

Synthesis and application of Zinc loaded Carboxymethyl tamarind kernel gum and xanthan gum-based superabsorbent hydrogels to investigate the effect on sesame plant growth.

A PROJECT REPORT

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD

OF THE DEGREE OF

MASTER OF SCIENCE

CHEMISTRY

(BATCH 2021-2023)

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CANDIDATE'S DECLARATION

We Ekta Yadav (2K21/MSCCHE/17) and Komal Pandey (2K21/MSCCHE/27) students of M.Sc. Chemistry, hereby certify that the work which is presented in the dissertation titled **“Synthesis and application of Zinc loaded Carboxymethyl tamarind kernel gum and xanthan gum-based superabsorbent hydrogels to investigate the effect on sesame plant growth”** in fulfilment of the requirement for the award of Degree of Master of Science in Chemistry and submitted to the Department of Applied Chemistry, Delhi Technological University (Formerly Delhi College of Engineering), New Delhi is an authentic record of our own carried out during a period from January 2023 to May 2023, under the supervision of Prof. Sudhir G. Warkar, Department of Applied Chemistry.

The matter presented in this report has not been submitted or previously formed the basis for the award of any Degree, Diploma, Associateship, Fellowship, or other similar title or recognition.

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CERTIFICATE

I hereby certify that the Project Dissertation titled “**Synthesis and application of Zinc loaded Carboxymethyl tamarind kernel gum and xanthan gum-based superabsorbent hydrogels to investigate the effect on sesame plant growth**” which is submitted by Ekta Yadav (2K21/MSCCHE/17) and Komal Pandey (2K21/MSCCHE/27) Department of Applied Chemistry, Delhi Technological University, New Delhi in partial fulfilment of the requirement for the award of the Degree of Master of Science is a record of the project work carried out by the students under my supervision and guidance.

To the best of my knowledge, this work has not been submitted in part or full for any Degree or Diploma to this University/Institute or elsewhere.

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ACKNOWLEDGEMENT

We feel immense pleasure in expressing my deep gratitude and an overwhelming sense of pride towards our guide, **Prof. Sudhir G. Warkar**, whose constant help and support, complete involvement, invaluable guidance and encouragement, and critical analysis of our result, led us to complete this project and gain preliminary knowledge of research. We owe our sincere thanks to him for giving us an opportunity to work under his guidance.

We would also like to take this opportunity to thank the HOD of the Department of Applied Chemistry, **Prof. Anil Kumar** for overlooking and enabling us to use all the facilities that were required and for going out of his way to help students in any matter.

We would like to express our deepest appreciation to **Indu Rani** for all her support, and continuous guidance in laboratory work and research during the project. We express our gratitude toward our families and colleagues for their kind cooperation and encouragement which help us in the completion of this project.

Without the help of fore mentioned individuals the project would not have been as easily carried out, and we would face many difficulties through it.

EKTA YADAV

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ABSTRACT

The novel superabsorbent hydrogel (SAH) was fabricated by interpenetrating xanthan gum and carboxymethyl tamarind kernel gum with sodium methacrylate. Various compositions of SAH were fabricated by varying the concentration of biopolymers, monomers, cross-linker, and initiators. The structural morphology of SAH was characterized by FTIR, FE-SEM, and TGA techniques. The swelling behavior of SAH was studied in different mediums viz. distilled water, 0.9 % NaCl, pH 4,9, and 12. Zinc Chloride was incorporate in SAH for the release zinc micronutrient. The Zinc Superabsorbent hydrogel was utilized for controlled-release studies of zinc micronutrients in soil and water. It was found that ZSAH showed 51.6 % release in water within 60 hours and 51.87 % release in soil within 60 days which were analyzed by atomic absorption spectroscopy (AAS) technique. Moreover, under the release kinetic studies, it was seen that the Korsmeyer-Peppas model fitted well in the zinc release pattern in soil and water. The estimated value of diffusion exponent (n) clearly indicated that the mechanism of zinc release followed fickian diffusion. Hence, the novel synthesized ZSAH acts as an excellent micronutrient carrier for agricultural applications.

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LIST OF ABBREVIATIONS

ABBREVIATION		EXPANSION
CMTKG	:	Carboxymethyl Tamarind Kernel Gum
XG	:	Xanthan Gum
APS	:	Ammonium Persulfate
MBA	:	N, N'-Methylenebisacrylamide
MAA	:	Methacrylic acid
SAH	:	Superabsorbent hydrogel
ZSAH	:	Zinc-loaded Superabsorbent hydrogel.
MWHC	:	Maximum water holding capacity.
D.S	:	Distilled water

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CHAPTER -1

INTRODUCTION

1.1 Overview

In polymer chemistry hydrogels took a great consideration due to their various properties. Hydrogels is defined as a three-dimensional crosslinked polymer network and referred to as aqua gels, are a series kind of soft and wet materials that have low volume-fraction, three-dimensional porous networks of polymer molecules, fibers, or particles, in which the water or aqueous phase acts as the dispersion medium [1]. Hydrogel or smart polymer enough to respond the alteration of environmental stimuli (ionic strength, pH, temperature, presence of enzyme, electric field, magnetic field etc) and swell or shrink accordingly. In the swollen state, they are soft, flexible, and spongy, look like the living tissue exhibiting excellent biocompatibility [2]. Hydrogels have a versatile properties and application in medicinal chemistry, biosensors, tissue engineering, novel drug delivery system, Films, nanocomposites, wastewater treatment, removal of heavy metal ions and agricultural fields. Hydrogels can be classified into three categories on their origin. Natural, Synthetic polymer and hybrid polymer.

- a) **Natural hydrogel**- Natural polymer hydrogels mainly which have natural origin such as collagen, gelation, alginate, and chitosan. These polymers are biodegradable, biocompatible, and good cell adhesion properties.
- b) **Synthetic Hydrogel**-Synthetic polymer hydrogels are synthesised using synthetic polymers such as polyethene glycol (PEG) and polyamides. Synthetic hydrogels are widely used as compared to natural hydrogel because they are easily available, low cost.
- c) **Hybrid Hydrogel**-Hybrid hydrogel are combination of both natural and synthetic polymer hydrogels. These hydrogels are more potent than natural or synthetic hydrogels. Chitosan (natural polymer) have been incorporated with synthetic polymers such as poly (N - isopropylacrylamide) and polyvinyl alcohol.

Hydrogels are classified based on polymeric composition into three groups.

- a) **Homopolymeric hydrogels** – Homopolymers are defined to as a polymer network formed from a single species of the monomer. Homopolymers can be prepare by using polyethylene glycol dimethacrylate as cross-linking agent, poly (2-hydroxyethyl methacrylate) (poly HEMA) as a monomer and benzoin isobutyl ether a as the UV-sensitive initiator.
- b) **Copolymeric hydrogels**- copolymeric hydrogels are synthesised using two or more distinct monomer species with at least one hydrophilic component, the properties of

copolymeric hydrogels can be tailored by varying the composition of the monomers, the cross-linking density, and the preparation conditions. Some examples of copolymeric hydrogels include poly (ethylene glycol)-diacrylate (PEG-DA) hydrogels, poly (ethylene glycol)-poly (lactic acid) (PEG-PLA) hydrogels, and poly (N-isopropylacrylamide-co-acrylic acid) (PNIPAAm-AAc) hydrogels.

- c) **Multipolymer interpenetrating polymeric hydrogel** - Multipolymer interpenetrating polymeric hydrogel (MPIP hydrogel) is a type of hydrogel made from two or more polymers, which are synthesized separately and then cross-linked together to form a network of interpenetrating polymer chains. MPIP hydrogels exhibit unique properties compared to other hydrogels due to the presence of multiple polymer networks. The interpenetration of the different polymer chains within the hydrogel structure leads to enhanced mechanical strength, greater stability, and improved responsiveness to external stimuli.

1.2 Applications

Hydrogels have many potential applications in various fields such as biomedicine, agriculture, personal care products, environmental remediation, and energy storage. They are commonly used in wound dressings, contact lenses, drug delivery systems, tissue engineering scaffolds, and biosensors [3].

1. **Biomedicine:** Hydrogels are widely used in biomedicine for applications such as wound dressings, drug delivery systems, tissue engineering, and biosensors. They can be designed to be biocompatible and provide controlled release of drugs or growth factors.
2. **Personal care products:** Hydrogels are used in personal care products such as cosmetics and skin care products for their moisturizing and hydrating properties.
3. **Environmental remediation:** Hydrogels can be used to remove pollutants from contaminated soil and water, making them useful in environmental remediation.
4. **Food industry:** Hydrogels can be used as thickeners, stabilizers, and gelling agents in the food industry.
5. **Energy storage:** Hydrogels have been explored for use in energy storage systems such as batteries and supercapacitors due to their high-water content and ion transport properties.
6. **Targeted drug delivery:** Hydrogels can be designed to target specific sites in the body by incorporating targeting moieties such as antibodies, peptides, or ligands. This enables the

drug to be delivered directly to the site of action, reducing side effects and improving therapeutic efficacy [4].

