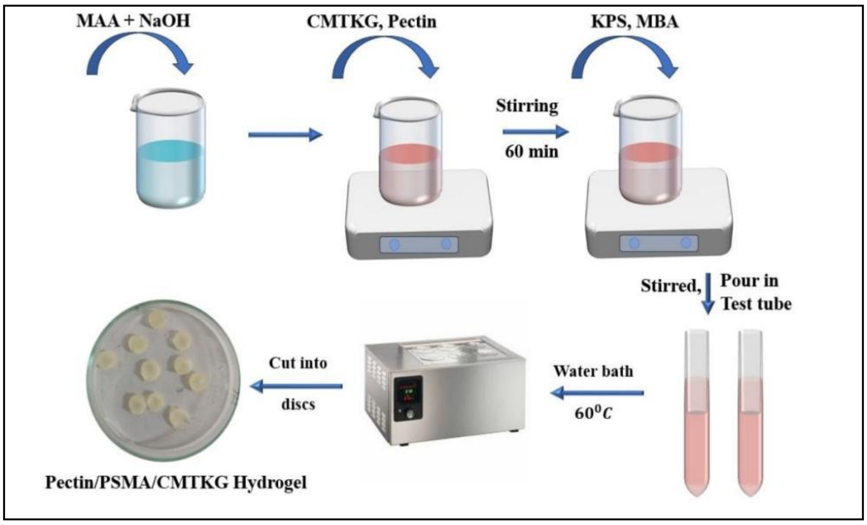

Fig. 2.1. Illustration of the synthesis of Pectin/PSMA/CMTKG hydrogel

Table 2.1 Amount of reactants used in the fabrication of Pectin/PSMA/CMTKG hydrogel

Sample code	**CMTKG (g)**	**Pectin (g)**	**MAA (ml)**	**NaOH (g)**	**MBA (mg)**	**KPS (mg)**
W-1	0.3	0.2	6	1.3	15	20
W-2	0.3	0.2	6	1.3	15	25
W-3	0.3	0.2	6	1.3	15	30
W-4	0.3	0.2	6	1.3	15	35
W-5	0.3	0.2	6	1.3	15	40
W-6	0.3	0.2	6	1.3	20	30
W-7	0.3	0.2	6	1.3	25	30
W-8	0.3	0.2	6	1.3	30	30
W-9	0.3	0.2	6	1.3	35	30

2.3. Fabrication of Cu-loaded Pectin/PSMA/CMTKG hydrogel

The Pectin/PSMA/CMTKG (W-3) hydrogel was opted for the synthesis of Cu-loaded hydrogel, as it showed the highest swelling ratio among all the formulations. The Cu-loaded Pectin/PSMA/CMTKG hydrogel was prepared by ex-situ loading of copper sulphate pentahydrate in the synthesized Pectin/PSMA/CMTKG hydrogel. For the synthesis, a fixed amount of dried hydrogel disc was immersed in 100 ml distilled water containing 20 mg $CuSO_4$ for 48 hr. Afterwards, the Cu-loaded Pectin/PSMA/CMTKG hydrogel disc was taken out and air-dried for 24 hr, followed by oven drying at 50 °C for 48 hr [18].

CHAPTER 3

EXPERIMENTAL SECTIONS

3.1. Swelling Studies

The swelling behaviour of all synthesized Pectin/PSMA/CMTKG hydrogels was examined based on gravimetric analysis. The accurately weighed dried hydrogel discs (W_{DG}) were immersed in distilled water. At certain time intervals, the swollen hydrogels were removed from the distilled water, and the extra water on the hydrogel disc was blotted off with the help of filter paper and weighed again (W_{SG})[22]. The equilibrium swelling ratio was determined for all synthesized hydrogels at equilibrium (maximum swelling) by using the given formula [23].

$$\text{Equilibrium Swelling Ratio} = \frac{W_{SG} - W_{DG}}{W_{DG}} \tag{1}$$

Moreover, the swelling analysis for Cu-loaded Pectin/PSMA/CMTKG hydrogel was carried out in distilled water, 0.9% NaCl, pH 4, 9, and 12 solutions, to study the effect of different mediums on the swelling capacity of the hydrogel [5].

3.2 Release analysis of Cu in soil and water

The two different experiments were conducted to quantify the Cu released from the synthesized Cu-loaded Pectin/PSMA/CMTKG hydrogel. To study the release of Cu in distilled water, a beaker was filled with 100 ml of distilled water and a fixed amount of Cu-loaded Pectin/PSMA/CMTKG hydrogel was immersed in it. The 10 ml of distilled water was taken out at fixed time intervals. Additionally, to ensure that volume remained steady throughout the experiment, an equal volume of fresh distilled water was poured into the beaker. The Cu amount in the withdrawn solution was quantified using AAS.

