NMHS-Himalayan Institutional Project Grant

NMHS-FINAL TECHNICAL REPORT (FTR)

Demand-Driven Action Research and Demonstrations

NMHS Grant Ref. No.:	GBPNI/NMHS-2018-19/SG 2

Date of Submission:	3	1	0	7	2	0	2	3
	d	**d**	**m**	**m**	**y**	**y**	**y**	**y**

PROJECT TITLE (IN CAPITAL)

"DEVELOPMENT OF BIODEGRADABLE SUPERABSORBENT HYDROGELS FOR AGRICULTURE APPLICATION TO CONTRIBUTE WATER CONSERVATION IN AGRICULTURAL FIELDS."

Project Duration: *from* (**10.01.2019**) *to* (**31.03.2023**).

***Submitted to*:**
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NMHS-Final Technical Report (FTR)

Demand-Driven Action Research Project

DSL: Date of Sanction Letter

1	2	1	2	**2**	**0**	**1**	**8**
d	d	m	m	y	y	y	y

DPC: Date of Project Completion

3	1	0	3	**2**	**0**	**2**	**3**
d	d	m	m	y	y	y	y

Part A: Project Summary Report

1. Project Description

i.	Project Grant Ref. No.:	GBPNI/NMHS-2018-19/SG 2					
ii.	Project Category:	Small Grant	X	Medium Grant		Large Grant	
iii.	Project Title:	"Development of biodegradable superabsorbent hydrogels for agriculture applications to contribute to water conservation in agricultural fields"					
iv.	Project Sites (IHR States/ UTs covered) (*Location Maps attached*):	Tripura					
v.	Scale of Project Operation:	Local	X	Regional		Pan-Himalayan	
vi.	Total Budget:	Rs. 31,91,000.00 (in lakh)					
vii.	Lead Agency:	Department of Chemical and Polymer Engineering., Tripura University (A Central University), Suryamaninagar, Tripura (W), India - 799022					
	Lead PI/ Proponent:	Dr. Sachin Bhaladhare Assistant Professor Chemical and Polymer Engineering Tripura University, Suryamaninagar, Tripura (W) – 799022, India					
	Co-PI/ Proponent:						
viii.	Implementing Partners:	Some more experiments are running in the lab to verify the repeatability of the results. After all the experiments, we will reach out to the stakeholders of the agriculture departments.					
	Key Persons (Contact Details, Ph. No., E-mail):						

2. Project Outcomes

2.1. Abstract/ Summary

***Background*:** Effective strategy and management of available water and fertilizers are imperative to improve agriculture production and food quality, including releasing them sustainably to the soil and plants. Polymeric hydrogels with three-dimensional (3D) networks can absorb ample water and soluble fertilizers without network dissolution. Subsequently, the absorbed water and fertilizers can be released to arid and semi-arid agricultural land to furnish enough moisture and nutrients for plant growth. In this study, carboxymethyl cellulose sodium salt (NaCMC) and hydroxyethyl cellulose (HEC) based hydrogels have been synthesized using citric acid (CA) as a crosslinker. The prepared hydrogels have shown a remarkable swelling ratio of ~1070% for hydrogel prepared using NaCMC/HEC: 2/1 and ~ 840% for NaCMC/HEC: 3/1, and a reduction in swelling ratio with increasing crosslinking density. Soil burial test for biodegradation study of prepared hydrogels revealed soil degradation of hydrogel, confirmed by FTIR analysis and visual appearance. Apart from regulating the irrigation frequency, superabsorbent hydrogels have demonstrated a positive effect on plant growth when mixed with the soil in appropriate amounts.

Objectives/ Aim:

1. Synthesis of superabsorbent hydrogel based on NaCMC-HEC for agriculture applications.
2. Complete characterization/analysis of hydrogel, such as Fourier transform infrared spectroscopy (FTIR) for chemical analysis, water swelling study, scanning electron microscope for hydrogel morphology, mechanical properties, etc.
3. Examining the suitability of hydrogels' composition as a water reservoir for agriculture applications.
4. Study the water retention capacity of the soil modified with hydrogels.
5. Study the effect of hydrogel-modified soil on plant growth.

Methodology/Approach:

1. NaCMC/HEC (2:1 and 3:1) based superabsorbent hydrogels were synthesized by polymerization and an absorbing 3D network of hydrogel was obtained using citric acid (CA) as a crosslinker (10%, 12 %, 14%, and 16%).
2. Synthesized hydrogels were completely analyzed using different characterization techniques, i.e., FTIR, SEM, DLS, swelling study, mechanical properties and soil burial (biodegradation), etc.
3. The water-retaining capacity of hydrogel-modified soil has been studied (on a weight basis) and compared with unmodified soil).
4. The effect of hydrogel-modified soil on plant growth (cucumber) using different performance indicators of plants, such as a change in weight, moisture content of plants, root-to-shoot ratio (R/S) of the plants, % germination, crop growth rate (CGR), chlorophyll production, and net assimilation rate (NAR), etc.

***Results/ Outcomes*:**

1. The obtained results of synthesized hydrogels were found to be very encouraging for agriculture applications. The prepared hydrogels have shown a remarkable swelling ratio of ~1070% for hydrogel prepared using NaCMC/HEC: 2/1 and ~ 840% for NaCMC/HEC: 3/1.
2. Soil burial test for biodegradation study of prepared hydrogels revealed soil degradation of hydrogel, confirmed by FTIR analysis and visual appearance.
3. Superabsorbent hydrogels have demonstrated a positive effect on plant growth when mixed with the soil in appropriate amounts.

Conclusions:

In this study, biodegradable cellulose hydrogels based on carboxymethyl cellulose (NaCMC) and hydroxyethyl cellulose (HEC) have been synthesized successfully using CA as a crosslinker. Hydrogels have shown good water absorption and retaining capacity with swell ability depending on crosslinking density of hydrogels and the pH of the swelling medium. The study revealed that incorporating CNFs into a hydrogel matrix significantly improved the mechanical properties of hydrogel nanocomposites, which is vital in maintaining the hydrogel's structural integrity in agriculture applications. The soil burial study confirmed the morphological and chemical changes in a hydrogel as a result of biodegradation by microorganisms in the soil. Moreover, superabsorbent hydrogels have demonstrated a positive effect on plant growth when mixed with the soil in appropriate amounts.

Recommendations/ Way Forward with Exit Strategy:

Superabsorbent biodegradable hydrogels as water reservoir for agriculture applications and plant growth could become a promising technology for proper management of available and irrigation water for agriculture. For proper implementation of this technology, It is important for hydrogels to absorb ample amount of water or water soluble fertilizers into their 3D network and release them in a sustainable and controlled manner, without loosing the structural integrity and no adverse effect on the environment.

2.2. Objective-wise Major Achievements

S#	Objectives	Major achievements (***in bullets points***)
1.	Synthesis of cellulose-based hydrogels using cellulose derivatives carboxymethyl cellulose (NaCMC) and hydroxyethyl cellulose (HEC) with crosslinker citric acid (CA). In addition, optimization of the synthesis process to obtain suitable composition of hydrogels for agriculture applications. **(Objective - 1 of sanction letter)**	1. Cellulose-based hydrogels were prepared using cellulose derivatives NaCMC and HEC of ratios 2:1 and 3:1. A 3D network (hydrogel network) of polymers was obtained using citric acid as a crosslinker. 2. NaCMC and HEC are hydrophilic polymers containing plenty of hydroxyl groups, leading to the high-water absorption capacity of hydrogels. 3. Hydrogels demonstrated porous structures in the FESEM microscope. 4. The prepared hydrogels have shown a remarkable swelling ratio of ~1070% for hydrogel prepared using NaCMC/HEC: 2/1 and ~ 840% for NaCMC/HEC: 3/1. 5. Moreover, the observation suggests a reduction in swelling ratio with increasing crosslinking density. **(Details in annexure 1)**

2.	Thorough characterization of prepared hydrogels **(part of objective – 1 of the sanction letter)**	Different characterization techniques have been used for the complete characterization of hydrogels. For instance, Fourier transform infrared spectroscopy (FTIR) for chemical functional groups analysis, scanning electron microscopy (SEM) for surface morphology, tensile test for mechanical properties, soil burial test for biodegradability of hydrogels, dynamic light scattering (DLS) for particle size analysis, and X-ray diffraction for crystallographic structure, etc. **(Details in annexure 1)**
3.	Study the ability of hydrogel to alter the water retention properties of soil. **(Objective – 2 of the sanction letter)**	1. It is crucial to evaluate the water retention behavior of NaCMC/HEC hydrogels for their agriculture applications. Hydrogels require to retain more water than the soil for such applications, where a hydrogel acts as a water reservoir that absorbs a significant amount of water and releases it to the ground and plants in a controlled and sustained manner. Water loss (evaporation) through hydrogels and soil was assessed periodically in open environmental conditions to evaluate water retention behavior. 2. Studies showed that hydrogel-modified soil needed thirteen (13) days to lose around 80% of water. In contrast, soil required nine (9) days for evaporation of 80% of water, suggesting better water holding capacity of the hydrogel-modified soil than the unmodified soil. **(Details in annexure 1)**

4.	Synthesis of Cellulose Nano Crystals as reinforcing agents to the hydrogel. **(Objective – 3 of the sanction letter)**	1. Crystalline cellulose nanocrystals (CNC) were extracted from cotton fibers through the acid (H_2SO_4) hydrolysis method. Extracted CNCs were used as reinforcing material to enhance the mechanical properties of the hydrogel. 2. The acid hydrolysis of bleached cotton fibers splits the amorphous regions of the fibers from the crystalline areas. It produced needle-like crystalline CNCs with an average length of ~ 600 nm and a diameter of 20-30 nm (L/D = 30). 3. Dynamic light scattering analysis showed the bimodal distribution of CNCs with a hydrodynamic diameter (*Dh)* of 599 nm and a polydispersity index (PDI) of 27%. The large number of CNCs is in the range of 240 – 1823 nm. 4. X-ray diffraction peaks indicate increased crystallinity of CNCs. **(Details in annexure 1)**
4.	Study the properties of hydrogel with and without reinforcing agents. **(Objective – 4 of the sanction letter)**	1. The mechanical analysis revealed improved tensile strength of hydrogel composites than the hydrogel without reinforcement (without CNCs). Increasing the CNC concentration from 0.2% to 0.7% in the hydrogel improved the mechanical strength of the hydrogel composite, indicating the reinforcing effect of crystalline CNCs. 2. Moreover, the elongation property has also improved for hydrogel composites compared to hydrogel, pointing to the fragile and brittle nature of the hydrogel. **(Details in annexure 1)**
5.	Study the effect of hydrogel-modified soil on plant growth and compared it with unmodified soil. (**(Objective – 4 of the sanction letter)**	1. A study of plant growth was carried out by measuring the performance indicators, such as fresh weight and dry weight of the plant at certain intervals, total moisture content, root and shoot ratio, crop growth rate, total chlorophyll produced by plants (chlorophyll A and chlorophyll B). 2. Data indicate that hydrogel-modified soil has a positive impact on plant growth. Hydrogel-modified soil can retent and deliver water for a longer time to the plants. **(Details in annexure 1)**

Note: Further details may be summarized in DPR Part-B, Section-5. Supporting materials may be enclosed as annexure/ appendix separately to the FTR.