7. **Controlled drug release:** Hydrogels can be designed to release drugs in a controlled manner by adjusting the cross-linking density, composition, and functional groups of the polymer network. This allows for sustained drug release over a prolonged period, reducing the need for frequent dosing.
8. **Agriculture:** Hydrogels can be used in agriculture to improve soil moisture retention, which can improve crop yields in dry areas [5].

There are mainly applications of hydrogels which are mentioned in above the points. We are working on agricultural applications of hydrogel.

1.3 Role of Micronutrients and Challenges

Agricultural production is largely reliant on rainfall and plays a crucial role in the global economy. In dry and semiarid regions, irregular rainfall patterns cause water shortages that annually cause unmanageable crop loss [6]. The world's population is expanding quickly, and as a result, highly productive agriculture operations must assure enough food safety [7].

For productive agriculture, it is necessary that there is enough water and micronutrients in soil [8]. Along with, the availability of micronutrients is essential because of their minimum availability is required in the plant growth [9].

As a result, micronutrients play a crucial role in ensuring crop productivity by influencing crop quality and yield. To achieve the optimum results, specific micronutrients should be made available to plants in a controlled manner [10].

Micronutrients have an impact on the growth cycle and metabolic activity of plants. These nutrients are involved in electron transport, energy storage, and enzyme activity. They are necessary for all plants and cannot be substituted because of the functions they carry out within the plant [11].

Micronutrients are important for boosting crop yields and enhancing the nutritional value of food since they are necessary building blocks for proteins and enzymes. At the optimum concentration, micronutrients including copper (Cu), manganese (Mn), iron (Fe), and zinc (Zn) are vital for plants.

In the past, generally nutrients were used to give the crops a heavy dose of fertilizers. Traditional methods for applying micronutrients have several drawbacks, including costly labour rates, difficult release control, reduced nutritional efficacy, and environmental pollution. Over the years, scientists and engineers have come up with different ways to get around these problems, such as controlled or slow-release system [12].

Superabsorbent hydrogel, in this perspective, has been researched as a new technique for water retention and soil conditioner in agricultural activities and regulated release of critical micronutrients [13]. Using the hydrogel polymer component as a soil conditioner to promote crop tolerance and growth in a sandy or light-weight gravel substrate looks to be quite effective in the agricultural industry [13].

Polymer hydrogel acts as slow-release carriers of nutrients in the soil and is considered a strategy for improving fertilizer efficiency by reducing nutrient losses by leaching, lowering costs, and reducing pollution for the environment [14], [15]. Hydrogels are very useful in agriculture because they can retain water and prevent soil erosion. In order to boost agricultural output and decrease soil water loss, hydrogel polymer has established itself as a soil conditioner.

Hydrogels are polymer substances made of cross-linked monomer networks that have a high absorption capacity for both water and solutes [16], [17]. Moreover, in the study of controlled delivery, hydrogels high water absorption rates make it easier for solutes to diffuse across porous, hydrophilic three-dimensional networks.

Superabsorbent hydrogels can be used to release agricultural nutrients under regulated conditions in soils with great performance. In just a few hours, they can absorb up to one hundred times their original weight in water, which they can then desorb under stress. When the soil near the root area of a plant starts getting dried out, hydrogel delivers water and nutrients to the roots. In addition, hydrogel application prevents micronutrients from leaching into water tables and increases water use efficiency. As an alternative, there are hydrogels that contain micronutrients and have regulated water release, allowing the micronutrient dose to be adjusted over time. The plant has access to the nutrient for a longer period [18].

As a micronutrient, zinc is extremely important in plants. Even though most plants require only a minimal amount of Zn, the proper amount is essential for the efficient functioning of various plant physiological pathways that play an important role in their growth and development.

Zinc serves as a regulatory co-factor for all the enzymes involved in the synthesis of chlorophyll, proteins, and carbohydrates [19]. Zinc deficiency has a considerable impact on the functioning of these enzymes, resulting in slowed plant growth and production. Zn is required for the enzyme rubisco to perform. As a result, it plays an important function in controlling the rate of photosynthesis in higher plants [20]. Zinc is required to sustain membrane function and accelerate the maturity of plant seed and stalk. Zn also plays an important part in the synthesis of auxin, which encourages plant growth. Therefore, Zn is vital to plant development and production. For the nutrient to release in the soil, hydrogels based on biopolymers have advantages over synthetic polymer. In a short period of time, they can absorb water up to a hundred times their initial weight, and they can also desorb that water when put under stress. When the soil around a plant's root zone begins to dry out [21] hydrogel delivers water and nutrients to the roots.

Also, application of hydrogel prevents micronutrients from washing into water tables and improves water use efficiency. As an alternative, there are hydrogels that contain micronutrients and have regulated water release, allowing the micronutrient dose to be adjusted over time. The plant has access to the nutrient for a longer period [22].

Out of many natural biopolymers, very few hydrogels based on carboxymethyl tamarind kernel gum (CMTKG) polymers have been synthesized for agricultural applications. Apart from this, hydrogel based on CMTKG has been used in drug delivery, wastewater treatment, tissue engineering and in developing hydrogels, films, composites, pellets, nanoparticles. Hydrogel based on CMTKG enhance swelling ability, high drug-holding capacity, broad pH tolerance, in situ gelation, hydrophilicity, stability, release of micronutrient and release kinetics [23]–[25]. CMTKG is made from the seeds of the *Tamarindus Indica* L. plant. Tamarind kernel gum (TKG) is a natural polymer that is also among the least expensive gums in the market [26]. Its molar ratios of xylose, galactose, and glucose are 1:2:3. Owing to its biodegradability, variable along with release kinetic studies. Solubility, non-toxicity, and susceptibility to microbial degradation, TKG and its derived compounds are being employed as a biopolymer a substitute for synthetic polymers. On the other side, xanthan gum is a natural polysaccharide with branched chains and an acidic property that is mostly synthesized aerobically by *Xanthomonas campestris* from sugarcane, corn, and their derivatives. The bacteria *Xanthomonas campestris* secretes xanthan gum (XG), an extracellular polysaccharide. It is a complex polysaccharide made up of a D-(1, 4) glucose backbone as its major chain, a branching

trisaccharide side chain made of D-(1, 2) mannose linked to D-(1, 4)-glucuronic acid, and final-d-mannose [27].

This study describes the synthesis of CMTKG and XG based superabsorbent hydrogels for the release study of Zinc as a micronutrient for agricultural applications. The aim of this research is to study the following objectives: (i) formulation of the various compositions of SAH by varying the concentration of CMTKG, XG, methacrylic acid monomer, cross-linker, and initiator; (ii) loading of zinc micronutrient in the best-swelled hydrogel composition (ZSAH) and their swelling studies in different pH solutions (iii) characteristic studies of SAH and ZSAH hydrogels by FTIR, SEM, TGA, and AAS techniques (iv) release of zinc (%) from ZSAH in water and soil.

CHAPTER -2

LITERATURE REVIEW

The study done by G. O. alkalın and M. Pulat on k-carrageenan(k-CG) hydrogels were prepared for the controlled release of copper and manganese micronutrients, glutaraldehyde (GA) was used as a crosslinker to synthesis hydrogels [8].

And the research performed by Khushbu, S. G. Warkar discussed the synthesis, unique properties, and applications of carboxymethyl tamarind Kernal gum. Gum CMTKG is derived from TKG (powder derived from Tamarindus Indica L seed powder). The paper concentrates on replacing synthetic polymers with natural polymers such as CMTKG and XG. The numerous properties of CMTKG and XG gum, such as significant swelling ability, hydrophilic nature, enhanced drug, retaining capacity, biodegradable properties etc., have been pointed out as the reason for this. Therefore, CMTKG and XG are used in agriculture for the controlled release of micronutrient (zinc) [28].

Also, the work done by T. Jamunongukan, S. kaewpironm reports the synthesis of controlled release fertilizer hydrogels from poly (viny alcohol), poly(vinyl-alcohol)/chitosan using glutaraldehyde as a crosslinker. The prepared hydrogel was tested for controlled release of fertilizer potassium. The released was lesser in the beginning and slowly increases then kept constant with time. Further Sukriti, Kaith B, and Kaur M researched on xanthan gum-based hydrogel and synthesised a hydrogel from xanthan gum and polyacrylic acid using the free radical mechanism. Urea was inserted into the synthesised hydrogel, and its release was studied. And

The paper was written by G.O. alkalın and M. Pulat on fabrication of sodium carboxymethyl cellulose hydrogel for controlled release of manganese micronutrient. The Swelling behaviour of the hydrogel was examined to confirm that it has excellent water retention. To investigate manganese release, the sample had been placed in distilled water and soil, where it exhibited slow-release characteristics.

Table 2.1 Many hydrogels which were used for different applications shown in below .