Moreover, for the release studies of Cu in soil, a fixed amount of dried Cu-loaded Pectin/PSMA/CMTKG hydrogel discs covered in chiffon packets were buried 2 cm deep in each different plastic pot, having 200 g of dry soil. To each pot, 100 ml of distilled water was added to retain moisture in the soil. After a particular time interval, one hydrogel packet was taken out from the soil. Thereafter, the 10 g soil sample was removed from the plastic pot and dried in the oven. The amount of Cu micronutrients released into the soil was quantified using AAS. Both experiments were conducted until the equilibrium Cu release value had been obtained [21].

3.3. Release kinetic studies

The Cu release data were fitted to various kinetic models to understand the Cu release mechanism, namely, Korsmeyer-Peppas, Zero Order, Higuchi, and First Order models, as illustrated in Table 4.1. The model that has the highest coefficient of determination (R^2) value was considered to be the best-fit model [24].

3.4. Maximum water holding capacity (MWHC)

To determine the maximum water holding capacity (MWHC) of soil, fully dried soil was taken and filtered with a sieve. The fixed amount of soil (100 g) was mixed with 0.1g, 0.2g, 0.3g, and 0.4g of Cu-loaded Pectin/PSMA/CMTKG hydrogel, while the untreated soil pot was used as a control for comparison. The soil was poured into a pot with tiny holes and filter paper at the bottom of the pot, and weighed. The pots were placed in the water bath for 4 hr for water absorption. Thereafter, the pot was removed, and extra water was drained out and weighed again. The MWHC of soil can be determined by the given formula[25] .

MWHC = Weight of [(Pot after water absorption) −(Pot containing dried soil+wet filter paper)] (2)

3.5. Tomato plant growth study

An experiment was conducted to examine the effect of the addition of Cu-loaded Pectin/PSMA/CMTKG hydrogel on the growth of a tomato plant for 25 days. For this study, the soil (200 g) was taken in two different pots and six tomato seeds (*Solanum lycopersicum*) were planted at 3 cm in each pot. In the first pot, a fixed amount (0.4 g) of Cu-loaded Pectin/PSMA/CMTKG hydrogel was added, while the second pot, having only soil without any hydrogel, served as a control. The 150 ml of water was added to both pots to maintain moisture in the soil [26]

3.6. Degradation Test

The synthesized Cu-loaded Pectin/PSMA/CMTKG hydrogel was tested for soil burial degradability for 60 days. In the well-moisturised soil, at a depth of 5-6 cm, the pre-weighed (W_i) amount of Pectin/PSMA/CMTKG hydrogel was buried. The hydrogel was removed at regular time intervals, weighed (W_f), and again buried in the soil for further degradation. The degradation (%) was calculated implying the given formula [27].

$$\text{Degradation \%} = \frac{W_i - W_f}{W_i} \times 100 \quad (3)$$

3.7. Characterization

The FTIR spectra of $CuSO_4$, MBA, Pectin/PSMA/CMTKG, and Cu-loaded Pectin/PSMA/CMTKG hydrogel were obtained using the ATR-FTIR Nicolet iS50 FTIR Tri-detector spectrometer within a wavenumber range of 4000-450 cm^{-1}. The TGA was captured for Pectin/PSMA/CMTKG and Cu-loaded Pectin/PSMA/CMTKG hydrogel using

PerkinElmer TGA 4000 within a temperature range of 30-850°C, at a uniform heating rate of 10°C/min. SEM was performed for Pectin/PSMA/CMTKG and Cu-loaded Pectin/PSMA/CMTKG hydrogel using JEOL Japan Mode: JSM 6610LV. AAS was carried out for Cu released data using a PerkinElmer A4000 model AAS.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Mechanism of synthesis of Pectin/PSMA/CMTKG hydrogel

Various formulations of Pectin/PSMA/CMTKG hydrogels were synthesized by varying concentrations of MBA and KPS, via a free radical mechanism. KPS is a redox initiator that decomposes to persulphate radical in thermal conditions (60°C). These radicals attack the vinyl bond of sodium methacrylate and generate radicals of sodium methacrylate, which undergo propagation and termination, thus resulting in the formation of PSMA. The sulphate radical also abstracts the proton from the -OH group of CMTKG and Pectin. Moreover, MBA acts as a bifunctional crosslinking agent and forms the covalent bond by joining all these radicals, leading to the formation of crosslinked Pectin/PSMA/CMTKG hydrogel, as represented in Fig. 4.1 [15].