2.3. Outputs in terms of Quantifiable Deliverables*

S#	Quantifiable Deliverables*	Monitoring Indicators*	Quantified Output/ Outcome achieved	Deviations, if any, & Remarks thereof:
1.	Synthesis of cellulose-based hydrogels	Absorption and swelling of the hydrogel as a water reservoir	1. Hydrogels have shown remarkable swelling of 800 – 1000 % of their dry weight.	
2.	Use of cellulose nanoparticles (CNCs) as reinforcing agents to improve the mechanical properties of hydrogel	The particle size of CNCs and mechanical strength of the hydrogel	1. The average particle size of 600 nm has been achieved for CNCs by the acid hydrolysis method. 2. Improved mechanical strength for CNCs reinforced hydrogels, tensile strength 16 MPa for composite hydrogel compared to 5 MPa for hydrogel.	
3.	Water retention capacity of the hydrogel	Comparison of water retention/evaporation capacity of hydrogel-modified soil vs. unmodified soil (control)	1. Results demonstrated that the evaporation of water in unmodified soil is larger (loss of 80% water in 9 days) as compared to hydrogel-modified soil (loss of 60% of water in 9 days). It took 13 days for 80% loss of water in modified soil. 2. ~ 30% more water has been retained by hydrogel-modified soil.	
4.	Impact of hydrogel on plant growth	Plant growth parameters such as fresh and dry weight of the plants, total moisture content of the plant, root-to-shoot ratio, crop growth rate, total chlorophyll production, and net assimilation rate.	1. Experimental results have shown improved parameters for hydrogel-modified soil. A more detailed analysis (with graphs) has been explained in Annexure 1 (section 5).	

*As stated in the Sanction Letter issued by the NMHS-PMU.

2.4. Strategic Steps with respect to Outcomes (in bullets)

S#	Particulars	Number/ Brief Details	Remarks/ Attachment
1.	New Methodology/ Technology developed, *if any*:	1. Novel hydrogel technology has been developed for the efficient management of water for agricultural applications. Developed hydrogels will absorb sufficient water/water soluble fertilizers into their structure and release them in a sustainable and controlled manner.	Details in Annexure 1
2.	New Ground Models/ Process/ Strategy developed, *if any*:	1. The process has been developed to synthesize robust, insoluble, and porous cellulose-based hydrogels capable of absorbing abundant water into their network. 2. The strategies have been carved out to study water retention capacity of hydrogels and their impact on plant growth and water conservation.	Details in Annexure 1
3.	New Species identified, *if any*:	NA	NA
4.	New Database established, *if any:*	-	-
5.	New Patent, *if any*:		
	I. Filed (Indian/ International)	-	-
	II. Technology Transfer, *if any*:	-	-
6.	Others, *if any*		

Note: Further details may be summarized in DPR Part-B, Section-5. Supporting materials may be enclosed as an annexure/ appendix separately to the FTR.

3. New Data Generated over the Baseline Data

S#	New Data Details	Status of Existing Baseline	Addition and Utilisation of New Data
1.	1. New data have been generated for the water retention capacity of developed hydrogels. 2. Data have been generated on the Impact of hydrogel-modified soil on plant growth in terms of total moisture content, crop growth rate (CGR), net assimilation rate (NAR), etc.	No comprehensive earlier research data is available as such to compare with. In this current research, we are trying to develop a comprehensive data set to help and promote researchers and industries to focus on this sustainable development project and product.	This developed new data will help in the sustainable development of agricultural plants' growth to meet ever-increasing demands for quality food.

Note: Further details may be summarized in DPR Part-B. Database files in the requisite formats (Excel) may be enclosed as annexure/ appendix separately to the soft copy of FTR.

4. Demonstrative Skill Development and Capacity Building/ Manpower Trained

S#	Type of Activities	Details with number	Activity Intended for	Participants/Trained			
				SC	**ST**	**Women**	**Total**
1.	Workshops	Some experiments are still under running to verify the repeatability of the obtained results, the workshop will be conducted thereafter.	The workshop will be intended: 1. To create awareness about climate change and its impact on agricultural production. 2. To create awareness of the impact of hydrogel-modified soil in conserving irrigated water and help plant growth in arid and semi-arid areas.				

2.	On-Field Trainings	Will be performed after collecting comprehensive research data including a repeatability study.	This exercise will be performed to do an on-field study of hydrogel-modified soil in a selected area of land.				
3.	Skill Development	1 Junior Research Fellow (JRF) has been skilled in this field from the synthesis of hydrogel, and their characterization to plant growth study.	JRF has been hired and skilled in generating comprehensive data under the guidance of PI				
4.	Academic Supports	-	-	-	-	-	-
	Others (if any)						

Note: Further details may be summarized in DPR Part-B. Supporting materials may be enclosed as annexure/ appendix separately to the FTR.

5. Linkages with Regional & National Priorities (SDGs, INDC, etc.)/ Collaborations

S#	Linkages /collaborations	Detail of activities (No. of Events Held)*	No. of Beneficiaries
1.	Sustainable Development Goals (SDGs)/ Climate Change/INDC targets addressed	A biodegradability study of developed hydrogels was conducted and the results show that the hydrogels are biodegradable and will not have an adverse impact on soil and the environment.	Public enlarge
2.	Any other:	-	-

Note: Further details may be summarized in DPR Part-B, Section-6. Supporting materials may be enclosed as an annexure/ appendix separately to the FTR.

6. Project Stakeholders/ Beneficiaries and Impacts

S#	Stakeholders	Support Activities	Impacts in terms of income generated/green skills built
1.	Line Agencies/ Gram Panchayats:	-	-
2.	Govt Departments (Agriculture/ Forest/ Water):	The government department, particularly the agriculture department is one of the major	-

		stakeholders to implement this project for sustainable development.	
3.	Villagers/ Farmers:	Farmers need to be trained properly and make aware of the impact of hydrogel-modified soil on water conservation and plant growth.	-
4.	SC Community:	-	-
5.	ST Community:	-	-
6.	Women Group:	-	-
	Others, *if any*:	-	-

Note: Further details may be summarized in DPR Part-B, Section-6. Supporting materials may be enclosed as annexure/ appendix separately to the FTR.

7. Financial Summary (Cumulative)

Please attach the consolidated and audited Utilization Certificate (UC) and Year-wise Statement of Expenditure (SE) separately, *ref*. **Annexure I.**

8. Major Equipment/ Peripherals Procured under the Project** (*if any*)

S#	Name of Equipment	Quantity	Cost (INR)	The utilization of the Equipment after the project
1.	Fourier Transform Infrared Spectroscopy (FTIR)	1	9,90,000.00	It is a spectroscopy technique that has been used for chemical analysis (functional groups). This instrument is always in demand and used for chemical analysis in multidisciplinary research.

Details should be provided in details **(*ref.*** **Annexure III &IV).**

9. Quantification of Overall Project Progress

S. No.	Parameters	Total (Numeric)	Remarks/ Attachments/ Soft copies of documents
1.	IHR States/ UTs covered:		

2.	Project Sites/ Field Stations Developed:		
3.	Scientific Manpower Developed (PhD/M.Sc./JRF/SRF/ RA):	*1 (JRF)*	
4.	Livelihood Options promoted		
5.	Technical/ Training Manuals prepared		
6.	Processing Units established, if any	*A hydrogel synthesis process unit and plant growth study have been established.*	
7.	No. of Species Collected, if any		
8.	No. of New Species identified, if any		
9.	New Database generated (Types):		
	Others (if any)		

Note: Further details may be summarized in DPR Part-B. Supporting materials may be enclosed as annexure/ appendix separately to the FTR.

11. Knowledge Products and Publications:

S#	Publication/ Knowledge Products	*Number*		*Total Impact Factor*	*Remarks/* Enclosures
		National	International		
1.	Journal – Research Articles/ Special Issue:		**3** (Starch Journal, Journal of Materials Chemistry B, ACS Applied Polymer Materials)	Starch: 2.3 JMCB: 7 ACS APM: 5	Details in Annexure 2
2.	Book – Chapter(s)/ Monograph/ Contributed:				
3.	Technical Reports:	3 yearly technical reports			
4.	Training Manual (Skill Development/ Capacity Building):				
5.	Papers presented in Conferences/Seminars:		2		
6.	Policy Drafts/Papers:				
7.	Others, if any:				

Note: Please append the list of KPs/ publications (with impact factor, DOI, and further details) with due Acknowledgement to NMHS. Supporting materials may be enclosed as annexure/ appendix separately to the FTR.

12. Recommendation on Utility of Project Findings, Replicability and Exit Strategy

Particulars	Recommendations
Utility of the Project Findings:	This innovative technology holds a potential to be commercialized and utilized in arid and semi-arid agriculture fields. Hydrogels have the capability of absorbing plenty of irrigation water and release it in a controlled and sustainable manner. Finding suggests that hydrogels can conserve up to 30% available water, depending on the environmental conditions.
Replicability of Project/ Way Forward:	Before applying at large scale, comprehensive data needs to be generated by applying hydrogels for different condition, variety of plants and soil.
Exit Strategy:	Technology requires creating an awareness among stakeholders, farmers, etc. Fields trials needs to be conducted for validity of the technology and its benefits.

Dr. Sachin Bhaladhare
Chemical and Polymer Engg.,
Tripura University
(**PROJECT PROPONENT/ COORDINATOR**)

(Signed and Stamped)

(**HEAD OF THE INSTITUTION**)

(Signed and Stamped)

Place: ………………..
Date: …../……/……

PART B: DETAILED PROJECT REPORT

The Detailed report should include an Executive Summary and it should have separate chapters on (i) **Introduction**, (ii) **Methodologies/Strategy/Approach**, (iii) **Key Findings and Results**, (iv) **Overall Achievements**, (v) **Project's Impacts in IHR** (vi) **Exit Strategy** and Sustainability, (vii) **References**, and (viii) **Acknowledgements** (acknowledging the financial grant from the NMHS, MoEF&CC, GoI).

Other necessary details/ Supporting Documents/ Dissemination Materials (*New Products/ Manuals/ Standard Operating Procedures (SOPs)/ Technology developed/Transferred, etc, if any*) may be attached as Appendix(ces).

1 EXECUTIVE SUMMARY

2 INTRODUCTION

2.1 Background

Hydrogel is a 3D crosslinked hydrophilic polymer network capable of absorbing, retaining, and releasing significant water in a controlled fashion. The polymer chains in a hydrogel network are usually crosslinked by physical, chemical, or dual crosslinking. Physical crosslinking involves the chains crosslinking by weak secondary forces, i.e., hydrogen bonding, electrostatic interactions, hydrophobic interactions, molecular entanglements, etc., and are called physical hydrogels. In chemical crosslinking, polymer chains are crosslinked by strong covalent bonds using a chemical crosslinker, such as divinyl sulfone, aldehydes, and their derivatives, epichlorohydrin, etc. Hydrogels, mainly designed and developed from natural polymers, have shown potential applications in biomedical, pharmaceutical, agriculture, water treatment, and food industries due to their biodegradability, biocompatibility, non-toxicity, and sustainability. Among natural polymers, cellulose, and its derivatives have been widely explored polymers for hydrogel synthesis due to its abundance and renewability. In addition, cellulose-based bioproducts satisfy the demands of the ecosystem for green development.