Hydrogels	Types of polymers	Applications
carboxymethyl tamarind kernel gum	Natural polymer	Agriculture (water retention capacity and slow release of micronutrients)
xanthan gum	Natural polymer	Drug delivery
Carboxymethyl cellulose (CMC)	Natural polymer	Drug delivery carrier (Anti-tumour)
k-carrageenan	Natural polymer	Agriculture (Effect on plant growth)
Chitosan	Natural polymer	Drug release control and mechanism
xanthan gum	Natural polymer	Food and Technology
Sodium Carboxymethyl cellulose (NaCMC)	Natural polymer	Agriculture (Soil enrichment)
carboxymethyl tamarind kernel gum	Natural polymer	Sustainable Agronomy
Guar- gum	Natural polymer	Drug delivery
Carboxymethyl Guar gum	Natural polymer	Disposable hygiene product

CHAPTER-3

METHODOLOGY

In this investigation, two distinct hydrogel combinations were synthesized first composition contained carboxymethyl tamarind kernel gum and xanthan gum, acrylamide, APS, and NaOH, while the second composition contained zinc inserted into the first composition. These 2 types of hydrogels were synthesized and cross-linked using CMTKG&XG to make a superabsorbent hydrogel and a zinc-loaded hydrogel, respectively. MBA was used as the crosslinker, and APS was used as the synthesis's initiator. The synthesized hydrogel pieces were evaluated by performing studies on swelling, gel content, MWHC, zinc micronutrient release, and plant growth.

3.1 Materials

The different materials used for synthesis of SAH is listed in table 1. All the solutions required for the experimental studies were prepared in distilled water.

Table 3.1: The materials used with their supplier and purity.

Material	Used As	Supplier	Purity
Carboxymethyl Tamarind kernel gum (CMTKG)	Natural biopolymer	Hindustan Gum and Chemical Ltd. Haryana	99 %
Xanthan gum (XG)	Natural biopolymer	SD Fine Chem Ltd.	99 %
MBA	Cross-linker	CDH New Delhi	98 %
Methacrylic acid (MAA)	Monomer	Merck Germany	98 %
Ammonium per sulphate (APS)	Initiator	CDH New Delhi	99 %
Zinc chloride	Micronutrient	Merck Germany	98%

3.2 Synthesis of SAH

The novel superabsorbent hydrogels based on CMTKG and XG were synthesized using APS as an initiator and MBA as a cross-linker by free radical polymerization mechanism. To synthesize hydrogel a desirable weight of CMTKG and XG was uniformly dispersed in 20 ml of distilled water. To this, a desirable amount of MAA and NaOH solution was added and stirred for 30 minutes. Afterward, a fixed weight of APS and MBA was added and stirred for 3 hours by using a magnetic stirrer. After 3 hours, the mixture that was made, put into test tubes, and kept for 5 hours at 60°C in a hot water bath. The hydrogels were then released from test tubes. They were then cut into equal thickness pieces [29]. The hydrogels were then put in D.S water overnight to eliminate of any chemical that had not yet reacted. The hydrogel discs were then dried at 60°C until they reached a constant weight.

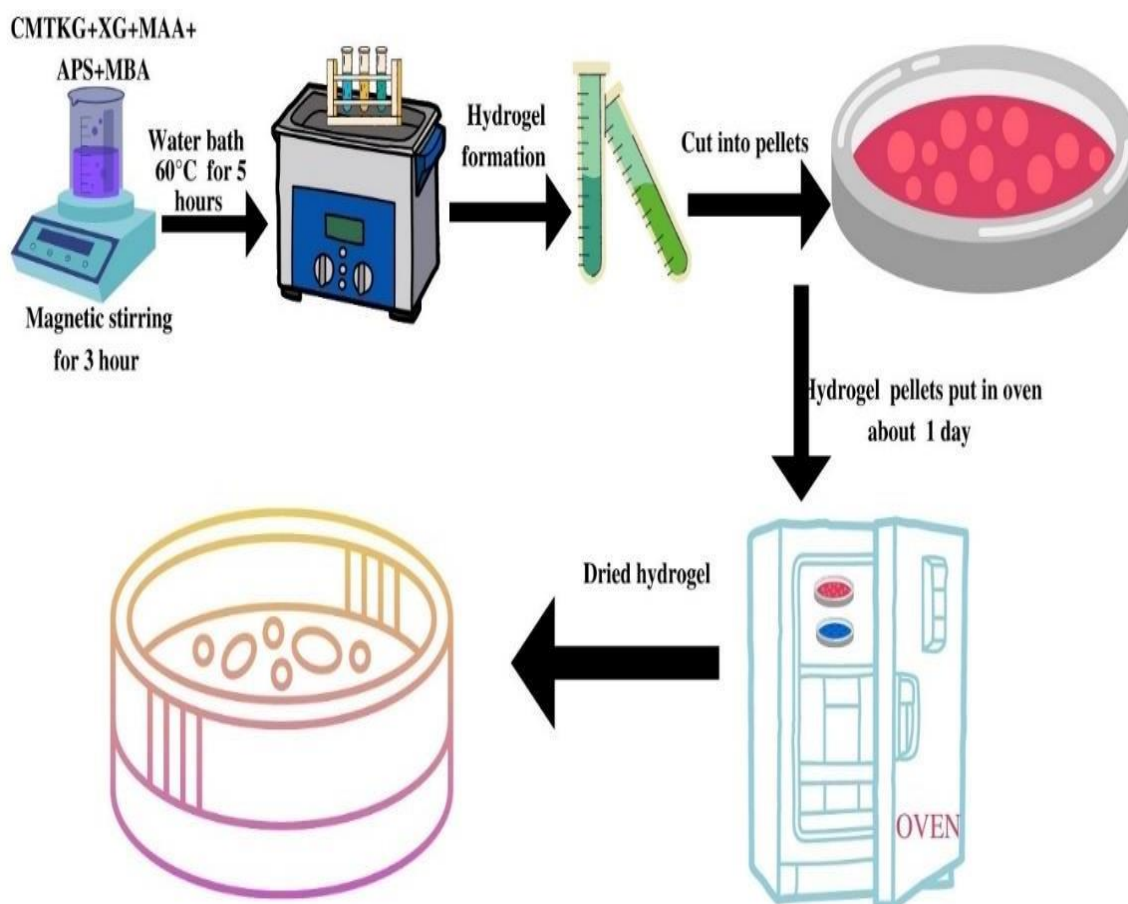


Figure 3.2: Illustration of synthesis of CMKTG/XG/NaMAA SAH

3.3 Synthesis of different SAH by varying composition of various reactant

SAH represent ation	CMK TG (g)	XG (g)	MAA (mL)	NaO H (g)	Distilled water (mL)	MBA (mg)	APS (mg)	Equilibriu m swelling index (g/g)	Gel content (%)
SAH-1	0.05	0.1	5	1	20	85	75	74.2	63
SAH-2	0.1	0.1	5	1	20	85	75	109.40	64
SAH-3	0.2	0.1	5	1	20	85	75	115.04	72.7
SAH-4	0.3	0.1	5	1	20	85	75	120.9	74.7
SAH-5	0.1	0.05	5	1	20	85	75	109.08	56.5
SAH-6	0.1	0.2	5	1	20	85	75	155.66	70.8
SAH-7	0.1	0.1	3	1	20	85	75	76.33	48.3
SAH-8	0.1	0.1	7	1	20	85	75	66.30	61.5
SAH-9	0.1	0.1	5	1	20	100	75	35.23	9.23
SAH-10	0.1	0.1	5	1	20	150	75	30.82	8.92
SAH-11	0.1	0.1	9	1	20	85	75	49.58	36.4
SAH-12	0.1	0.1	5	1	20	200	75	24.55	13.50
SAH-13	0.1	0.1	5	1	20	85	55	34.45	35
SAH-14	0.1	0.1	5	1	20	85	95	42	40.45
SAH-15	0.1	0.1	5	1	20	85	110	33	40.90

Table 3.3: Composition of various reactants used in synthesis of different SAH, their swelling index and gel content (%)

3.4 Synthesis of Zinc loaded SAH.

Based on the equilibrium swelling index listed in Table 2, the SAH-6 sample was selected for the zinc release studies. The SAH-6 hydrogel exhibited the highest swelling index (155.66 g/g) in distilled water. By using the traditional entrapment method, Zinc chloride was in situ loaded in the SAH-6. In order to synthesize ZSAH-6 hydrogel, 0.5g of Zn was added in a beaker containing 0.1g of CMKTG and 0.2 g of XG with 20 mL of D.S water. To this, a measured amount of MAA (5mL) and NaOH solution was added and stirred for 20 minutes. Then the specified amount of APS (85 mg) and MBA (75 mg) was incorporated, and the mixture

was stirred for 1 hour. The reaction mixture was put into a test tube and placed in 60°C hot water for 3 hours. Then, the test tubes were broken to release ZSAH6 SAH and dried in vacuum oven at 60°C for the complete removal of moisture.