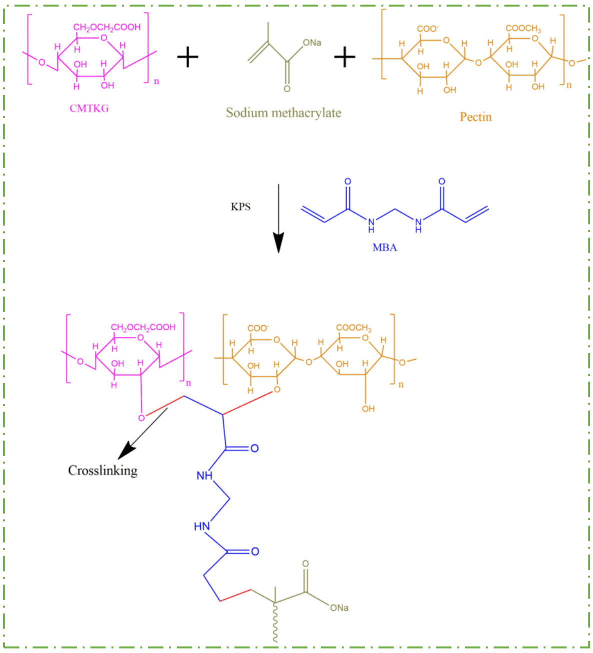

Fig. 4.1. Mechanism of fabrication of Pectin/PSMA/CMTKG hydrogel

4.2. Swelling studies

Swelling studies of all synthesized Pectin/PSMA/CMTKG hydrogels were carried out in distilled water to determine the effect of the initiator and crosslinker on the equilibrium swelling ratio, as presented in Fig. 4.2.(a), (b). Additionally, the swelling studies of Cu-loaded Pectin/PSMA/CMTKG hydrogel were performed in 0.9% NaCl, pH 4, 9, 12, and distilled water, as shown in Fig. 4.2. (c).

4.2.1. Effect of crosslinker

The effects of crosslinker on the equilibrium swelling ratio of Pectin/PSMA/CMTKG hydrogels were studied, as presented in Fig. 4.2 (a). The highest swelling ratio of 235.86 ± 0.89 g/g was observed at 15 mg concentration of crosslinker. The swelling analysis revealed that on increasing the MBA amount, the equilibrium swelling ratio decreases. This is accredited to an increase in the crosslinking density of the polymeric network, which reduces the free space within the polymeric matrix, and hence the water absorption capacity decreases [28].

4.2.2. Effect of the initiator

The amount of initiator plays an important role in the swelling behavior of the hydrogel. The maximum equilibrium swelling ratio of 235.86 ± 0.89 g/g was noticed at 30 mg of initiator for W-3 formulation. It was observed that on increasing the concentration of KPS (20-30 mg), the equilibrium swelling ratio increases, as shown in Fig.4.2 (b). This can be associated with an increase in the number of free radicals, which increases the rate of polymerization, and hence, the equilibrium swelling ratio increases. However, beyond 30 mg of the KPS, a decrease in the equilibrium swelling ratio was observed. It can be attributed to the fast generation of free radicals, which led to an increase in the formation of shorter chains, i.e. oligomers, that are soluble in water, and hence the equilibrium swelling ratio decreases [5].

4.2.3. Swelling analysis of Cu-loaded Pectin/PSMA/CMTKG hydrogel

The swelling was performed in 0.9% NaCl, pH 4, 9, 12, and distilled water for Cu-loaded Pectin/PSMA/CMTKG hydrogel, as illustrated in Fig. 4.2 (c). It was noticed that the swelling ratio was maximum in distilled water. It is due to the absence of interfering ions, which may interact with the oppositely charged ions present in the hydrogel. Additionally, it was also observed that as the pH of the solution increased from 4 to 12, the swelling capacity of the hydrogel increased. This is attributed to the carboxylate ions (COO^-) generated in an alkaline medium because of the deprotonation of the carboxylic acid (−COOH) group present on the polymeric chain. Additionally, due to the electrostatic repulsion between these COO^- ions, more free spaces are available, leading to faster water imbibition, hence swelling increases [29][30]. However, the lower swelling ratio observed at pH 4 is attributed to the non-ionization of −COOH groups present in the polymeric network [31]. Furthermore, the lowest swelling was observed in 0.9% NaCl solution, which is because the sodium ions (Na^+) of NaCl interact with the COO^- present within the hydrogel. This reduces the charge density, making the hydrogel less able to attract water molecules, and the swelling ratio decreases [32].