Despite attractive properties, hydrogels are soft and fragile materials demonstrating weak mechanical properties. For many applications, the mechanical properties of hydrogels are vital to preserving their shape, stiffness, and robustness during use. The mechanical properties of hydrogels are generally enhanced by incorporating strong fibers or nanoparticles into the matrix. Strong natural fibers, such as cotton, flax, hemp, and jute, have already been explored as reinforcing agents for polymer and hydrogel composites. Lately, nanocrystals, particularly cellulose nanocrystals (CNCs), have attracted significant attention as reinforcing fillers in hydrogel composites due to their high strength, crystallinity, surface area, and aspect ratio. CNCs have been used as reinforcing agents for gelatin hydrogel for 3D printing applications and demonstrated increased properties with 10% CNF content in the matrix. The CNCs-reinforced hydrogels have been significantly researched in biomedical applications, such as tissue scaffolding and regeneration, and wound healing, where hydrogels' shape and robustness are critical.

In the current study, we prepared CNCs-reinforced cellulose hydrogel nanocomposites based on hydrophilic cellulose derivatives, carboxymethyl cellulose sodium salt (NaCMC), and hydroxyethyl cellulose (HEC), for agriculture applications. The prepared hydrogel nanocomposite will act as a water reservoir by absorbing and holding the water in the network and releasing it to the plants in a controlled manner resulting in reduced irrigation efficiency and improved plant growth. The natural crosslinker citric acid (CA), found in citrus fruits, was used to crosslink polymer chains to form a hydrogel network. The NaCMC alone constructs a weak hydrogel due formation of intramolecular bonds instead of intermolecular interaction between polymer chains. Incorporating HEC promotes intermolecular interactions between chains to form a hydrogel network, resulting in a comparatively robust hydrogel. The CNCs were extracted from cotton fibers using acid (H_2SO_4) hydrolysis. The obtained CNCs from cotton fibers with small particle size distribution have been used as reinforcing agents in hydrogel matrix to improve mechanical strength. To our knowledge, no study has reported on CNFs reinformed hydrogel composite for agriculture applications.

2.2 Overview of the major issues addressed

Climate change and increasing demands for food and water have significantly affected the volume and quality of food globally. Agricultural food production largely depends on the quality of the soil and the supply of adequate water. The mismanagement of soil by human activities, such as soil pollution, and deforestation, results in soil erosion and reduced fertile land, limiting food production. Most importantly, insufficient rainfall and inefficient use of available water significantly affect food production and quality. The proper management of accessible water using promising technologies is imperative to overcome the existing limitations and to improve quality and volume for global demands. The technologies and materials need to be developed that can efficaciously absorb water and water-soluble fertilizers and release them expeditiously in a sustained and controlled manner. The hydrogels as superabsorbents are considered potential materials due to their appealing properties, such as the high absorption capacity of water and water-soluble substances, i.e., fertilizers, into their network. Subsequently, the absorbed water and fertilizers can be released to arid and semi-arid agricultural land to furnish enough moisture and nutrients for plant growth. This practical water management exercise can conserve water to improve the water-retaining capacity of agricultural soil.

2.3 Baseline Data and Project Scope

- **Water conservation in the Agriculture field**

The addition of hydrogel into the soil (hydrogel-modified soil) can increase the water retention capacity of soil by ~ 50% with proper amendment with various dosages of soil-to-hydrogel ratio. Consecutively soil bulk density can be reduced by 8-10 %. The expected upward trend in saturated water volumetric content of the soil with increasing doses of hydrogel will show clear signs of an increase in agricultural water use efficiency in arid and semi-arid regions. This will have a positive impact on the net plant yield. Hydrogel will directly influence soil permeability, density, structure, texture, evaporation, and infiltration rates of water. Irrigation frequency, compaction tendency, and run-offs will decrease while aeration & microbial activity is promoted. Water stress due to scarcity of moisture around root zones is often associated with premature leaf shedding, decreasing chlorophyll content, reduced seed yield, and less fruit and flower yield per plant. The use of hydrogel can help moderate these impacts caused by deficit irrigation. Being a water retaining agent greatly increases the irrigation period of cultivation, enhancing irrigation efficiency, particularly in arid & semi-arid belts.

- **Drought Stress Reduction**

Drought stress can lead to the production of Oxygen radicals that result in increased lipid peroxidation and oxidative stress in the plants. Visible effects include stunned height, decrease in leaf area and foliar matrix damage, etc. Hydrogel can reduce drought impact on plants leading to reduced stress and oxygen radical formation. This in turn provides scope for better growth and yield even in unfavorable climatic conditions.

- **Enhanced Fertilizer Efficiency**

Irrigation technology has major constraints in the fields of application of fertilizers, herbicides and germicides. Studies suggest the use of synthetic fertilizers can be greatly reduced when hydrogel agriculture is practiced without hindering crop yield and nutritional value. It would indeed be a more appropriate practice for sustainable agriculture in arid and semi-arid conditions and regions with similar ecological constraints.

- **Biodegradability of hydrogel**

Biodegradability of Hydrogel Polymer Studies have confirmed that hydrogel is sensitive to the action of UV rays, and degrades into oligomers. Cellulose-based hydrogels become much more sensitive to aerobic and anaerobic microbiological degradation and can degrade at rates of 10-15 per year into the water, carbon dioxide, and nitrogen compounds. The hydrogel molecules are too voluminous to be absorbed into plant tissue and have zero bioaccumulation potential.

2.4 Project Objectives and Target Deliverables (as per the NMHS-Sanction Order)

S#	Objectives	Major achievements (***in bullets points***)
1.	Synthesis of cellulose-based hydrogels using cellulose derivatives carboxymethyl cellulose (NaCMC) and hydroxyethyl cellulose (HEC) with crosslinker citric acid (CA). In addition, optimization of the synthesis process to obtain suitable composition of hydrogels for agriculture applications. **(Objective - 1 of sanction letter)**	6. Cellulose-based hydrogels were prepared using cellulose derivatives NaCMC and HEC of ratios 2:1 and 3:1. A 3D network (hydrogel network) of polymers was obtained using citric acid as a crosslinker. 7. NaCMC and HEC are hydrophilic polymers containing plenty of hydroxyl groups, leading to the high water absorption capacity of hydrogels. 8. Hydrogels demonstrated porous structures in the FESEM microscope. 9. The prepared hydrogels have shown a remarkable swelling ratio of ~1070% for hydrogel prepared using NaCMC/HEC: 2/1 and ~ 840% for NaCMC/HEC: 3/1. 10. Moreover, the observation suggests a reduction in swelling ratio with increasing crosslinking density. **(Details in annexure)**

2.	Thorough characterization of prepared hydrogels **(part of objective – 1 of the sanction letter)**	Different characterization techniques have been used for the complete characterization of hydrogels. For instance, Fourier transform infrared spectroscopy (FTIR) for chemical functional groups analysis, scanning electron microscopy (SEM) for surface morphology, tensile test for mechanical properties, soil burial test for biodegradability of hydrogels, dynamic light scattering (DLS) for particle size analysis, and X-ray diffraction for crystallographic structure, etc. **(Details in annexure)**
3.	Study the ability of the hydrogel to alter the water retention properties of soil. **(Objective – 2 of the sanction letter)**	3. It is crucial to evaluate the water retention behavior of NaCMC/HEC hydrogels for their agriculture applications. Hydrogels require to retain more water than the soil for such applications, where a hydrogel acts as a water reservoir that absorbs a significant amount of water and releases it to the ground and plants in a controlled and sustained manner. Water loss (evaporation) through hydrogels and soil was assessed periodically in open environmental conditions to evaluate water retention behavior. 4. Studies showed that hydrogel-modified soil needed thirteen (13) days to lose around 80% of water. In contrast, soil required nine (9) days for evaporation of 80% of water, suggesting better water holding capacity of the hydrogel-modified soil than the unmodified soil. **(Details in annexure)**

4.	Synthesis of Cellulose Nano Crystals as reinforcing agents to the hydrogel. **(Objective – 3 of the sanction letter)**	5. Crystalline cellulose nanocrystals (CNC) were extracted from cotton fibers through the acid (H_2SO_4) hydrolysis method. Extracted CNCs were used as reinforcing material to enhance the mechanical properties of the hydrogel. 6. The acid hydrolysis of bleached cotton fibers splits the amorphous regions of the fibers from the crystalline areas. It produced needle-like crystalline CNCs with an average length of ~ 600 nm and a diameter of 20-30 nm (L/D = 30). 7. Dynamic light scattering analysis showed the bimodal distribution of CNCs with a hydrodynamic diameter (*Dh)* of 599 nm and a polydispersity index (PDI) of 27%. The large number of CNCs is in the range of 240 – 1823 nm. 8. X-ray diffraction peaks indicate increased crystallinity of CNCs. **(Details in annexure)**
4.	Study the properties of hydrogel with and without reinforcing agents. **(Objective – 4 of the sanction letter)**	3. The mechanical analysis revealed improved tensile strength of hydrogel composites than the hydrogel without reinforcement (without CNCs). Increasing the CNC concentration from 0.2% to 0.7% in the hydrogel improved the mechanical strength of the hydrogel composite, indicating the reinforcing effect of crystalline CNCs. 4. Moreover, the elongation property has also improved for hydrogel composites compared to hydrogel, pointing to the fragile and brittle nature of the hydrogel. **(Details in annexure)**
5.	Study the effect of hydrogel-modified soil on plant growth and compared it with unmodified soil. (**(Objective – 4 of the sanction letter)**	2. A study of plant growth was carried out by measuring the performance indicators, such as fresh weight and dry weight of the plant at certain intervals, total moisture content, root and shoot ratio, crop growth rate, total chlorophyll produced by plants (chlorophyll A and chlorophyll B). 3. Data indicate that hydrogel-modified soil has a positive impact on plant growth. Hydrogel-modified soil can retent and deliver water for a longer time to the plants. **(Details in annexure)**

3 **METHODOLOGIES/STRATEGY/ APPROACH –** _supporting documents to be attached._

3.1 Methodologies used

- **Synthesis of NaCMC/HEC hydrogel**

Superabsorbent, biodegradable cellulose hydrogel based on cellulose derivatives NaCNC and HEC (2:1 and 3:1) were synthesized through polymerization using natural citric acid (CA) as a crosslinker (Fig. 1). Prepared hydrogels were thoroughly characterized using the following characterization techniques:

1. Fourier transform infrared spectroscopy (FTIR) was used for the chemical analysis of functional groups present in NaCMC, HEC, and NaCMC/HEC hydrogels.

2. A scanning electron microscope (SEM) was used to study the surface morphology of prepared hydrogels.

3. Mechanical properties of hydrogels and hydrogel composites (reinforced with CNCs) were performed using a universal tensile machine (UTM)

Fig. 1: Synthesis process for NaCMC/HEC-based hydrogels

- **Extraction of cellulose nanoparticles (CNCs) from cotton fiber**

CNCs were extracted from cotton fiber using acid (H_2SO_4) techniques and the particle and shape were analyzed using SEM and dynamic light scattering techniques.