3.5 Swelling Studies

Gravimetric analysis was used to investigate the swelling behaviour of the synthesized CMKTG/XG/NaMAA hydrogels. For this purpose, dried hydrogels were precisely weighed and put in 0.9 % NaCl, pH 4, 9, and 12 and distilled water as shown table 3. After that, swollen hydrogels were removed at regular intervals of time and measured after the surface water was removed with filter paper. Thus, the equilibrium swelling index (SI) were determined for all the synthesized hydrogels by using equation (1) [30].

$$\text{Swelling index (SI)} = \frac{W_2 - W_1}{W_1} \quad (1)$$

W_2 is the weight of the swelled SAH, and W_1 is the original weight of the Xerogels. The observations are recorded in triplicate. Equilibrium swelling index is calculated by using the maximum weight of swollen hydrogels.

3.6 Gel Content (%)

The gel content of the synthesized SAH is determined by using equation no. 2, where W_1 is the weight of dried hydrogels that are swollen in distilled water for 48 hours at room temperature. The hydrogels were then removed from D.S water and dried completely to remove moisture and reweighed W_2 .

$$\text{Gel Content (\%)} = \frac{W_2}{W_1} \times 100 \quad (2)$$

3.7 Maximum Water holding Capacity of soil.

A certain amount of completely air-dried soil was screened through a 3 mm filter and mixed with 0.05%, 0.1%, and 0.15% of crushed ZSAH-6 with a particle size of 100-120 mesh. A sample of controlled soil was set aside as a control for comparison. To find out how much water the ZSAH-6 soil sample could hold, a measured amount of the soil samples was placed in a pot with tiny holes in the base and tissue paper inside. The soil samples were left in the water bath so that the soil could soak up as much water as it could. After 5 hours, the ZSAH-6 samples were removed from the water bath and any extra water was drained. Thus, MWHC of soil was determined using the equation (3).

$$\text{MWHC of soil} = \text{Weight of [whole pot - (empty pot + wet tissue paper)]} \quad (3)$$

3.8 Release Studies of zinc in water and soil

Studies on release were conducted using two distinct experimental sets, one of which involved continuous releasing in water, while the other involved releasing in soil [31]. A beaker made of glass was filled with 20 mL of distilled water, and ZSAH-6 was put into it. In order to observe the release and ensure that the volume held steady throughout the experiment, aliquots of 20 mL were taken from the medium at various time intervals. The release was always as sink conditions. The use of an atomic absorption spectrometer provided for the estimation of the quantity of the micronutrient that was liberated by the hydrogel (AAS, PerkinElmer A4000). In order to determine the equilibrium release value, the measurements were continued until the equilibrium point was reached. The other release investigations were conducted in the soil as well. A dry ZSAH-6 was put in a permeable chiffon package to keep the soil from sticking to the sample. At a depth of 2 cm, a package was buried in a plastic beaker with 200 g of dry soil. Eight beakers were made in this manner. Then, 100 mL of distilled water was added to each beaker, and the temperature of the beakers was maintained at room temperature. Throughout the period, one package was taken from the beaker at a specific time interval (every 72 hours). The total amount of micronutrients was extracted from the hydrogel into the soil, determined with the use of AAS. Therefore, the quantity of the micronutrient that was released into the soil was determined by applying. This procedure was repeated until the equilibrium release value was determined to have been obtained.

CHAPTER- 4

CHARACTERIZATION TECHNIQUES

4.1 FTIR

FTIR spectroscopies, all infrared spectroscopies are based on the idea that some infrared (IR) radiation is absorbed when it goes through a sample. The amount of radiation that gets through the sample is recorded down. Because the shapes of molecules are different, their spectra are also different. This means that spectra can be used to identify and tell molecules apart. FTIR spectroscopy is used in food analysis, organic synthesis, polymer science, petrochemical engineering, and the pharmaceutical business.

Covalent bonds in a molecule will only receive light with certain wavelengths, which changes the bond's vibrational energy. The type of vibration caused by infrared light (stretching or bending) depends on the atoms that make up the bond. Different molecules have different transmission patterns because different bonds and functional groups absorb different frequencies. (Absorbance is the other side of transmittance.) On a graph, the spectrum is shown with the wavenumber (cm^{-1}) on the X-axis and the transmission on the Y-axis.

4.2 TGA

TGA is utilized to establish the relationship between weight change and temperature change. The obtained curve provides numerous pieces of information, such as a change in the composition of the sample and the kinetic parameters for a chemical reaction occurring in the sample.

There are numerous additional information's that TGA provides, including:

1. Reaction rate and activation energy.
2. Moisture loss, desorption, and evaporation.
3. Determine the lifetime of a sample (in relation to its thermal stability).
4. Oxidation of metals in air, thermal decomposition in an inert environment, and oxidative decomposition of organic substances in air/O₂.
5. The influence of a reactive or deleterious atmosphere on a material.

The sample loses mass due to the disruption of chemical bonds, the loss of volatiles with increasing temperature, or desorption. In contrast, sample weight gain is caused by oxidation, absorption, or absorption.

4.3 SEM

SEM uses a focused beam of high-energy electrons to make different signals on the surface of solid objects. The signals produced when electrons come into contact with a sample provide information regarding the sample's external form (texture), chemical composition, crystal structure, and the way the sample's constituent materials. The majority of application data are collected over a specific area of the sample's surface, and a 2-D image is created to illustrate how these properties vary over space. Usually, the SEM is used to produce high-resolution images of the contours of objects (SEI) and to reveal spatial variations in chemical compositions: 1) obtaining elemental maps or conducting spot chemical analyses .

4.4 AAS

AAS is Spectro analytical techniques for the quantitative analysis of chemical elements utilizing gaseous, liberated atoms. AAS depends on the light absorption of free metallic ions.

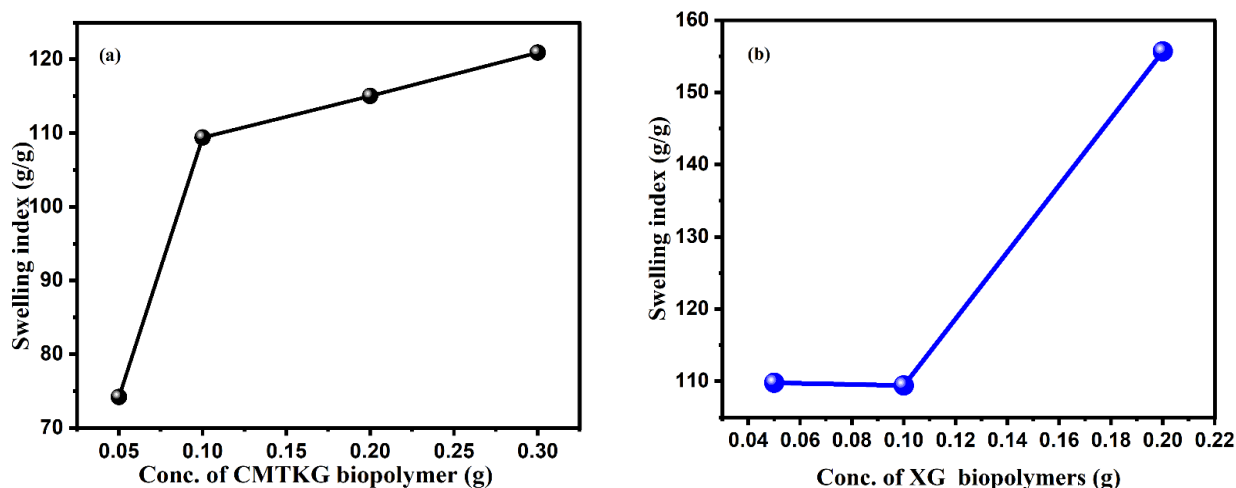
In analytical chemistry, the method is used to figure out how much of a certain element (called the "analyte") is in an analysis sample.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Effect of Biopolymers concentration