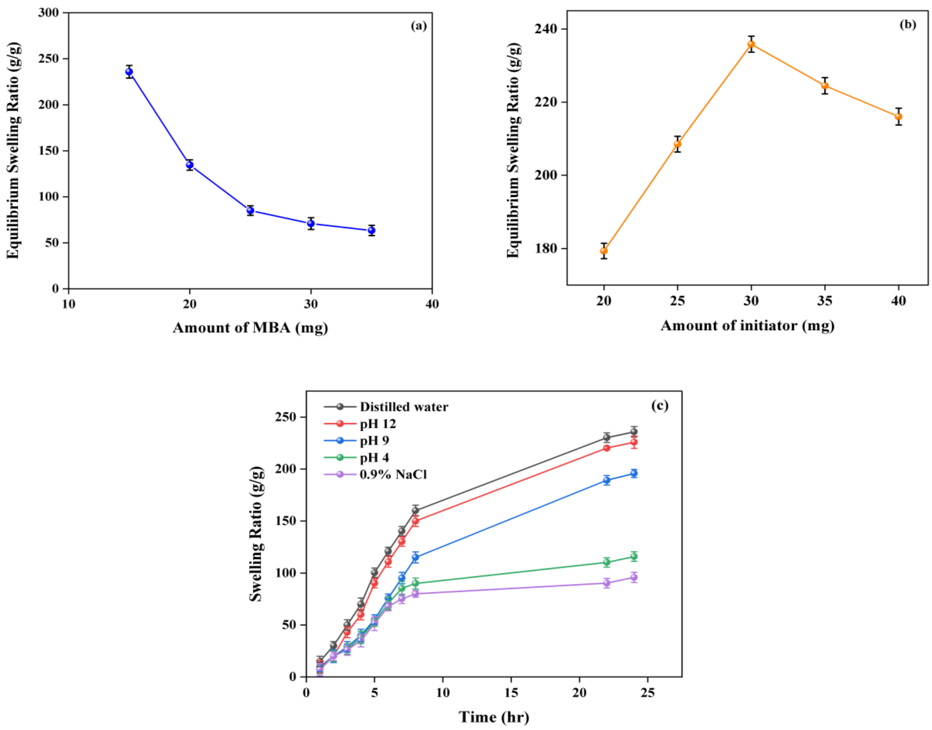

Fig. 4.2. Impact of **(a)** crosslinker, **(b)** initiator, on equilibrium swelling ratio, and **(c)** swelling vs time for Cu-loaded Pectin/PSMA/CMTKG hydrogel

4.3. Maximum water holding capacity (MWHC)

The MWHC of control soil and soil containing varying amounts of synthesized hydrogel was shown in Fig. 4.3. The MWHC was found to be 39±0.648% for control soil, i.e., the soil held 39 g of water per 100 g of soil. Moreover, the soil containing 0.1 g, 0.2 g, 0.3 g, and 0.4 g Cu-loaded Pectin/PSMA/CMTKG hydrogel was found to hold 45 g, 48 g, 52 g, and 57 g of water per 100 g of soil respectively, which indicates an increase in MWHC, as compared to control soil. Hence, it can be concluded that the amount of hydrogel directly affects the MWHC of soil [33].

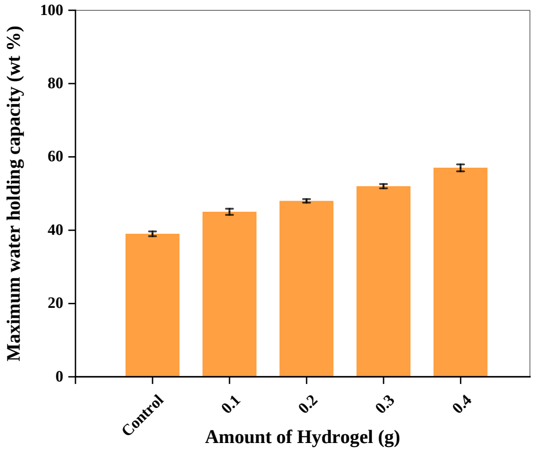

Fig. 4.3. MWHC plot for control and Cu-loaded Pectin/PSMA/CMTKG hydrogel

4.4. SEM

SEM micrographs of Pectin/PSMA/CMTKG and Cu-loaded Pectin/PSMA/CMTKG hydrogel are presented in Fig. 4.4. The micrographs showed that Pectin/PSMA/CMTKG hydrogel has a porous and smooth surface morphology. However, the Cu-loaded Pectin/PSMA/CMTKG hydrogel possesses a rough layered surface, which may be due to the intercalation of Cu into a Pectin/PSMA/CMTKG hydrogel matrix [32]. This proves the successful loading of Cu in Pectin/PSMA/CMTKG hydrogel, mostly on the surface, which enhances the likelihood of Cu release in soil to counter micronutrient deficiency.

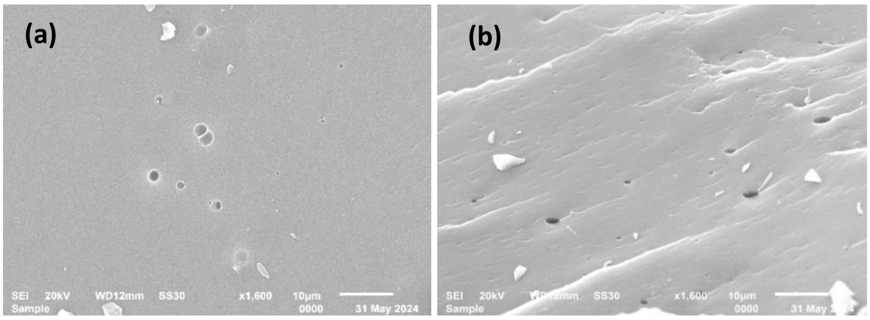

Fig. 4.4. SEM of (a) Pectin/PSMA/CMTKG, and (b) Cu-loaded Pectin/PSMA/CMTKG hydrogel