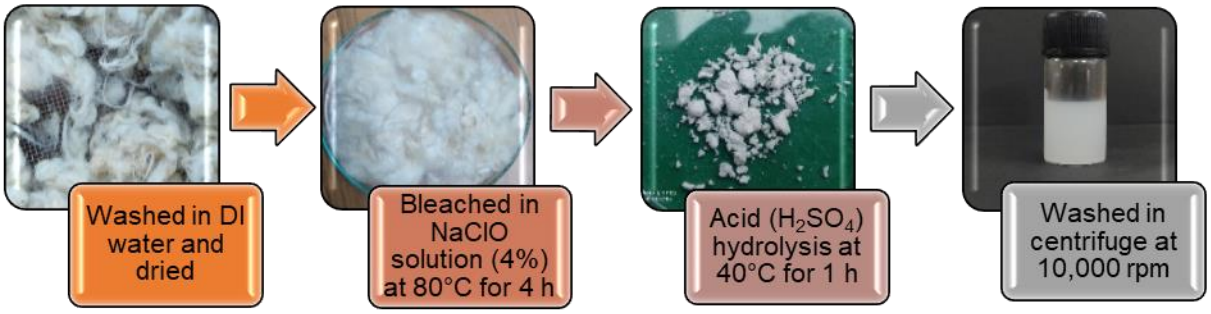


Fig. 2: extraction of crystalline CNFs from cotton fibers through acid (H_2SO_4) hydrolysis

- **Hydrogel mixing with the soil to form hydrogel-modified soil**

  The prepared hydrogel was grounded into the granular form (size: > 2 mm) and mixed with black clay soil available in Tripura state. 2% (wt %) of hydrogel (based on total soil weight) was used to prepare hydrogel-modified soil. Hydrogel-modified soil was watered (irrigated) for plant germination and to study the water retention test. One reference pot with only soil (control) was also irrigated for comparison.

Fig. 3: soil mixed with hydrogel for hydrogel-modified soil

3.2 Data collected and Equipments utilized

Various data collection methods and equipment have been utilized during the entire study. Some of the methods and equipment mentioned in characterization techniques.

1. **Hot air oven** to carry out the polymerization reaction at 75°C for the synthesis of NaCMC/HEC hydrogels.
2. **Fourier transform infrared spectroscopy (FTIR)** was used for the chemical analysis of functional groups present in NaCMC, HEC, and NaCMC/HEC hydrogels.

3. **A scanning electron microscope (SEM)** was used to study the surface morphology of prepared hydrogels and CNCs.
4. Mechanical properties of hydrogels and hydrogel composites (reinforced with CNCs) were performed using a **universal tensile machine (UTM).**
5. **Differential scanning calorimetry (DSC)** for thermal analysis of hydrogels and CNCs.
6. **Centrifuge machine** (R.P.M.: 10,000) for removing unreacted chemicals and washing CNCs.
7. **X-Ray diffractometer (XRD)** to study the crystallographic structure of cotton, CNCs, and hydrogels.
8. **Weighing balance** for measuring weights.
9. **Moisture analyzer probe** to measure moisture contents in the soil and hydrogel-modified soil.

3.3 Strategic Planning for each activity with a time frame

Activity	**Time frame**															
	1st year				**2nd year**				**3rd year**				**4th year**			
Hiring manpower (JRF), procuring chemicals and equipment	■	■	■	■	■	■										
Synthesis of cellulose-based (NaCMC/HEC) hydrogels and optimization of the synthesis process	■	■	■	■	■	■	■	■								
Complete characterization and analysis of prepared hydrogels using different characterization techniques, i.e., FTIR, DSC, SEM, XRD, etc.			■	■	■	■	■	■	■	■	■	■				
Extraction of cellulose nanocrystals (CNCs) from cotton fiber using acid hydrolysis.			■	■	■	■	■	■	■	■	■	■				
Study the water retention capacity of hydrogel-modified soil and compared it with unmodified soil (control).			■	■	■	■	■	■	■	■	■	■				
Study the effect of hydrogel-modified soil on plant growth. (project time has been extended for 1 more year due to covid-19. Many experiments haven't been finished because of the closer of university and lab during covid-19).										■	■	■	■	■	■	■

4 KEY FINDINGS AND RESULTS – *supporting documents to be attached.*

4.1 Major Activities/ Findings

Major Activities	Findings
Synthesis of cellulose-based (NaCMC/HEC) hydrogels and optimization of the synthesis process	1. Hydrogels demonstrated porous structures in the FESEM microscope. 2. The prepared hydrogels have shown a remarkable swelling ratio of ~1070% for hydrogel prepared using NaCMC/HEC: 2/1 and ~ 840% for NaCMC/HEC: 3/1. 3. Moreover, the observation suggests a reduction in swelling ratio with increasing crosslinking density.
Extraction of cellulose nanocrystals (CNCs) from cotton fiber using acid hydrolysis.	1. The acid hydrolysis of bleached cotton fibers produced needle-like crystalline CNCs with an average length of ~ 600 nm and a diameter of 20-30 nm (L/D = 30). 2. Dynamic light scattering analysis showed the bimodal distribution of CNCs with a hydrodynamic diameter (*Dh)* of 599 nm and a polydispersity index (PDI) of 27%. The large number of CNCs is in the range of 240 – 1823 nm. 3. X-ray diffraction peaks indicate increased crystallinity of CNCs. 4. Hydrogels reinforced with CNCs demonstrated increased tensile strength as compared to non-reinforced hydrogels.
Study the ability of the hydrogel to alter the water retention properties of soil.	1. Studies showed that hydrogel-modified soil needed thirteen (13) days to lose around 80% of water. In contrast, soil required nine (9) days for evaporation of 80% of water, suggesting better water holding capacity of the hydrogel-modified soil than the unmodified soil.
Study the effect of hydrogel-modified soil on plant growth and compared it with unmodified soil.	1. A study of plant growth was carried out by measuring the performance indicators, such as fresh weight and dry weight of the plant at certain intervals, total moisture content, root and shoot ratio, crop growth rate, total chlorophyll produced by plants (chlorophyll A and chlorophyll B).

	2. Data indicate that hydrogel-modified soil has a positive impact on plant growth. Hydrogel-modified soil can retent and deliver water for a longer time to the plants

4.2 Key Results

1. Hydrogels demonstrated porous structures in the FESEM microscope.
2. The prepared hydrogels have shown a remarkable swelling ratio of ~1070% for hydrogel prepared using NaCMC/HEC: 2/1 and ~ 840% for NaCMC/HEC: 3/1.
3. Moreover, the observation suggests a reduction in swelling ratio with increasing crosslinking density.
4. The acid hydrolysis of bleached cotton fibers produced needle-like crystalline CNCs with an average length of ~ 600 nm and a diameter of 20-30 nm (L/D = 30).
5. Dynamic light scattering analysis showed the bimodal distribution of CNCs with a hydrodynamic diameter (*Dh)* of 599 nm and a polydispersity index (PDI) of 27%. The large number of CNCs is in the range of 240 – 1823 nm.
6. X-ray diffraction peaks indicate increased crystallinity of CNCs.
7. Hydrogels reinforced with CNCs demonstrated increased tensile strength as compared to non-reinforced hydrogels.
8. Studies showed that hydrogel-modified soil needed thirteen (13) days to lose around 80% of water. In contrast, soil required nine (9) days for evaporation of 80% of water, suggesting better water holding capacity of the hydrogel-modified soil than the unmodified soil.
9. A study of plant growth was carried out by measuring the performance indicators, such as fresh weight and dry weight of the plant at certain intervals, total moisture content, root and shoot ratio, crop growth rate, total chlorophyll produced by plants (chlorophyll A and chlorophyll B).
10. Data indicate that hydrogel-modified soil has a positive impact on plant growth. Hydrogel-modified soil can retent and deliver water for a longer time to the plants

4.3 Conclusion of the study

1. In this study, biodegradable cellulose hydrogels based on carboxymethyl cellulose (NaCMC) and hydroxyethyl cellulose (HEC) have been synthesized successfully using CA as a crosslinker.
2. Hydrogels have shown good water absorption and retaining capacity with swell ability depending on the crosslinking density of hydrogels and the pH of the swelling medium.
3. The study revealed that incorporating CNFs into a hydrogel matrix significantly improved the mechanical properties of hydrogel nanocomposites, which is vital in maintaining the hydrogel's structural integrity in agriculture applications.
4. The soil burial study confirmed the morphological and chemical changes in a hydrogel as a result of biodegradation by microorganisms in the soil.
5. A plant growth study shows that the hydrogel-modified soil kept the soil moist for a longer time and had a positive impact on plant growth.

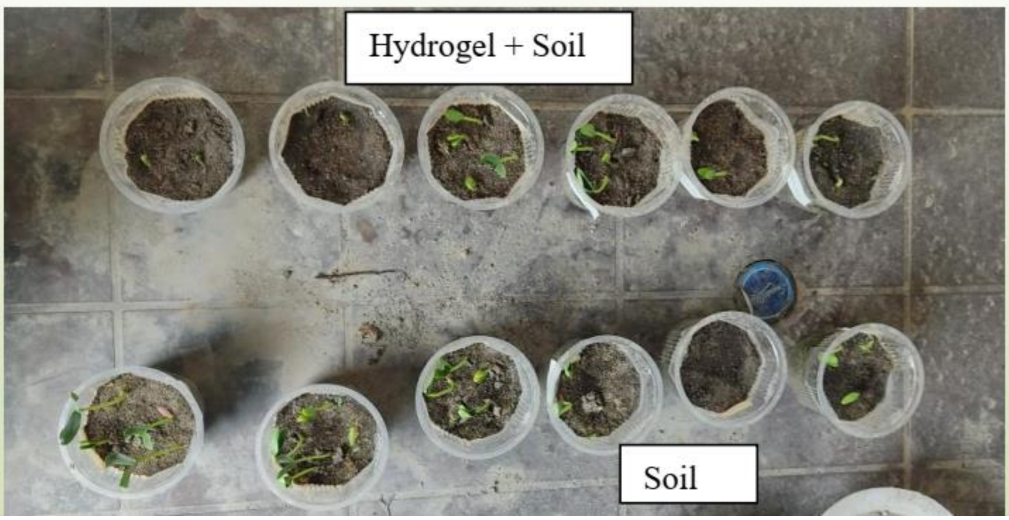
5 OVERALL ACHIEVEMENTS – *supporting documents to be attached.*

5.1 Achievement on Project Objectives/ Target Deliverables

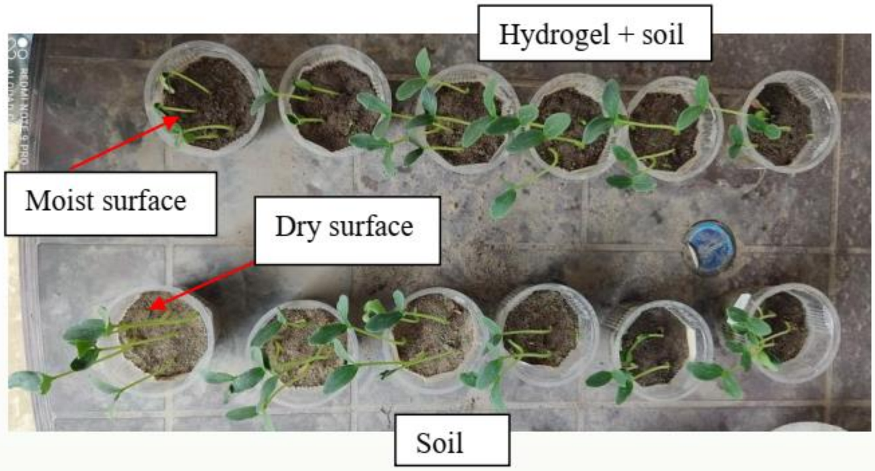
The prime objective of this study is to synthesize cellulose-based superabsorbent hydrogels which should be able to absorb ample amount of water and release it in a sustained and controlled manner. As achievement mentioned in the aforementioned sections that prepared hydrogels were capable of absorbing plenty of water into their network and releasing it in a controlled way into the plants.