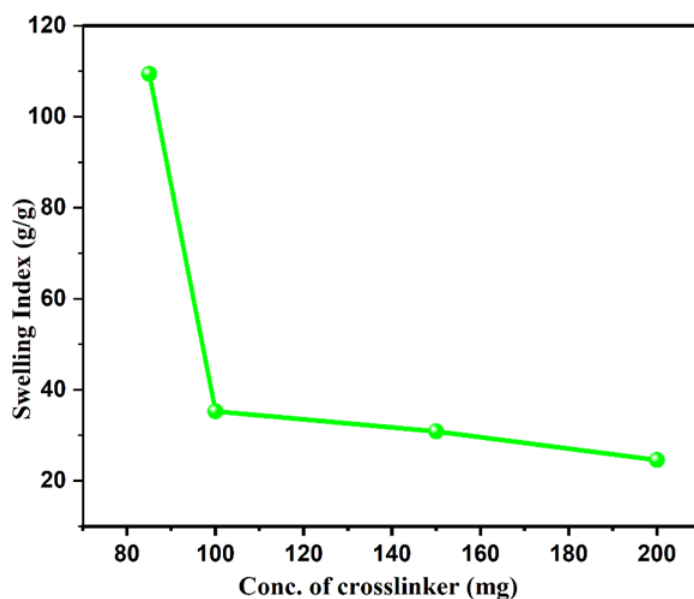
A swelling study of SAH was carried out by varying the concentration of both biopolymers viz. CMTKG and XG. The amount of carboxymethyl tamarind kernel gum varied from 0.05 g to 0.3 g by keeping the amount of XG (0.1 g) constant and the swelling index was calculated as evident in graph 5.1 (a). It was noticed that, as the amount of carboxymethyl tamarind kernel gum increased, the swelling index increased and attained the highest value 120.9 g/g at 0.3 g of CMTKG. This may be due to an increase in the number of COO⁻ groups which would increase the electrostatic repulsions between the like groups. Secondly, the number of counter ions Na⁺ ions also increased which would enhance the osmotic swelling pressure and chain relaxation in the gel network of hydrogel [32]. On the other side, the effect of the concentration of XG was studied on the swelling behavior of hydrogel by varying the concentration from 0.05 g to 0.2 g of XG by keeping the amount of CMTKG (0.1 g) constant as shown in Figure 5.1 (b) It was noticed that the swelling index of SAH increased from 109.08 g/g to 155.66 g/g. This may be attributed to the increase in the hydrophilicity and repulsive forces between anionic sites present on the surface of xanthan gum [33].



Graph 5.1: Effect of biopolymers concentration on swelling index (a) Conc. Of CMTKG (b) Conc. Of XG

5.2 Effect of Crosslinker concentration

The effect of cross-linker was studied on the swelling index of SAH. Generally, the cross-linking density of hydrogels is directly related to the concentration of the cross-linker. The concentration of MBA was varied from 85 mg to 200 mg to study the effect of cross-linker on the swelling index of the hydrogel as shown in graph 5.2 the highest swelling index was observed at 85 mg concentration of cross-linker. After that, a further increase in the concentration of MBA led to a decrease in the swelling index of the hydrogel. This may be attributed to increasing the crosslinking density of the polymeric network which resulted in reducing the pore spaces among the polymeric chains [34]. Therefore, the available volume required for water absorption got reduced. Thus, the swelling index of hydrogel reduced with increasing the concentration of cross-linker.

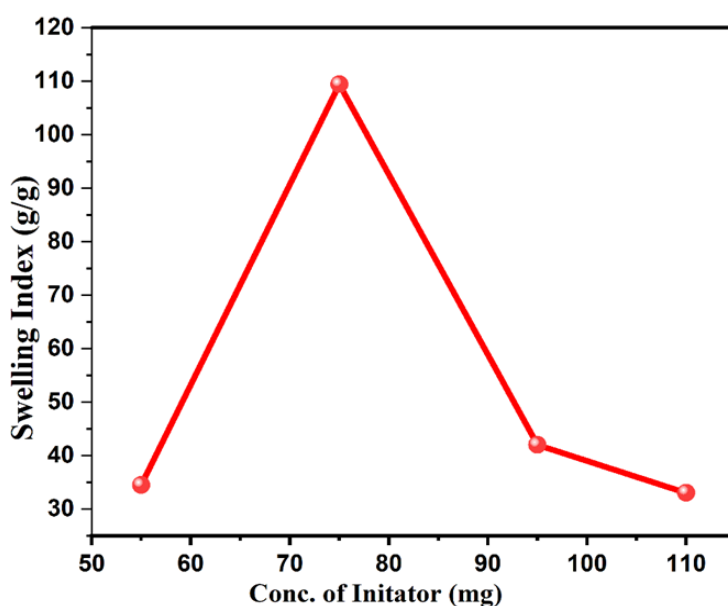


Graph 5.2: Effect of Crosslinker concentration on swelling index

5.3 Effect of Initiator concentration

The initiator APS is responsible for the synthesis of SAH because it creates active sites on the polymer chains. Keeping the concentration of crosslinker (75mg) and biopolymers (0.1 g) constant, the concentration of APS was varied and its effect on the swelling index of SAH was studied as shown in graph 5.3. The maximum swelling index (g/g) i.e., 109.40 g/g was observed at a concentration of 75 mg initiator. Initially, it was noticed that the swelling index of hydrogels

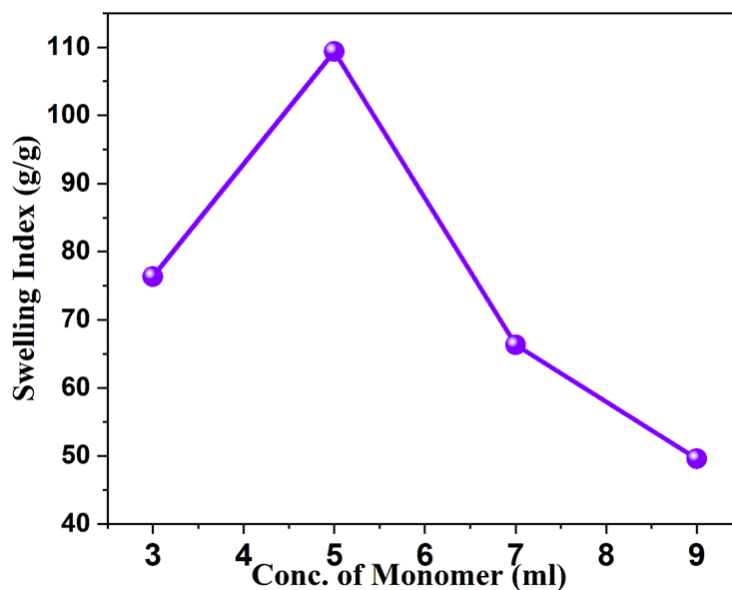
increased with the concentration of the initiator from 55 mg to 75 mg. This may be attributed to an increase in the number of free radicals due to the fast disintegration of the initiator which resulted in an increase in the rate of polymerization with monomers. However, further, increasing the concentration of the initiator beyond 75 mg led to a decrease the swelling index of the hydrogel. This may be due to the fast rate of consumption of monomers because of the generation of a large number of free radicals [35] this resulted in an increase in the formation of shorter chains, and oligomer content in the cross-linked network of the hydrogel. Therefore, the swelling index of SAH decreased above 75 mg of the initiator.



Graph 5.3: Effect of initiator concentration on swelling index

5.4 Effect of Monomer concentration

The effect of the concentration of monomers was studied on the swelling index of the hydrogel. The concentration of monomers varied between 3 to 9 ml as shown in graph 5.4. The maximum swelling index i.e., 109.40 g/g was observed at 5 ml monomer concentration. It was seen that below this concentration, a lower value of the swelling index was observed. It may be due to the slow diffusion rate, and a smaller number of active sites which resulted in a slow rate of free radical polymerization [36]. However, when the concentration of monomer increased above 5 ml, again swelling index starts to decrease. This could be caused by to increased rigidity, crosslinking and dense network of hydrogel with increased concentration of monomer. Therefore, the swelling index was decreased [37].



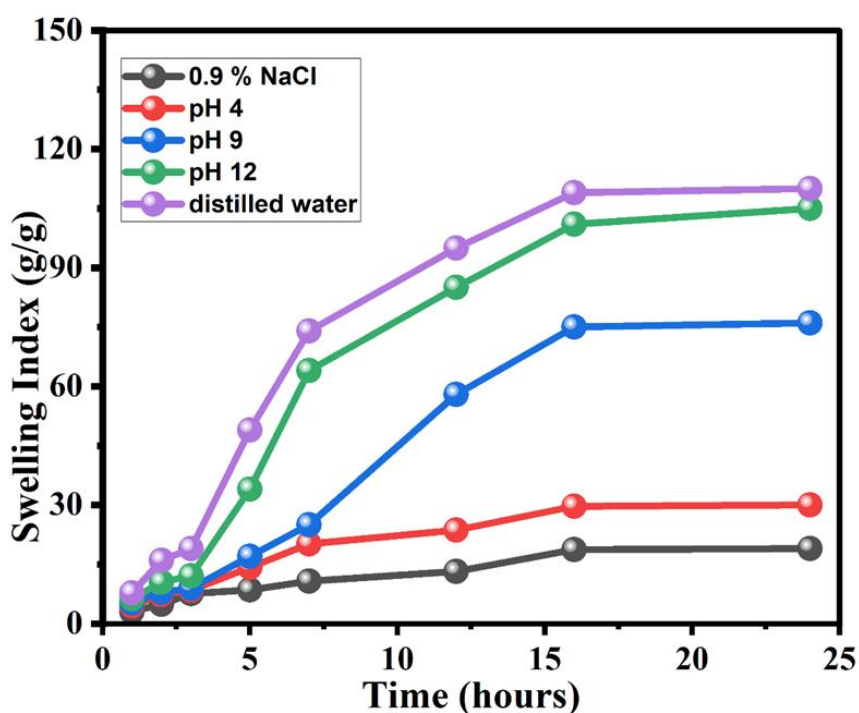
Graph 5.4: Effect of Monomer concentration on swelling index

5.5 Swelling study in different pH and saline solution

Swelling studies of ZSAH have been done in different mediums viz 0.9% NaCl, pH 4, 9, 12 and D.S water as shown in Table 5.5. Among the various medium, the highest swelling index (110 g/g) was observed in distilled water. It was observed that as the pH of the medium increased from 4 to 12, the water absorption capacity of hydrogels increased as shown in graph 5.5. In pH4, the lowest swelling was observed which may be due to incomplete ionization of -COOH groups due to their protonation. But in the case of an alkaline medium, a higher number of carboxylate ions are generated which increased the electrostatic repulsion between the similar groups. Thus, a higher swelling was observed in an alkaline medium [38]. However, in the situation of 0.9 % NaCl solution, the significant lowest swelling was observed. It may be due to the high ionic atmosphere around the inner and outer phase of osmotic pressure which is the factor that makes it hard for water molecules to get inside the plastic network.