4.5. TGA

TGA was carried out for Pectin/PSMA/CMTKG, and Cu-loaded Pectin/PSMA/CMTKG hydrogel, to ascertain their behaviour at higher temperatures. The thermograms of both the hydrogels showed weight loss in three different zones, as presented in Fig. 4.5. In the first zone (30-235°C), weight loss of 18.8% & 16.7% was observed for Pectin/PSMA/CMTKG and Cu-loaded Pectin/PSMA/CMTKG hydrogel, respectively, due to the loss of moisture. In the second zone (235-517°C), weight loss of 32.2% & 31.36% was noticed, corresponding to the decomposition of the polymeric backbone. Finally, the weight loss of 20.22% & 18.63%, respectively, observed between 517-850°C, was due to the complete degradation of the remains of polymers [34].

Additionally, the residual mass of Pectin/PSMA/CMTKG and Cu-loaded Pectin/PSMA/CMTKG hydrogel was found to be 28.78% & 33.31%, respectively. Cu, which is an inorganic element that does not degrade, may have contributed to the thermal stability of Cu-loaded hydrogel[35]. Hence, it can be concluded that the thermal stability of Pectin/PSMA/CMTKG hydrogel was increased with the incorporation of Cu micronutrient into the polymeric matrix.

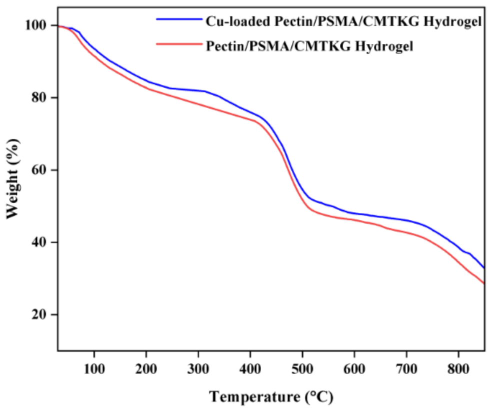

Fig. 4.5. TGA plot of Pectin/PSMA/CMTKG, and Cu-loaded Pectin/PSMA/CMTKG hydrogel

4.6. FTIR

The FTIR spectra of MBA, $CuSO_4$, Pectin/PSMA/CMTKG, and Cu-loaded Pectin/PSMA/CMTKG hydrogel, are illustrated in Fig. 4.6. In the FTIR spectrum of $CuSO_4$, the peaks observed at 3106 cm^{-1}, 1668 cm^{-1}, 1054 cm^{-1} and 865 cm^{-1} correspond to O-H stretching vibration, H_2O stretching vibration, O-H bending vibration and SO_4^{2-} bond respectively[36]. Moreover, in the FTIR spectra of Pectin/PSMA/CMTKG and Cu-loaded Pectin/PSMA/CMTKG hydrogel, the peaks observed at 2883 cm^{-1} and 2946 cm^{-1} indicate the C-H stretching vibration. Further, the peaks at 1390 cm^{-1} and 1394 cm^{-1} are attributed to COO^- symmetric stretching, respectively, while the peaks at 1554 cm^{-1} and 1539 cm^{-1} represent COO^- asymmetric stretching vibration. Additionally, the peaks found at 1683 cm^{-1} and 1681 cm^{-1} is due to C=O stretch and peaks at 3382 cm^{-1} and 3367 cm^{-1} respectively, are due to -OH stretch [34].

In the FTIR spectrum of MBA, the =C-H wagging peak observed at 993 cm^{-1} disappears in Pectin/PSMA/CMTKG hydrogel and Cu-loaded Pectin/PSMA/CMTKG hydrogel [37]. Hence, this confirms the successful synthesis of crosslinked Pectin/PSMA/CMTKG and Cu-loaded Pectin/PSMA/CMTKG hydrogel. Additionally, in the comparison of FTIR spectra of Cu-loaded Pectin/PSMA/CMTKG hydrogel with Pectin/PSMA/CMTKG hydrogel, no new peak is observed, which indicates that there is no chemical interaction between Cu and Pectin/PSMA/CMTKG hydrogel; only physical interaction is present[18].