Cucumber seeds were planted in hydrogel-modified soil and unmodified soil and observed the plant growth for 30 days. Pots were watered (irrigated) in appropriate intervals (every 48 hrs.) Observed the plant growth and available water to the plants.

4th Day Growth



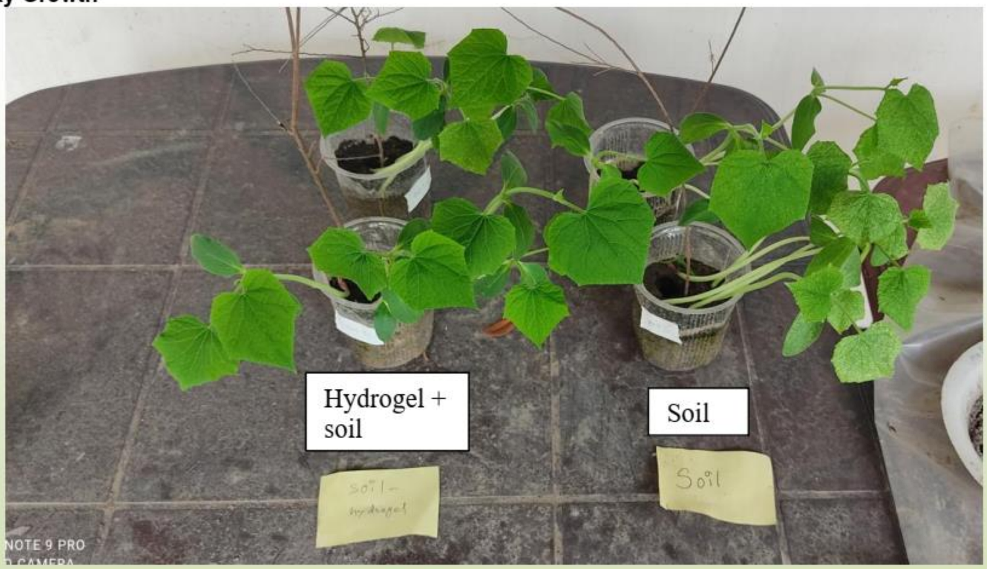
6th Day Growth



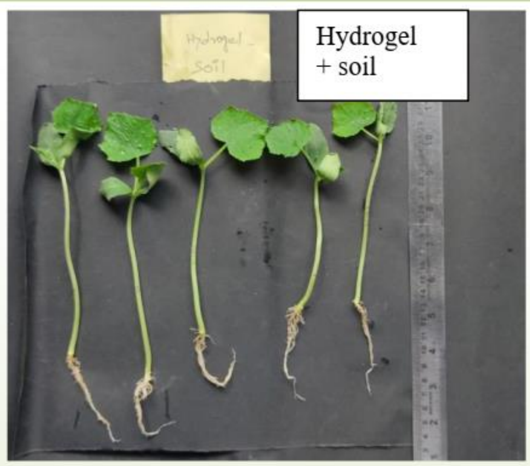
10th Day Growth

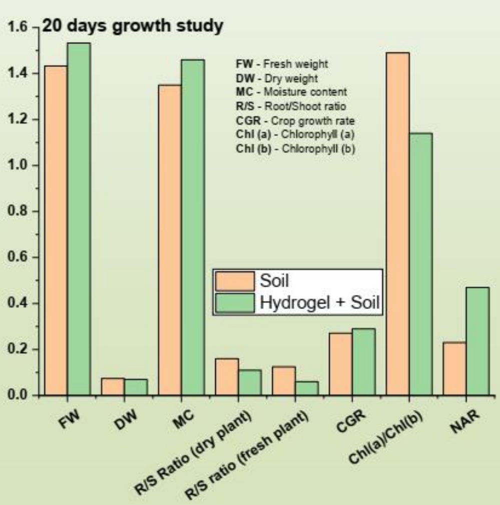
20th Day Growth

30th Day Growth



Step 5: Analysis of growth by different performance parameters





Data shows that hydrogel modified soil keep the soil moist for longer time as compared to non-modified soil, hence will reduce the irrigation frequency. Moreover, hydrogel modified soil has positive impact on plant growth as shown by different performance parameters in the graph.

5.2 Interventions

It is learned while experimenting that the particle sizes of hydrogel granules affect the swelling capability as well. Smaller the size (~ 2 mm) of granules absorb more water due to their relatively high surface area. More experiments need to be done repetitively to analyze the effect of hydrogel-modified soil on different plant growths. Bulk production of hydrogels needs to be carried out to see its feasibility and possibility.

5.3 On-field Demonstration and Value-addition of Products

Some more trial experiments on plant growth are running in the laboratory to establish the hypothesis. Results are very encouraging and show hydrogel's potential for water conservation in agriculture fields. Hydrogels are biodegradable and non-toxic, so offer no adverse effect on the environment. Besides water conservation, hydrogels are capable of preventing the loss of chemical fertilizers into the environment, leads to positive impact on environmental pollution. Field demonstration needs to be carried out after proven hypothesis.

5.4 Addressing Cross-cutting Issues

6 PROJECT'S IMPACTS IN IHR – *supporting documents to be attached.*

6.1 Socio-Economic impact

Agriculture is the major source of sustenance and support for the people of Tripura State. Approximately 40-42 % of Tripura's population directly depends on agriculture and about 30-33 percentage of GDP is contributed by the agriculture sector. The tribes of Tripura (mainly schedule tribes-ST community) constitute a major population of the state. About 19 tribes reside in the state of Tripura and agriculture is their main occupation for livelihood. About 0.28-million-hectare cultivable land is available in Tripura state with an irrigation potential of 0.12 million hectares. The major agricultural crops produced by farmers are Rice, potatoes, tomatoes, and Pulses, however, pulses are the major crop in non-irrigated areas. Horticulture is a rising sector in the state with the cultivation of exotic flowers and fruits produced for increasing their export potential. The tribal population in Tripura state mostly practices Jhum (shifting) cultivation and has a livelihood status. The reason is most of the farmers are marginal and small farmers and soil fertility of Jhum land is decreasing. Almost all the tribes are fully dependent on biomass generation in the field for the use as fertilizer (organic agriculture), the productivity is less hence income from Jhum is also less. So, most of Jhumia's socioeconomic condition is low or medium. Hence, the majority of them belong to the low to medium livelihood status category. Agricultural research is the only active connection between research & development and farmers. In an agricultural economy in the state, where the majority of farmers are marginalized and small landholders, research in any way related to agriculture turns the most significant element in agriculture and allied sectors. Not only in Tripura state but in the whole of India, the agriculture sector is a cause of concern because of drought, salinity of water, and increasing temperature. These situations are likely to get worse because of land degradation, urbanization, and climate change. In India, most of the area is situated in arid and semi-arid regions. The availability of irrigation water is limited, which requires the development of water-efficient technologies to conserve water in agricultural fields.

The development of “superabsorbent hydrogels” is necessary in order to absorb (swelling) and release the water through a diffusion mechanism into the growing plants. In this manner, irrigated water will not be lost through drainage or evaporation as being efficiently supplied to plant roots when needed. Moreover, hydrogel granules increase in size upon swelling resulting in enhancing soil porosity and offering better oxygenation to the roots. In agriculture, chemically synthesized fertilizers are normally used in large quantities than actually required by the plants. This causes nitrate accumulation in the soil (usually in dry areas) with a negative impact on the environment as well as on product quality. The use of hydrogels could significantly reduce the amount of fertilizers used and/or limit nitrate accumulation in the soil.

6.2 Impact on Natural Resources/ Environment

As stated earlier, cellulose is the most abundant biodegradable natural polymer and a source of many advanced materials for many applications in biomedicals, electronics, agriculture, food, etc. Consequently, developed hydrogels from cellulose and its derivatives are also biodegradable and non-toxic, and impose no adverse effect on the environment. Moreover, these hydrogels can absorb water-soluble fertilizers and release them into the plant in a controlled manner, resulting in the prevention of runoff to the environment and reduction in wastage. Hydrogels can bind heavy metals into their structure through weak secondary forces and prevent the plants get affected by them.

6.3 Conservation of Biodiversity/ Land Rehabilitation in IHR

Agriculture soil fertility can be conserved using hydrogels as water reservoirs for plant growth. Hydrogel granules increase in size upon swelling resulting in enhancing soil porosity and offering better oxygenation to the roots. In agriculture, chemically synthesized fertilizers are normally used in large quantities than actually required by the plants. This causes nitrate accumulation in the soil (usually in dry areas) with a negative impact on the environment as well as on product quality. The use of hydrogels could significantly reduce the amount of fertilizers used and/or limit nitrate accumulation in the soil.

7 EXIT STRATEGY AND SUSTAINABILITY – *supporting documents to be attached.*

7.1 Utility of project findings

The development of “superabsorbent hydrogels” is necessary in order to absorb (swelling) and release the water through a diffusion mechanism into the growing plants. In this manner, irrigated water will not be lost through drainage or evaporation as being efficiently supplied to plant roots when needed. Moreover, hydrogel granules increase in size upon swelling resulting in enhancing soil porosity and offering better oxygenation to the roots. In agriculture, chemically synthesized fertilizers are normally used in large quantities than actually required by the plants. This causes nitrate accumulation in the soil (usually in dry areas) with a negative impact on the environment as well as on product quality. The use of hydrogels could significantly reduce the amount of fertilizers used and/or limit nitrate accumulation in the soil.

7.2 Other Gap Areas

Apart from the scarcity of water and loss of fertilizers, the high concentration of toxic heavy metals (Cu II, Hg II, Cd II, Ni II, etc.) in the soil also adversely affects the soil quality and impacts human health. Hydrogels synthesized from cellulose and its derivatives carry a large number of functional groups in polymer backbones, which are capable of immobilizing or binding these toxic metals through secondary forces, resulting in a reduction in soil toxicity.

7.3 Major Recommendations/ Way Forward

The experimental data indicate that cellulose-based hydrogels have the potential to conserve a significant amount of water and reduce irrigation frequency. Properly implementing bulk production and process optimization, prepared hydrogels can be effectively used for agriculture applications. After laboratory experiments on plant growth with repeatability of results, hydrogels should be implemented for field trials. Initially, the production should be carried out at a pilot plant, and thereafter it needs an industry partner for the synthesis and development of hydrogel for bulk production. The whole process requires proper training before implementation.

7.4 Replication/ Upscaling/ Post-Project Sustainability of Interventions

1. As mentioned above, the repeatability of experimental results should be tested carefully (which are already under process).

2. Cellulose is an abundant polymer, available almost in every plant cell wall, and be extracted easily, so will be no shortage of raw materials. Prepared hydrogels are biodegradable as depicted by the soil burial test, hence no adverse effects on the environment.

3. The Hydrogel production process is facile and can be done at the bulk level. Moreover, no harmful chemicals are required for the production of cellulose-based hydrogels. Water has been used as a synthesis medium during production.