Table 5.5: Swelling studies of ZSAH -6 in different PH and saline solution

Solution	Duration of swelling (hours)						
Different pH	1hr	2hr	3hr	5hr	7hr	12hr	16hr
Distilled water	6.27	10.5	12.1	34.7	64.2	91.5	108.1
pH 9	5.28	9.95	11.7	32.5	67.9	90.7	107.8
pH 4	7.82	16.1	19.1	49.7	73.8	87.3	106.0
pH 12	4.46	7.37	8.4	14.2	20.1	23.6	29.7
0.9% NaCl	3.09	4.90	7.63	8.54	10.7	13.2	18.7



Graph 5.5: Swelling studies of ZSAH in different pH medium

5.6 SEM

SEM of SAH (a, b) and ZSAH (c) at different magnifications, are shown in Figure 5.6. The study was done to investigate the effect of zinc loading on the morphology of hydrogel.

This analysis of SAH showed a smooth surface, distinct boundaries, and interstitial voids while the ZSAH showed a highly aggregated, rough, and fractured appearance which may be due to the intercalation of zinc into a polymeric network [39]. It was observed that ZSAH appeared more amorphous after loading the zinc into hydrogel matrix [40].

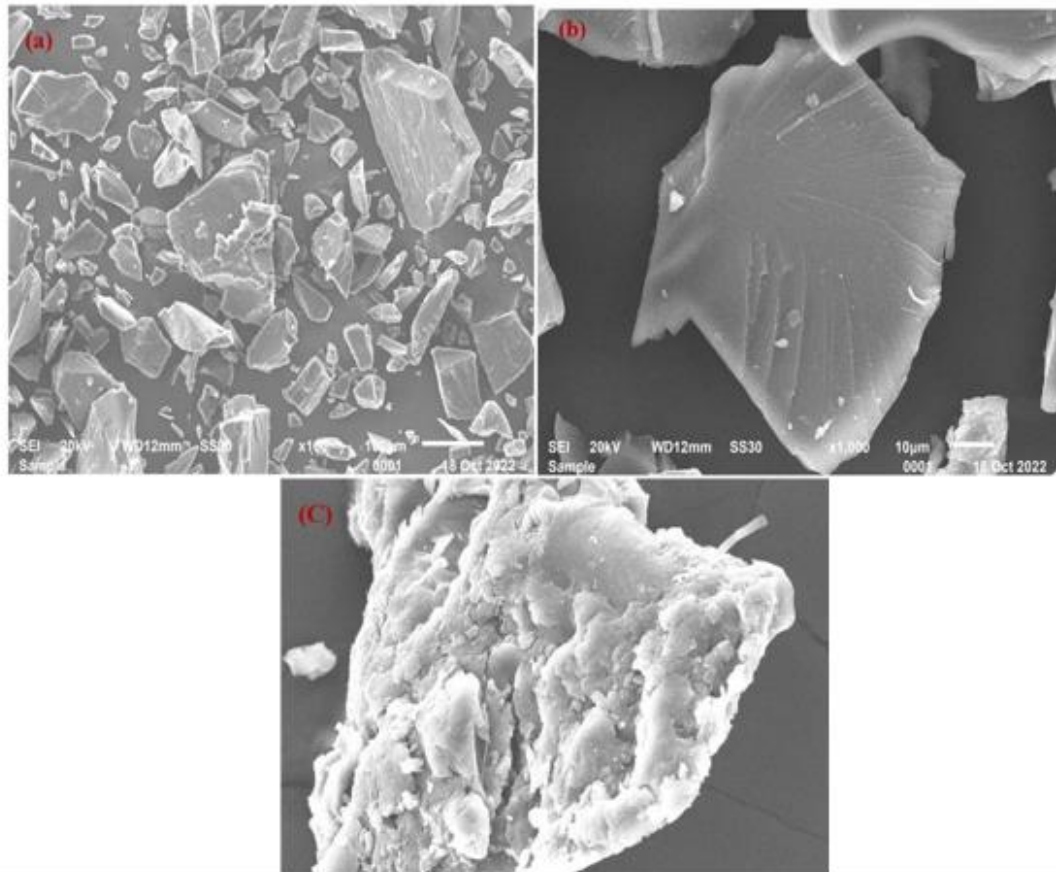
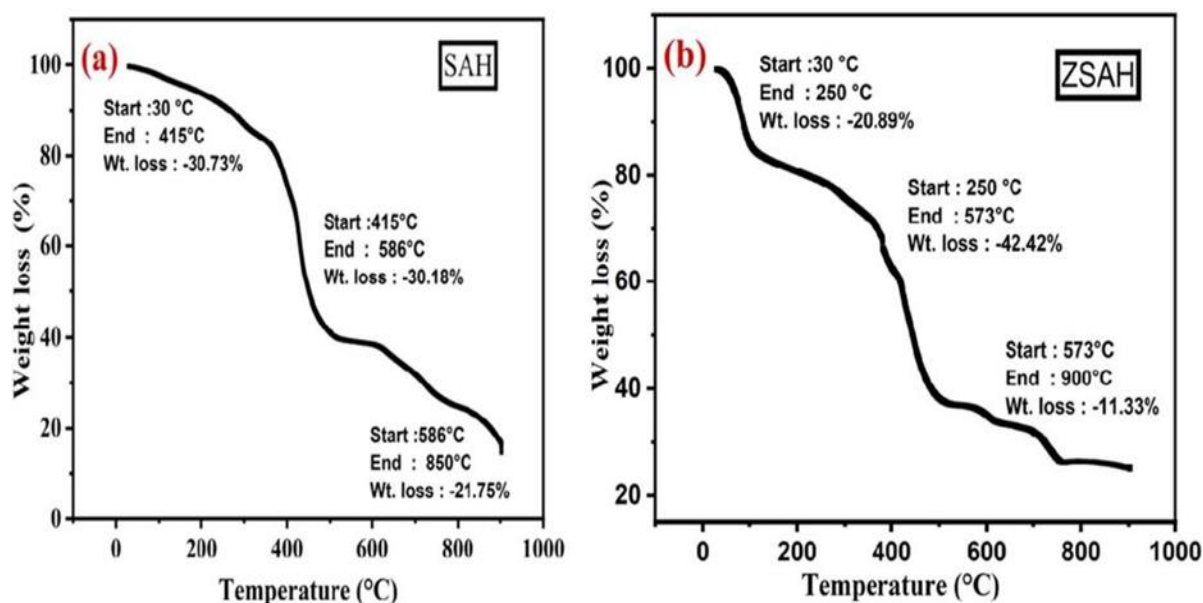


Figure 5.6: SEM images of SAH (a, b) and ZSAH (c)

5.7 Thermogravimetric Analysis

The thermogravimetric analysis of SAH and ZSAH was studied as shown in graph 5.7 (a, b) to determine the thermal stability at high temperatures. In the case of the thermogram of SAH, weight loss was found in 3 different regions as shown in graph 5.7 (a). It was noticed that the removal of moisture from SAH caused a weight loss of 30.73 % in the first region (30– 415°C) [19]. In the second region (415°C - 586°C), a weight reduced by 30.18% was observed due to the breakdown of a cross-linked network of the polymeric chain. In the end, the third and final weight reduced by (21.97%) took place in the range of 586–900°C. However, in the case of ZSAH, the weight reduced was found in 3 region as shown in 5.7 (b). A weight reduced by 30.73 % in the first region of 30–250°C was observed due to the removal of water from the

crosslinked network of ZSAH while in the second region between 250°C - 573°C, a weight reduced by 42.42% was due to the breakdown of the cross-linked bonds between the hydroxyl group of the polymer backbone and the cross-linker in the ZSAH network [41]. However, for the third region 573–900°C, there was a weight reduced by 11.33%. It was noticed that the residual mass of SAH and ZSAH was 17.37 and 25.37 % respectively [42]. Hence, the thermal stability of SAH was increased by addition of zinc as a micronutrient.