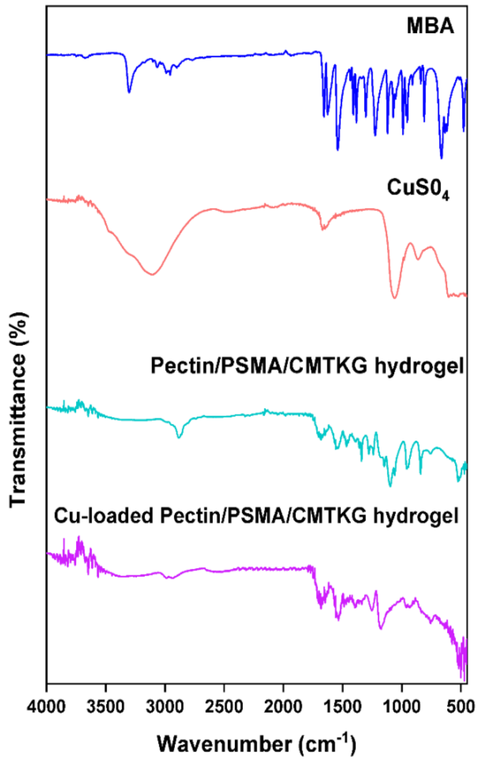

Fig. 4.6. FTIR spectra of MBA, $CuSO_4$, Pectin/PSMA/CMTKG, and Cu-loaded Pectin/PSMA/CMTKG hydrogel

4.7. Release analysis of Cu in soil and water

The release of Cu from Cu-loaded Pectin/PSMA/CMTKG hydrogel was studied for 30 hr, as shown in Fig. 4.7. (a). In 1st hr, the Cu release from Cu-loaded Pectin/PSMA/CMTKG hydrogel was determined to be 6.75%, which increased with time, reaching 61.17% in 30 hr. Additionally, the release of Cu in soil was studied over 60 days, as illustrated in Fig. 4.7.(b). The Cu-loaded Pectin/PSMA/CMTKG hydrogel exhibited 26.44% Cu released in soil on the 5th day, which significantly enhanced up to 67.02% on the 60th day. This result showed the slow release of Cu in the soil as compared to the water. This controlled release of Cu in the soil occurs in three stages, as noticed in Fig. 4.7.(b). Firstly, during the initial 10 days, the Cu released may be due to the wetting time of Cu-loaded Pectin/PSMA/CMTKG hydrogel.

Secondly, the released observed upto 30 days, corresponds to the release of Cu from the external layers of Cu-loaded Pectin/PSMA/CMTKG hydrogel. Finally, the Cu released was noticed between 30-60 days, which may be due to the diffusion of Cu from the inner layer of hydrogel [27]. Thus, it may be concluded that the synthesized Cu-loaded Pectin/PSMA/CMTKG hydrogel exhibited a controlled release of Cu in soil

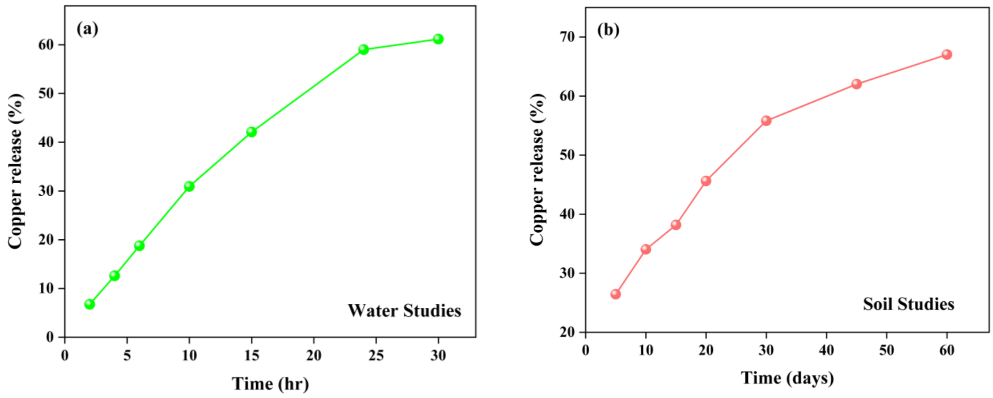

Fig. 4.7. Release plot of Cu in **(a)** water and **(b)** soil

4.8. Release Kinetic studies

The Cu release data were analyzed using various kinetic models such as zero order, first order, Higuchi, and Korsmeyer-Peppas to predict the release mechanism of copper based on the correlation coefficient (R^2). In Table 4.1 M_t and M_∞ represent the quantity of Cu released at determined time intervals and the amount of Cu present in the hydrogel initially, respectively, while k and k_H represent the release rate constant, and n is the release exponent, which indicates the release mechanism. [38]. The R^2 values for zero order, Higuchi, and Korsmeyer-Peppas Model are acceptable for the release of Cu, but are independent of concentration according to the first order model due to the poor R^2 value[39]. The release data best followed the Korsmeyer–Peppas model in both soil and water, as this model has the highest R^2 value, as shown in Fig. 4.8. The Korsmeyer-Peppas model has an R^2 value of 0.9965 in water and 0.9830 in soil. Moreover, the diffusion exponent value (n) was found to be 0.483 in water and 0.41 in soil, as observed in Table 4.1. This concludes that the Fickian diffusion method is responsible for Cu diffusing out from the hydrogel matrix. This revealed that the Cu micronutrient is released solely through diffusion from the higher concentration (hydrogel) to the lower surrounding (soil). Thus, the Cu-loaded Pectin/PSMA/CMTKG hydrogel can be utilized in agriculture, owing to its capacity to transport Cu micronutrients [40,41].