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9 ACKNOWLEDGEMENTS

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Appendix-1

(Details on Technical Activities)

1. Synthesis of NaCMC/HEC hydrogels and hydrogel nanocomposites

The NaCMC/HEC hydrogels were prepared using different ratios of NaCMC/HEC, i.e., 2:1 and 3:1, with varying concentrations of CA crosslinker (10%, 12%, 14%, and 16%). To prepare a hydrogel, an appropriate weight of NaCMC was initially dissolved in 100 ml of distilled water (DI) in a 250 ml glass beaker with continuous stirring. After that, HEC was slowly added to the solution and stirred until it completely dissolved. Then the required concentration of CA crosslinker was added to the clear cellulose solution and dissolved thoroughly. The solution was kept in a hot-air oven at 45°C for 24 h to evaporate the water partially. Then the temperature increased to 75°C for carrying out the hydrogel synthesis reaction and allowed the reaction to take place for 27 h. The prepared hydrogel was washed entirely in methanol and DI water to remove unreacted monomers and dried for further experiments. To prepare a CNCs-reinforced hydrogel nanocomposite, the required amount of CNCs was added into the NaCMC/HEC solution with continuous stirring. Then the reaction was carried out as described above. The 2:1 ratio of NaCMC/HEC and 10% of CA with varying percentages of CNCs were used to prepare hydrogel nanocomposites. The cellulose hydrogel network was formed by a reaction between hydroxyl groups of cellulose derivative and anhydride groups of crosslinked CA with the formation of diester linkage. The compositions for prepared hydrogels and the hydrogel reaction mechanism are given in Table 1 and Figure 1, respectively.

Table 1: compositions of prepared NaCMC/HEC hydrogels and hydrogel nanocomposites

Hydrogels (HG)	NaCMC/HEC ratio	Weight of NaCMC (g)	Weight of HEC (g)	CA crosslinker (%)	CNC (%)
$HG_{21}CA_{10\%}CNC_{0\%}$	2/1	2	1	10	0
$HG_{21}CA_{12\%}CNC_{0\%}$	2/1	2	1	12	0
$HG_{21}CA_{14\%}CNC_{0\%}$	2/1	2	1	14	0
$HG_{21}CA_{16\%}CNC_{0\%}$	2/1	2	1	16	0
$HG_{31}CA_{10\%}CNC_{0\%}$	3/1	3	1	10	0
$HG_{31}CA_{12\%}CNC_{0\%}$	3/1	3	1	12	0
$HG_{31}CA_{14\%}CNC_{0\%}$	3/1	3	1	14	0
$HG_{31}CA_{16\%}CNC_{0\%}$	3/1	3	1	16	0

$HG_{21}CA_{10\%}CNC_{0.2\%}$	2/1	2	1	10	0.2
$HG_{21}CA_{10\%}CNC_{0.5\%}$	2/1	2	1	10	0.5
$HG_{21}CA_{12\%}CNC_{0.7\%}$	2/1	2g	1g	10	0.7

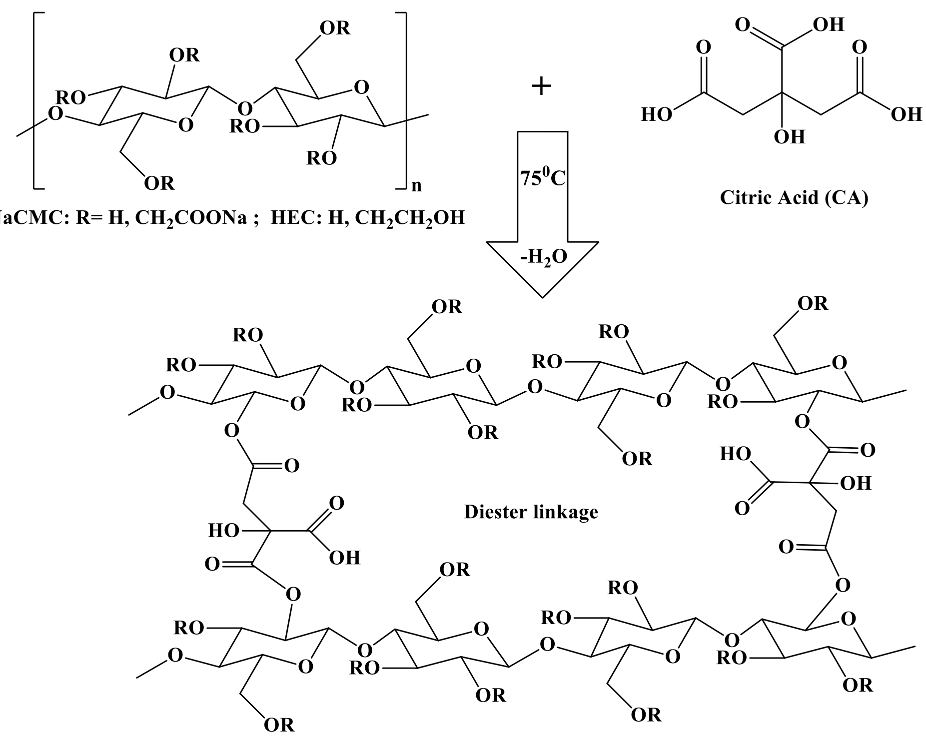


Fig. 1: reaction mechanism and hydrogel network formation with diester linkage

2. Extraction of crystalline cellulose nanofibers (CNCs) from cotton fibers

The CNCs were extracted from cotton fiber by acid (H_2SO_4) hydrolysis. Initially, raw cotton was thoroughly washed in distilled water (DI) to remove foreign particles and other impurities and then dried in sunlight for 48 hrs. The dried cotton was then bleached in 500 ml of 4% sodium hypochlorite (NaClO) solution at 80°C for 4 hrs. Bleached cotton fibers were filtered and washed five (5) times in DI water to remove residual NaClO. After that, 10g of washed cotton was acid hydrolyzed at 40°C for 1 hr to obtain crystalline CNCs using 100 ml sulfuric acid (50% conc.) solution. Obtained CNCs were washed five times in a centrifuge for 10 minutes at 10000 rpm. Washed CNCs were dried thoroughly and analyzed for their particle size and distribution using dynamic light scattering (DLS). The flow chart of the CNCs extraction process from cotton is shown in Figure 2.

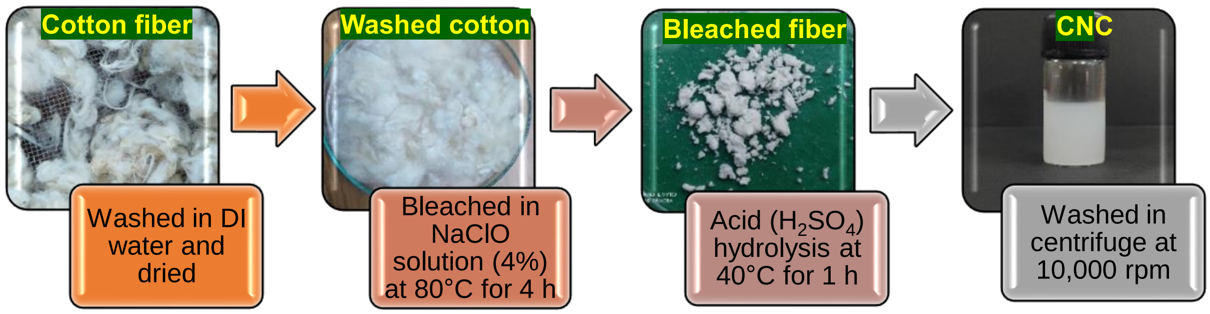


Fig. 2: extraction of crystalline CNCs from cotton fibers through acid (H_2SO_4) hydrolysis.

3. Characterization

3.1. Fourier transform infrared (FTIR) spectroscopy.

The chemical analysis of cellulose derivatives (NaCMC and HEC) and prepared hydrogels were performed by Fourier transform infrared spectroscopy (FTIR) using Shimadzu IR (model: IRspirit) spectroscopy. The KBr pellets were prepared using a hydraulic press, and spectra were recorded in the 4000 cm^{-1} - 400 cm^{-1} wavenumber range with 45 scans.

3.2. Differential scanning calorimetry (DSC)

The thermal analysis of hydrogels was performed using differential scanning calorimetry (Netzsch DSC 2914 calorimeter, Germany). The weighed sample (5-10 mg) of hydrogel was placed in a sample holder and thermally scanned from 25˚C to 500˚C with a heating rate of 10°C/ min. in a nitrogen (N_2) atmosphere to obtain a DSC thermogram.

3.3. Particles size analysis (DLS)

The particle size, size distribution, and zeta potential of the nanogels were measured by dynamic light scattering (Litesizer 500, Anton Paar, Austria) equipped with a zeta sizer, using the Electrophoretic light scattering principle (ELS). The angle measurement was 175° with a laser light source of wavelength 658 nm.

3.4. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) patterns were measured for raw cotton fibers, their CNCs, NaCMC, HEC, and NaCMC/HEC hydrogels using an X-ray diffractometer (PANalytical, X'pert pro) with CuKα radiation (λ = 1.54 A°) at 45 Kv and 40 mA. The scattered radiation was detected in the range of 2θ = 5° - 90° at a scan rate of 2°/min. The crystallinity index (C_rI) (Eq^n iii) was evaluated using a crystalline intensity peak of 200 planes (I_{200}) (2θ ~ 22.5°) and minimum intensity of amorphous region (I_{am}) (2θ ~ 18.5°) between 200 (I_{200}) and 110 (I_{110}) planes.

$$Crystallinity\ Index\ (C_rI)(\%) = \frac{(I_{200} - I_{am})}{I_{200}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (iii)$$

3.5. Field emission scanning electron microscopy (FESEM)

The surface morphology of prepared hydrogels was analyzed using field emission scanning electron microscopy (Sigma-300, ZEISS, Germany). The cryo-fractured hydrogel sample was mounted on the substrate and gold-sputtered before capturing FESEM images. FESEM machine works at a high voltage of 20kV.

3.6. Swelling Study

Swelling tests of hydrogels were carried out in three steps. In the first step, the dry hydrogel was weighed (dry weight) and immersed in DI water to swell at room temperature. The swollen hydrogel was removed from the swelling medium at regular intervals, and the surface water was removed using filter paper. Then the hydrogel was weighed (swollen weight) and placed again into the same swelling medium, maintaining the constant volume. The tests were continued until the swelling reached equilibrium. The swelling ratio was calculated using the following formula.

$$\text{Swelling ratio (SR)} = \frac{(Ws-Wd)}{Wd}\times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(i)$$

Where W_d is the dry weight, and W_s is the swollen weight of the hydrogel.

3.7. Water retention capacity of the hydrogel

To investigate the water retention behavior of a hydrogel in soil, 2% of dried hydrogel in particulate form was mixed and added to the soil (50 g) in a plastic container. 20 ml of DI water was added to the soil with and without hydrogel (reference sample) and kept in an open environment. The loss % of water (evaporation) from hydrogel and reference samples was measured every 24 h till the water was evaporated entirely. Recorded initial weights of soil with (W_0) and without hydrogel (W), and after every 24 h (W_t) was used to calculate the water retention capacity of the hydrogel using the following formula.

$$\text{Water retention (WR) (\%)} = \frac{Wt-W}{Wo-W}\times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(ii)$$

3.8. Mechanical properties (UTM test)

The mechanical properties of prepared hydrogels and hydrogel nanocomposites were performed using 5KN electromechanical universal testing matching (UTM) (ZwickRoell, Model: Z005TNProline, Germany). The dimensions of the measured samples were length = 8 cm, width = 3.2 cm, and thickness = 0.5 cm). Three (3) replicates were measured for each sample, and average values of tensile stress and strain at break were mentioned to estimate mechanical properties.

3.9. Biodegradation (soil burial) test

A soil burial test assessed the biodegradability of NaCMC/HEC hydrogels. Hydrogel samples were cut into rectangular shapes and definite sizes and buried (~ 20 cm deep) into the soil containing plastic containers. The samples were kept outside in an open environment, and soil moisture was maintained (to allow microorganisms growth) during the experiment. Hydrogel samples were taken out every 15 days and evaluated by FTIR for any changes in chemical structures during biodegradation. The entire investigation was carried out for 60 days.