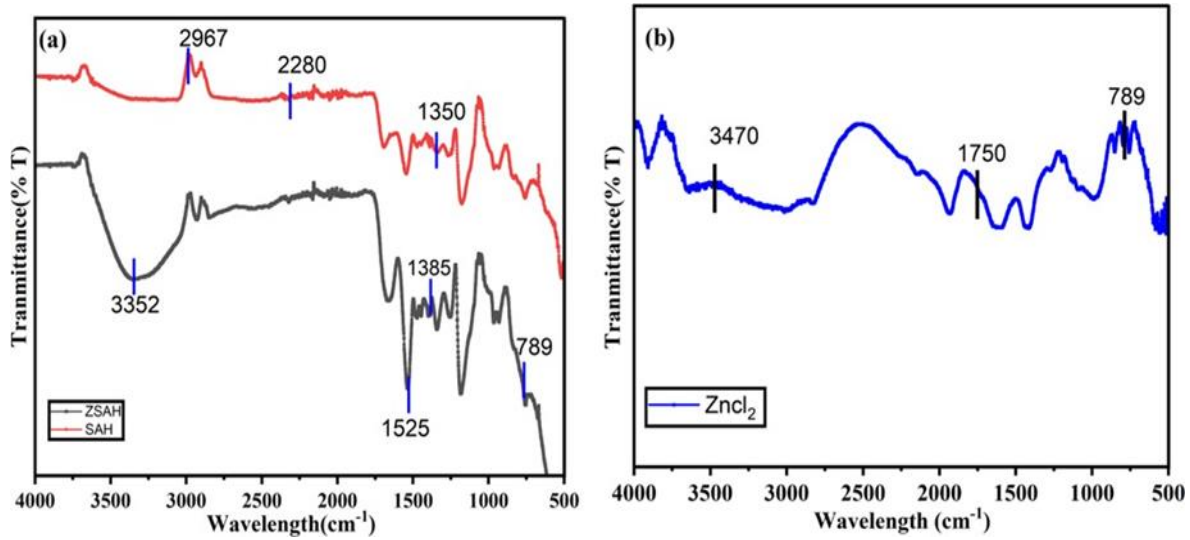


Graph 5.7: TGA thermogram of SAH (a) and (b) ZSAH

5.8 FTIR

The FTIR analysis of the, SAH, ZSAH and $ZnCl_2$ are shown in graph 5.8. The FTIR were recorded in the range 500-4000 cm^{-1} at room temperature and are presented in graph 5.8(a, b). From SAH spectra show a peak at 2900 cm^{-1} which belongs to the C-H stretching vibrations. Further 2280 cm^{-1} peak lies in this range (2280-2200 cm^{-1}) which belong to the $C\equiv N$ stretching vibrations [43]. Last peak 1350 cm^{-1} lies in the range (1390-1300 cm^{-1}) which belongs to the NO_2 stretching vibrations. In ZSAH spectra, a broad band (3352 cm^{-1}) is associated with -OH stretching vibration, whereas around 1525 cm^{-1} and 1385 cm^{-1} shows asymmetric and symmetric vibrations, respectively for $-COO^-$ moiety [44]. A sharp transmittance peak around 1525 cm^{-1} was observed for C=O stretching vibration. In the FTIR of $ZnCl_2$ graph 5.8 (b), the peak 3470 cm^{-1} corresponds to the -OH stretching vibration. At 1750 cm^{-1} peak corresponds to the C=O stretching vibration. In ZSAH and $ZnCl_2$ there is one common peak which is at 798 cm^{-1} [45]. Also, there is no change in the frequency shift. Therefore, we concluded that there is

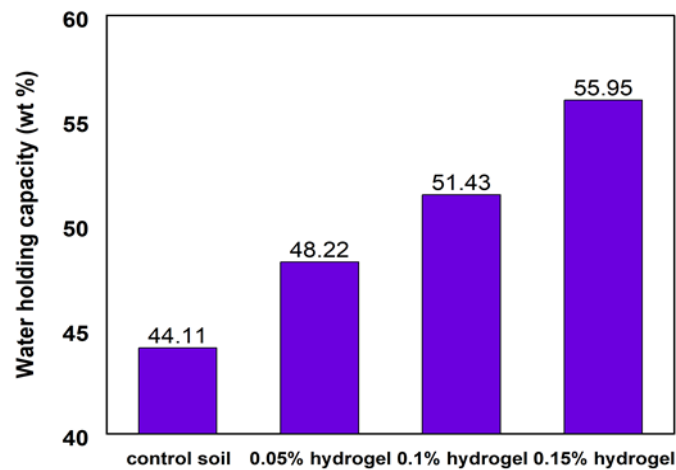
only physical interaction (weak van der Waals force present) of zinc with the polymeric network of hydrogel.



Graph 5.8: FTIR spectra of (a) SAH, ZSAH (b) ZnCl₂

5.9 Maximum Water Holding Capacity

Subsequently treating the soil with ZSAH, the investigation showed that its maximum water-holding capacity went remarkably higher. Graph 5.9 shows that ZSAH at doses of 0.05%, 0.1%, and 0.15% helped to increase the MWHC of the soil. The MWHC of the controlled soil was determined to be 44.11%, signifying that 100 g of dried soil can contain 44.11 g of water to reach saturation. The MWHC increased up to 48.22%, 51.43%, and 55.95% after being treated with powdered ZSAH at concentrations of 0.05%, 0.1%, and 0.15%. This experiment shows that when ZSAH is mixed with soil, the MWHC of the soil increases by a significant amount.



Graph 5.9: maximum water holding capacity.

5.10 Gel Content (%)

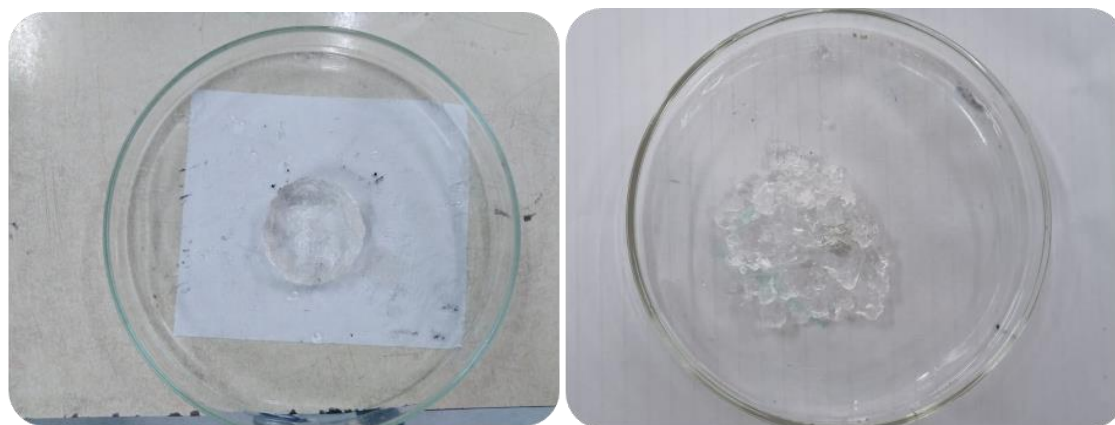


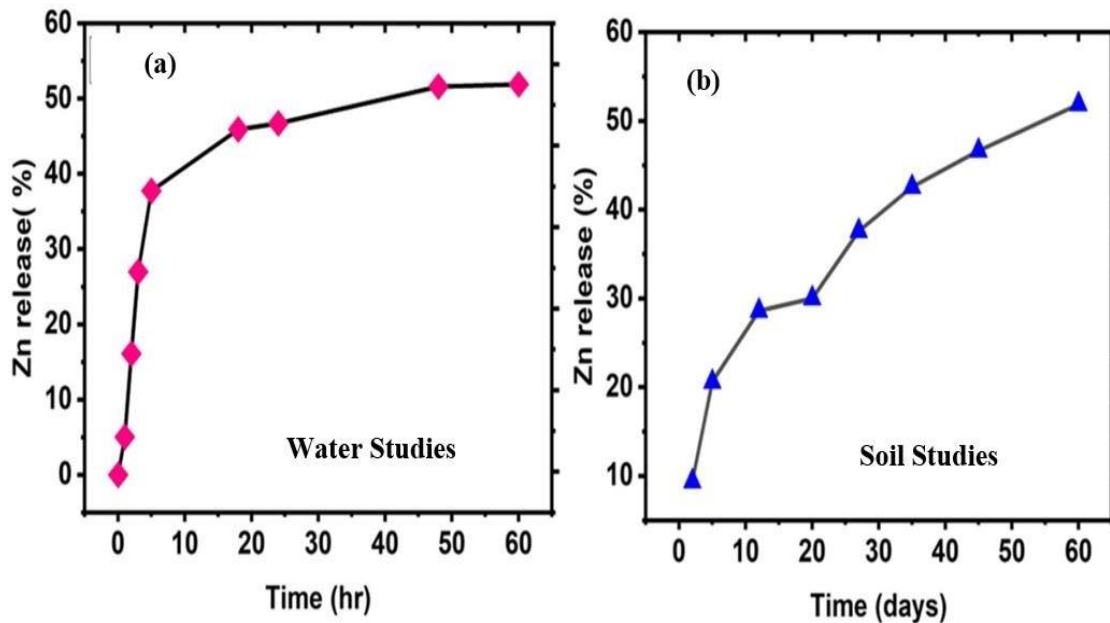
Figure 5.10: (a) Swollen Hydrogel (b) SAH-12 showed the lowest value of gel content

The value of gel content (%) is directly related to cross-linking yield and consumption of reactants used in the synthesis of hydrogels. Therefore, this was measured for all synthesized formulations using Eq. (2) as shown in Table 3.3. From the table, SAH-12 showed the lowest value of gel content (13.50 %) while SAH-6 showed the highest value of gel content (70.8 %).