Table 4.1. Kinetic modelling data of Cu-loaded Pectin/PSMA/CMTKG hydrogel

Model	**Equation**	**Water**		**Soil**		**Ref.**
		R^2 value	**n value**	**R^2 value**	**n value**	
Zero Order	$M_t = M_\infty + k_0 t$ k_0 is the rate constant	0.9792	-	0.9803	-	[38]
First Order	$\text{Log}M_t = \text{Log}M_\infty + \frac{kt}{2.303}$ k is the rate constant	0.7922	-	0.8915	-	[38]
Higuchi	$F = M_t/M_\infty = k_H t^{1/2}$ k_H is the kinetic constant	0.9908	-	0.9819	-	[38]
Korsmeyer–Peppas	$F = M_t/M_\infty = kt^n$ k is the kinetic constant n is the diffusion exponent 1. Fickian Diffusion ($n < 0.5$) 2. Non-Fickian Diffusion ($0.89 \geq n \geq 0.5$) 3. Case II transport ($n > 0.89$)	0.9965	0.483	0.9830	0.41	[42]

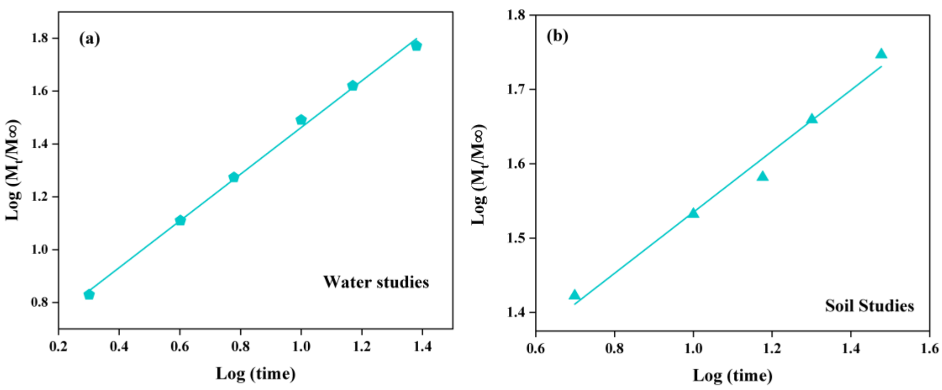

Fig. 4.8. Release kinetics curve according to Korsmeyer-Peppas model in **(a)** Water, and **(b)** Soil

4.9. Tomato plant growth study

The effect of Cu-loaded Pectin/PSMA/CMTKG hydrogel on tomato plant growth was illustrated in Fig. 4.9. The germination count was noticed after 4 days in both pots, while the average plant height was noted after 25 days. Both the number of germination and the average height of tomato plants were found to be higher in the case of the pot containing Cu-loaded Pectin/PSMA/CMTKG hydrogel compared to the control soil sample pot, as observed in Table 4.2. Thus, it can be concluded that the synthesized Cu-loaded Pectin/PSMA/CMTKG hydrogel has the potential to reduce the deficiency of Cu micronutrient in plants [43].

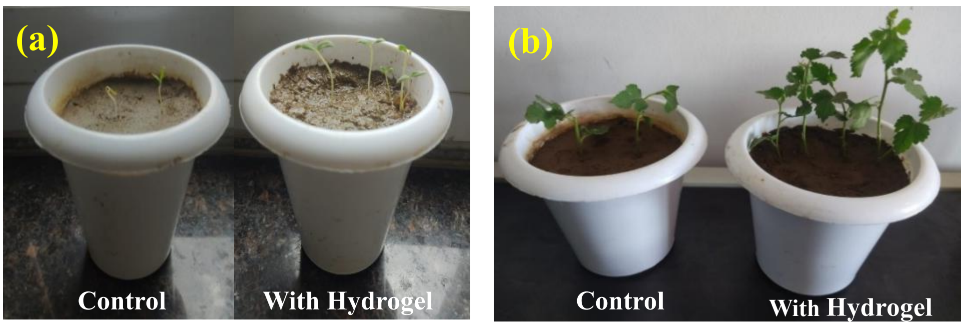

Fig. 4.9. (a) Number of germinated tomato seeds, and **(b)** Average tomato plant height treated with control and hydrogel

Table. 4.2. Impact of hydrogel on tomato seed germination and plant height

Sample	Number of germinated seeds on 4th day	Average Tomato plant height (cm) on the 25th day
Controlled soil	2	13
Soil containing Cu-loaded Pectin/PSMA/CMTKG hydrogel	5	22.5

4.10. Degradation Test

The degradation analysis of Cu-loaded Pectin/PSMA/CMTKG hydrogel was carried out in soil for 60 days. The degradation profile showed a two-step degradation process, as presented in Fig.4.10. The degradation profile of Cu-loaded Pectin/PSMA/CMTKG hydrogel demonstrates a faster degradation within the initial 50 days. The organic content (CMTKG, Pectin) and oxygen were high during the initial period of degradation, leading to a fast degradation rate. Moreover, the degradation becomes slower between 50-60 days. It may be due to the anaerobic conditions which lowered the microbial activity, thus lesser diffusion of oxygen into the hydrogel which lowered degradation [15]. The degradation of synthesized Cu-loaded Pectin/PSMA/CMTKG hydrogel was found to be 54 ±0.78% within 60 days, which seems good for agricultural applications.