4. Results and discussion

4.2. FTIR Analysis

The FTIR spectra of raw cotton (untreated) and extracted CNCs (acid hydrolyzed) from raw cotton are shown in Figure 3A. The absorption peaks at 3432 cm^{-1}, 2920 cm^{-1}, 1061 cm^{-1}, and 1644 cm^{-1} belong to the hydroxyl group (O-H) stretching, C-H stretching, C-O stretching, C=O stretching, respectively, typical characteristic peaks of polysaccharides. For untreated cotton, a peak at 1731 cm^{-1} is attributed to the ester linkage of the carboxyl group (ferulic acid) of hemicellulose and the carboxyl group (p-coumaric acid) of lignin. Moreover, the peak at 1250 cm^{-1} belongs to the C-O stretching of the alkyl aryl group of lignin. The peaks at 1731 cm^{-1} and 1250 cm^{-1} completely disappeared for treated fiber to extract crystalline CNCs, demonstrating that hemicellulose and lignin were successfully washed-out during bleaching and hydrolysis of raw cotton. Additionally, a band at 1373 cm^{-1} attributed to the twisting vibration of C-H in the aromatic ring, and a band at 896 cm^{-1} belongs to the symmetric stretching of glycosidic linkage, which had been reduced in the intensity for CNCs.

The FTIR spectra of NaCMC, HEC, and NaCMC/HEC hydrogel are shown in Figure 3B. The strong and broad bands between 3446 cm^{-1} are attributed to a hydroxyl group (O-H) stretching.

However, the band is narrow for the hydrogel compared to NaCMC and HEC, probably due to the crosslinking reaction between O-H groups of cellulose and CA crosslinker. The peaks at 2931 cm^{-1} and 1432 cm^{-1} belong to the C-H stretching and C-H bending vibrations of CH_3 and CH_2, respectively. The absorption band at 1648 cm^{-1} belongs to C=O stretching, and a band at 1076 cm^{-1} is attributed to C-O stretching. The peak at 1321 cm^{-1} is ascribed to O-H bending vibrations. Additionally, a new peak was noticed for NaCMC/HEC hydrogel at 1731 cm^{-1}, which is attributed to the carbonyl group (C=O) of ester linkage formed during crosslinking reaction between CA and cellulose chains. It confirms the formation of a crosslinked network of the hydrogel.

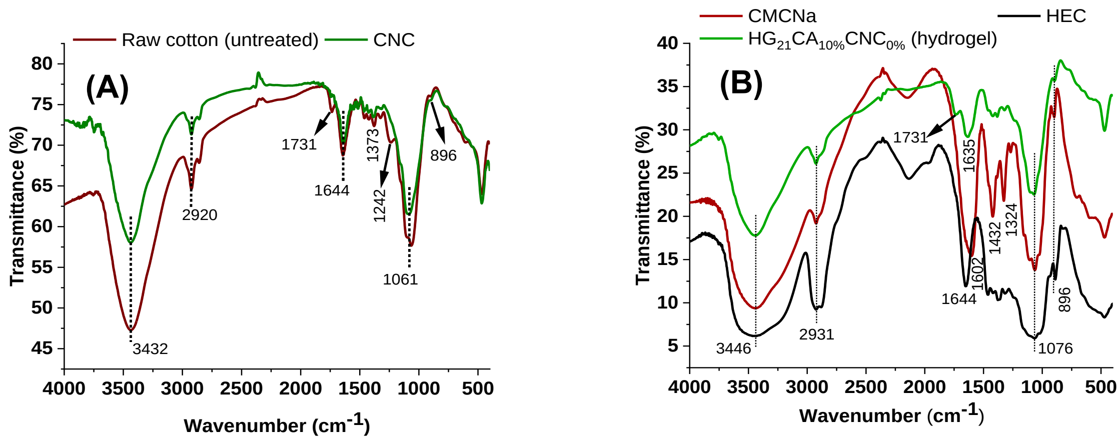


Fig. 3: FTIR spectra of (A) raw cotton and CNCs, (B) NaCMC, HEC, and NaCMC/HEC hydrogel.

4.3. DSC analysis

The DSC thermograms of raw cotton (untreated) and treated cotton by acid hydrolysis to extract crystalline CNCs are shown in Figure 4A. The DSC thermogram of raw cotton demonstrates two exothermic peaks, first at 345°C (broad) and second at 461°C (sharp). The first exothermic peak is associated with the decomposition of cotton into byproduct levoglucosan and other volatile compounds. The second peak belongs to the oxidation of decomposed compounds. In the case of treated cotton (CNCs), mentioned exothermic peaks disappeared or broadened, indicating the thermal stability of CNCs due to the crystalline nature of the fibers. Both treated and untreated cotton fibers show a broad endothermic peak at about 244°C, probably attributed to cellulose's melting temperature. An endothermic peak at 70°C for CNCs is due to the evaporation of bound water.

Likewise, the thermal analysis of NaCMC, HEC, hydrogel, and cotton CNCs-reinforced hydrogel composite was also performed by DSC, and DSC thermograms are shown in Figure 4B. An endothermic peak at ~ 112°C and ~ 80°C for NaCMC and HEC, respectively, is attributed to the evaporation of residual water. These peaks for NaCMC/HEC hydrogel and hydrogel composite disappeared due to the participation of hydroxyl groups of cellulose in crosslinking reaction with the CA, resulting in reduced water absorption and low or no evaporation of water at elevated temperature. The DCS for NaCMC exhibits two exothermic peaks at 306°C (sharp) and 411°C. The peak at 306°C represents the decomposition of glycosidic linkages in the cellulose molecule and cellulose chains, and the peak at 411°C reveals the degradation of decomposed products. DSC for HEC shows a broad exothermic peak at ~ 295°C lower than NaCMC, starting from 260°C to 325°C, attributed to less Intra and inter-molecular interactions in HEC molecules than NaCMC causing transition at appear at a lower temperature. For hydrogel and hydrogel composite (CNCs = 0.2%), DCS thermograms depicted broad exothermic peaks around 297°C and peaks shift at 337°C, indicating that crosslinking in hydrogel formation has improved the thermal stability of the hydrogel by increasing decomposition temperature. The slightly high decomposition temperature (340°C) for hydrogel with 16% CA crosslinker has been noticed than hydrogel with 10% CA crosslinker, suggesting high crosslinking density and improved thermal stability with increased crosslinker percentage.

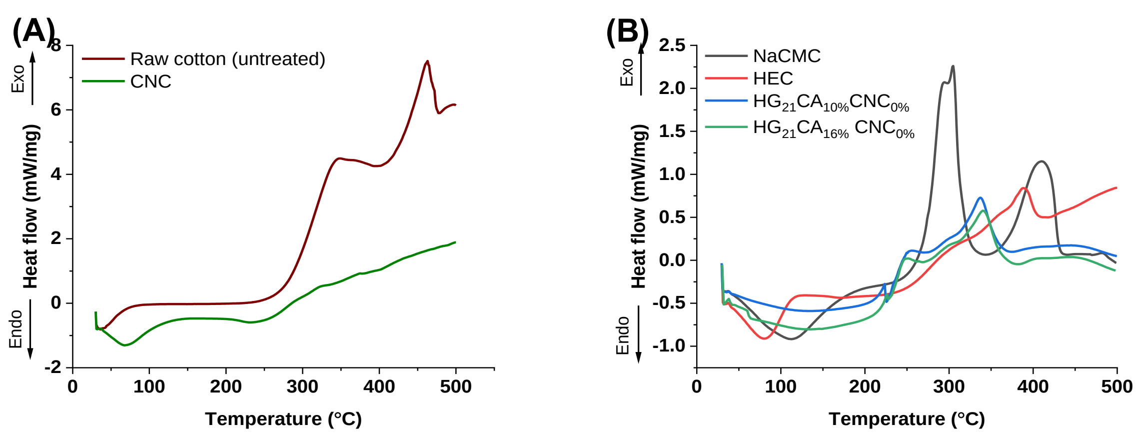
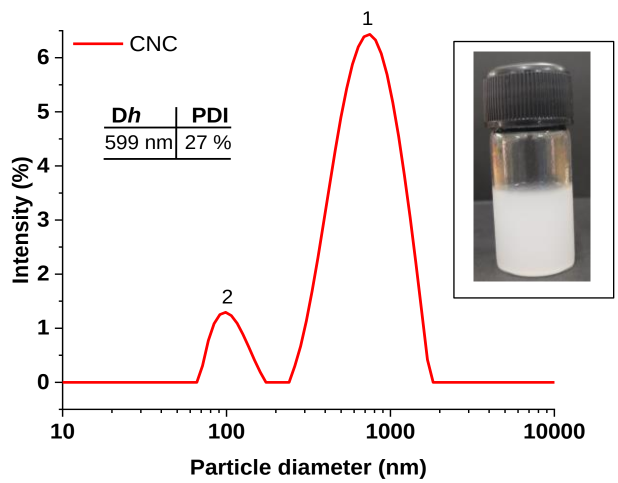


Fig. 4: DSC thermograms of (A) raw cotton and CNCs, (B) NaCMC, HEC, and NaCMC/HEC hydrogels

4.4. Particle size analysis (DLS)

Dynamic light scatting (DLS) has been utilized to determine crystalline CNCs size distribution, their average diameter (hydrodynamic diameter, D*h*), and polydispersity index (PDI), shown in Figure 5. The DLS graph shows the bimodal distribution of CNCs with *Dh* 599 and PDI 27%. The large number of CNCs is in the range of 240 – 1823 nm. The CNCs particle size is larger than the actual size because DLS was measured when particles are suspended in DI water and CNCs hydrophilic nature.



Parameters	DLS values
Hydrodynamic diameter (D*h*)	599 nm
Polydispersity index (PDI)	27%
Peak intensity 1	766 nm
Area intensity 1	91%
Peak intensity 2	105 nm
Area intensity 2	9%
D10 intensity	278 nm
D50 intensity	648 nm
D90 intensity	1142 nm

Fig. 5: particle size distribution of extracted CNC by DLS, and DLS parameters and values.

4.5. XRD analysis

The XRD diffraction patterns for raw cotton and CNCs obtained by acid hydrolysis are shown in Figure 6A. The diffractogram for raw cotton shows crystalline peaks at 2θ = 16°, 22.5°, 30.9°, and 34.5° and for CNCs at 2θ = 16°, 22.5°, 26.7°, 34.8°, and 39.4°. The peaks at 2θ = 16° (110 planes), and 22.5° (200 planes), typical characteristic peaks of cellulose, have sharpened for CNCs due to increased crystallinity during acid hydrolysis. The crystallinity index (C_rI) calculated for CNCs was 56% compared to raw cotton (41%). The acid hydrolysis treatment of bleached cotton helped remove the amorphous region of the cellulose.

The XRD diffractograms of NaCMC, HEC, and hydrogels ($HG_{21}CA_{10\%}CNC_{0\%}$ and $HG_{21}CA_{10\%}CNC_{0\%}$) are shown in Figure 6B. The diffractogram for NaCMC shows crystalline peaks at 19.6°, 12°, and 37.8° (broard) with C_rI:15% and for HEC at 20.4°, 31.7°, and 45° with C_rI: 26%. The NaCMC shows lower crystallinity and peak shift at 19.6° with lower intensity (cellulose I peak) than HEC due to the reduction of hydrogen bonds by substituting the carboxymethyl groups at some of the hydroxyl groups of cellulose. Similar observations have been noticed in earlier studies, and it was also observed that the degree of substitution in NaCMC has significantly affected the crystallinity of cellulose I. The hydrogels of NaCMC/HEC have shown an XRD peak at 19.6 with C_rI: 21%, and all other peaks are disappeared. The cross-linking reaction between the CA and cellulose molecules during hydrogel formation has affected the crystallinity of the hydrogel.