5.11 Release studies in soil and water

The zinc release from ZSAH in water is shown in (a). A graph 5.11 (a) linear trend of zinc release was observed for 60 hours. Initially, during the first hour, the zinc release percentage was determined to be just 5.06% while in 60 hours, the release percentage (%) increased to 51.6%. The release percentage increased dramatically over time which can be attributed to the diffusion of zinc micronutrient due to the difference in concentration between the outer and inner structures of hydrogels [46]. In the case of soil, at regular interval release of zinc from ZSAH was studied over 60 days as shown in graph 5.11(b). ZSAH showed a 30% release of zinc in soil on the 20th day, which significantly increased to 51.87% on the 60th day. Also, in case of soil, ZSAH showed a gradual rise in zinc release with an increase in the number of days. Initially, zinc was released because of the soaking time of ZSAH [47]. Subsequently, zinc was released from the external layers of ZSAH as a result of the diffusion mechanism. Finally, zinc diffused through the internal layers by establishing equilibrium with the exterior

network of ZSAH [48]. Thus, it may be concluded that the ZSAH exhibited a slight increase in the pattern of zinc release in soil with time.



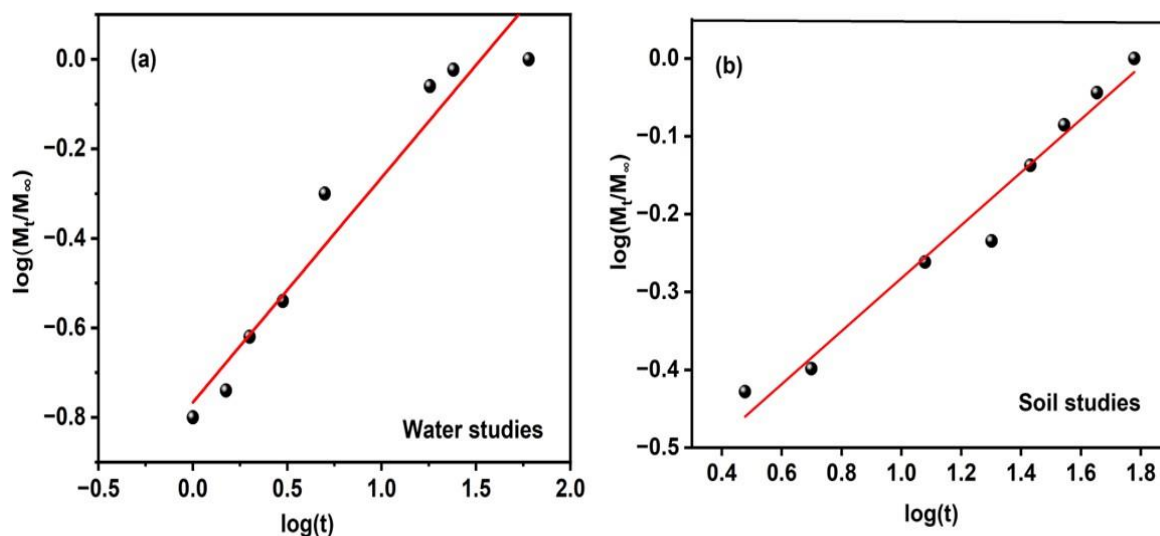
Graph 5.11: Release studies in water (a) and soil (b)

5.12 Kinetic release of Zinc in soil and water

In order to understand the release kinetics of zinc micronutrients from the ZSAH-6 matrix, release data were analysed in accordance with the various kinetic equations [49], [50]. The entire release data for the Korsmeyer-Peppas model had a coefficient of determination values (R^2) that were close to unity, ZSAH -6 followed the Korsmeyer-Peppas model Table 5.12. The Korsmeyer- Peppas model was recommended as the appropriate model that quantitatively described the release kinetic behaviour of zinc from ZSAH-6 based on the value R^2 in Table 5.12. Zinc released in the water had a diffusion exponent value (n) as shown in graph 5.12 of 0.23 and an R^2 of 0.94, both of which significantly indicated Fickian diffusion occurring as a result of the simple diffusion procedure through the hydrogel network. Zinc eluted out of ZSAH-6 in soil shown in Fig. 13 that its n value was 0.34 and its R^2 value was 0.98. This clearly shows that Fickian diffusion was the only method the zinc diffused out. This means that zinc is thought to move through the structure of the hydrogel network just by diffusion processes. ZSAH-6 is a strong candidate for use in agriculture due to its advantageous properties, which include its capacity to conserve water and, more significantly, transport zinc micronutrients.

Table 5.12 Mathematical model used for released kinetic from ZSAH -6

Model	Mechanism proposed in the model	Equation	Water		Soil		Ref.
			n	R ²	n	R ²	
Korsmeyer-peppas	(a) Fickian diffusion (n<0.45)	$M_t/M_\infty = Kt^n$	0.23	0.94	0.34	0.98	
	(b) non-Fickian diffusion (0.89≥n≥0.45)	K=kinetic constant					
	(c) superbase II (n>0.89)	n=diffusion constant					
Higuchi	Fickian diffusion	$M_t/M_\infty = K_H t^{1/2}$ K_H =kinetic constant	—	0.90	—	0.97	



Graph 5.12: Kinetic release studies of zinc micronutrient in water (a) and soil (b)

5.13 Effect of hydrogels sesame plants on plant growth

The pot test was carried out on sesame plants as shown in Figure 5.13 to study the effect of zinc-loaded hydrogels [51]. The length of sesame plants were measured through the number of germination of seeds and changes in their height. The average plant length and the number of seed-germinated sesame plants in soil containing ZSAH-6 and without hydrogels were

investigated. The number of germination of seeds count for the ZSAH-6 hydrogels was significantly greater than those for the without hydrogel as shown in Figure 5.13. Thus, we concluded that zinc loaded hydrogel has excellent potential for application in agriculture because it fulfils the deficiency of zinc micronutrient, and the growth of plant was more enrichment as compared to without hydrogel. The pot experiment was determined by following the changes of plant growth. The average of plant height and the number of seed germinated of sesame plants in soil containing ZSAH-6 and controlled soil was investigated table 5.13.

Sample	Average number of germinated seed (per pot) at 7 th day	Average plant height (cm) at 15 th day
Controlled soil	7±2	12.5 ±0.5
ZSAH loaded soil	15±2	20.8±0.5

Table 5.13: Effect of hydrogel on plant development.



Figure 5.13: Shows the average number of germination seed with (a) ZSAH hydrogel (b) controlled soil, (c) the average plant height with controlled soil and (d) ZSAH hydrogel.

CHAPTER 6

CONCLUSION

Novel degradable SAH was synthesized by using biopolymers CMTKG and XG and sodium methacrylate monomer. The effect of varied amounts of CMTKG and XG biopolymers, sodium methacrylate monomer, MBA cross-linker and APS as initiator was also studied on the swelling behaviour of hydrogels. The swelling assessment of all the synthesized hydrogels was analysed with distilled water. In this study, the highest swelling index was noticed up to 155.66 g/g for SAH -6 hydrogel composition. Moreover, zinc chloride was in situ incorporated in SAH-6 for the micro-nutrient release study. Along with this, Zinc release investigations were conducted in water and in soil with respect to time. The structural morphology of SAH, ZSAH hydrogels was characterized by SEM and FTIR techniques concluded that there is only physical interaction of zinc with the polymeric network of hydrogel. In soil, ZSAH exhibited a zinc discharge of 28.60% on the 12th day, which significantly increased to 51.9% on the 60th day. Both water and soil release kinetic experiments were analysed, with the Korsmeyer-Peppas model fitting best because its R^2 values were closer to unity. It was also found that the release of zinc from ZSAH in soil and water followed the Fickian diffusion mechanism and was largely independent of the morphology of the polymeric network. Zinc-loaded hydrogels improved the plant growth and germination of seed. So, ZSAH's equisetetic properties make it a strong competitor in the field of cultivation, both as a water-rationing operator and, most importantly, as a zinc micronutrient transporter.

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