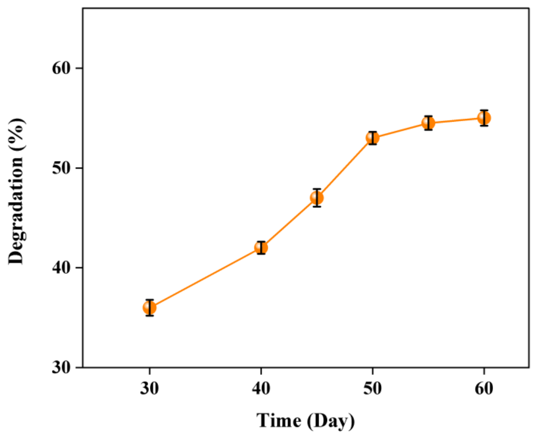

Fig. 4.10. Degradation profile of Cu-loaded Pectin/PSMA/CMTKG hydrogel

CHAPTER 5

CONCLUSION, FUTURE SCOPE, AND SOCIAL IMPACT

The synthesis of Cu-loaded Pectin/PSMA/CMTKG hydrogel was successfully done and its effect on germination and growth of tomato seeds was studied. The highest swelling ratio of about 235.86±0.89 g/g was observed in distilled water. The swelling ratio was found to decrease with an increase in the concentration of MBA and increase with the KPS amount. The Pectin/PSMA/CMTKG hydrogel was observed to increase the water holding capacity of soil from about 39% in the control soil to 57% in the soil containing 0.4 g of hydrogel. The Cu release study showed the maximum release of Cu as 61.17% in water and 67.02% in soil, respectively. Among various kinetic studies, the Cu release data were best fitted with the Korsmeyer-Peppas model. The degradation studies revealed that the hydrogel was bio-degradable, showing 54±0.78% degradability within 60 days. Thus, the Cu-loaded Pectin/PSMA/CMTKG hydrogel was confirmed to counter Cu deficiency in plants.

This research focuses on the synthesis of a novel hydrogel that incorporates copper (Cu) into a matrix of pectin, PSMA, and CMTKG. The study evaluates the performance and characteristics of this Cu-loaded hydrogel, examining its potential applications and effectiveness in various chemical reactions. The incorporation of Cu is expected to enhance the catalytic properties of the hydrogel, making it suitable for applications in environmental and biomedical fields. Overall, the findings from this study contribute to the ongoing development of advanced materials for diverse application

The strength of the Cu-loaded Pectin/PSMA/CMTKG hydrogel will play a key role in its reproducibility and usefulness in agriculture. Therefore, mechanical strength testing could be a potential pathway forward. The Cu release from Cu-loaded Pectin/PSMA/CMTKG hydrogel was tested for only one type of soil. However, the Cu release can be checked in different types of soil, such as alluvial, black, and red soil. In the present work, ex-situ loading of Cu was done, while the effectiveness of in-situ loading can also be tested.

The synthesized Cu-loaded Pectin/PSMA/CMTKG hydrogel has various socially viable properties. The superabsorbent hydrogel can be valuable in water-stressed regions, as seen by the MWHC study. The increase in germination and height of tomato plants containing Cu-loaded Pectin/PSMA/CMTKG hydrogel compared to control soil shows better plant productivity, which can be critical for ensuring food security, especially in regions where water scarcity and micronutrient deficiency are major challenges. Since Cu is an essential micronutrient and can counter various development issues in plants, it can also reduce the nutrient dependency in agriculture and synchronously cut the cost for farmers. The synthesized Cu-loaded Pectin/PSMA/CMTKG hydrogel was found to be biodegradable, so it also avoids the long-term soil damage.

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LIST OF PUBLICATIONS, CONFERENCES AND THEIR PROOFS

1. Presented poster at the *“2nd International Conference on Advanced Materials for Green Chemistry and Sustainable Environment”* organized by the K. R. Manglam University and Shivaji College, University of Delhi, held at the Department of Chemistry, K. R. Mangalam University on 20 & 21 March 2025.

PROOF OF CONFERENCE

AMGSE-2025

2nd International Conference

on

Advanced Materials for Green Chemistry and Sustainable Environment

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