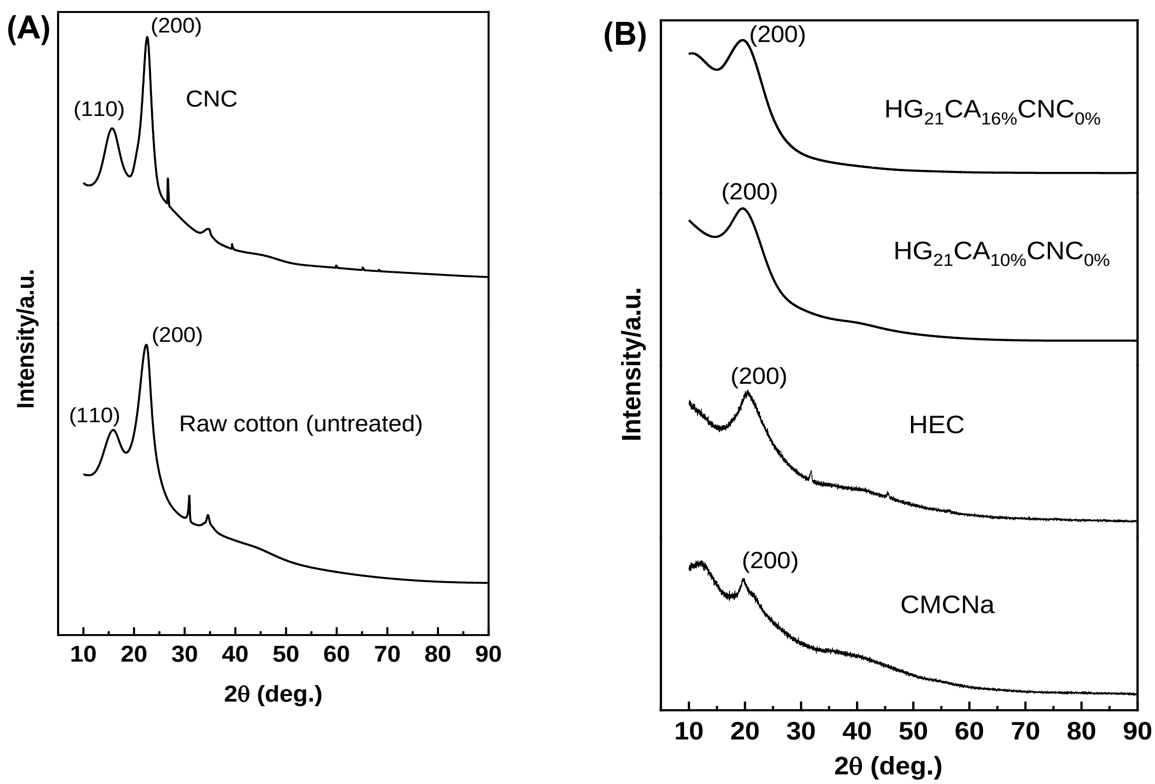


Fig. 6: XRD diffractograms of (A) raw cotton and CNCs and (B) NaCMC, HEC, and NaCMC/HEC hydrogels.

4.6. FESEM analysis

The morphologies of bleached cotton, crystalline CNCs, and hydrogels are characterized by field FESEM and are shown in figures 7A, 7B, 7C, 7D, 7E, and 7F. The bleached fibers are flat, straight, and slightly wrinkled. The bleaching has distorted the fibrillated structure of cotton fibers and destructed cellulose molecules and intramolecular hydrogen bonds between hydroxyl groups of cellulose chains, resulting in opened molecular chains and narrow valley-like structures (figure 7A). The acid hydrolysis of bleached fibers splits the amorphous regions of the fibers from the crystalline areas. It produces needle-like crystalline CNCs with an average length of ~ 600 nm and a diameter of 20-30 nm (L/D = 30) (figure 7B). The dimensions of CNCs are smaller than the values reported in the DLS analysis. It is due to FESEM characterization being performed on dried CNCs, whereas suspended and swollen CNCs are used for DLS analysis. The FESEM images of hydrogel samples show the porous structure, a vital characteristic of hydrogels for their applications as superabsorbents in agriculture applications. However, the hydrogel prepared with less concentration of CA crosslinker (10%) displays uniform and better pore structure (figure 7C) than the hydrogels with more concentration of CA crosslinker (12%, 14%, and 16%). It is due to the increased crosslinking density in a hydrogel with increasing crosslinker concentration, causing reduced pore size and swelling ratio of the hydrogel. Moreover, increased crosslinking density created a brittle structure of the hydrogels where cracks have been propagated between the pores due to the development of internal stress during the drying process of FESEM sample preparation (figures 7D, 7E, and 7F). FESEM results are in agreement with the swelling.

FESEM images of cryo-fractured hydrogel nanocomposites are shown in Figures 7G, 7H, 7I, and 7J. FESEM images showed uniform and interconnected porous structures for all hydrogel nanocomposites. The pore walls of composites, as observed in FESEM, demonstrated that CNC fibers are completely assimilated in a hydrogel matrix, which is required for better mechanical properties. In contrast, non-reinforced hydrogels showed smooth pores in FESEM images.

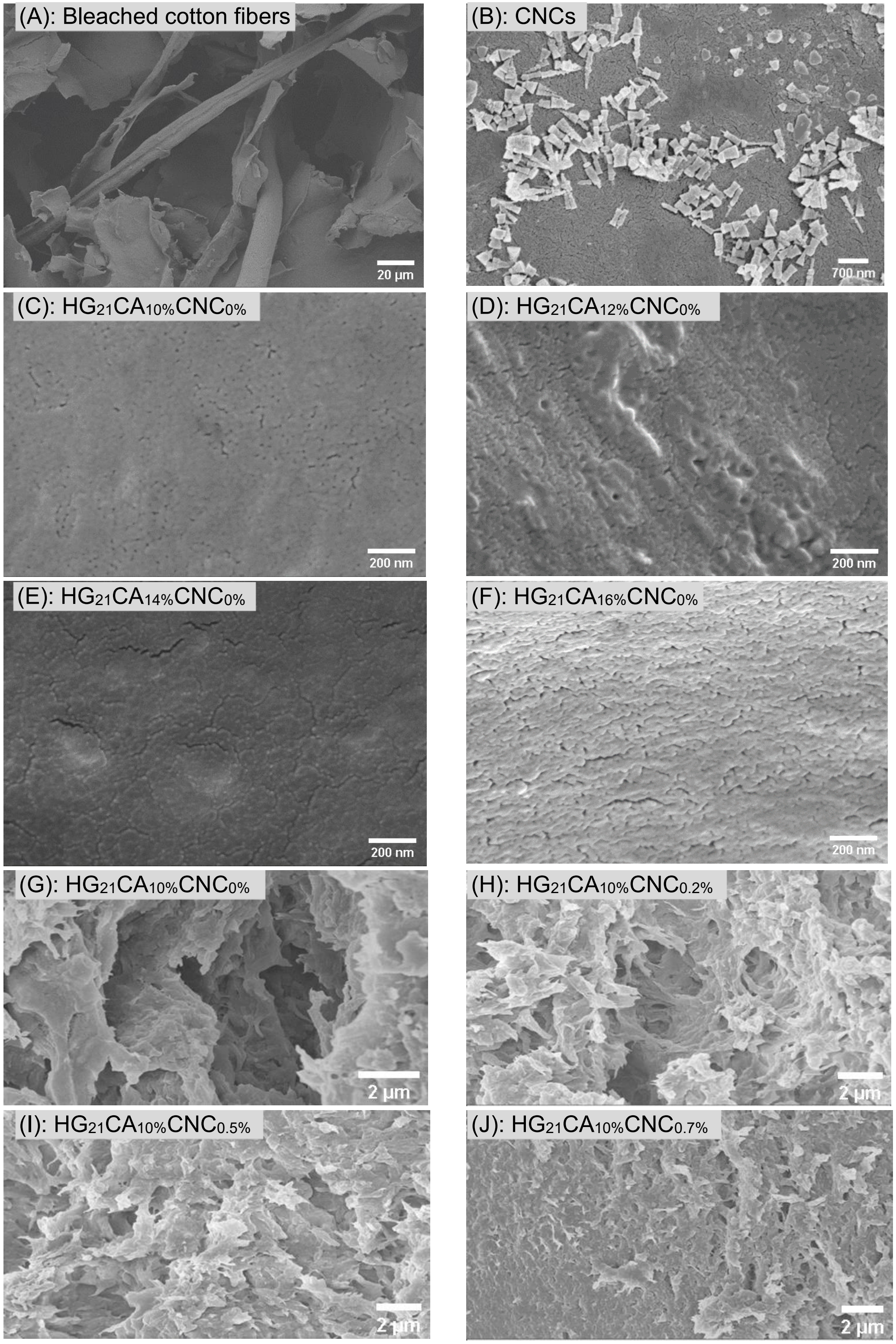

(A): Bleached cotton fibers
20 µm
(B): CNCs
700 nm
(C): HG21CA10%CNC0%
200 nm
(D): HG21CA12%CNC0%
200 nm
(E): HG21CA14%CNC0%
200 nm
(F): HG21CA16%CNC0%
200 nm
(G): HG21CA10%CNC0%
2 µm
(H): HG21CA10%CNC0.2%
2 µm
(I): HG21CA10%CNC0.5%
2 µm
(J): HG21CA10%CNC0.7%
2 µm

Fig. 7: FESEM images of (A) bleached cotton fibers, (B) CNCs, NaCMC/HEC hydrogels with a crosslinker CA (C) 10%, (D) 12%, (E) 14%, (F) 16%, and hydrogel nanocomposites with (G) 0% CNC, (H) 0.2% CNCs, (I) 0.5% CNCs, and (J) 0.7% CNCs.

4.7. Swelling Study

A hydrogel's water absorption (swelling) capacity is vital for its application in agriculture. Hydrogel acts as a water reservoir and releases water in a sustained and controlled manner to the plants. The attached hydrophilic groups, i.e., -OH, -COOH, to cellulose chains are responsible for ' 'hydrogel's capability to absorb water. The water swelling capacities of prepared hydrogels and CNCs-reinforced hydrogel composite are given in Figures 8A, 8B, and 8D. NaCMC/HEC -based hydrogels have shown ~ 1070% water absorption for NaCMC/HEC: 2/1 (figure 8A) and ~840% for a 3/1 ratio (figure 8B) using a 10% CA crosslinker. However, increasing the NaCMC/HEC (3/1) ratio in hydrogels reduces the water absorption capacity (figure 8B). It is probably due to the increased intramolecular bonds between hydroxyl (-OH) groups causing a reduction in available hydrophilic -OH groups for water absorption as increasing the NaCMC contents in hydrogels. All hydrogels absorbed water rapidly in the initial stage, and the water absorption reached equilibrium in about 12 h for all prepared hydrogels. The percentage (%) of CA crosslinker in hydrogels significantly affects the swelling capacity. The hydrogels' swelling capacity was markedly reduced by increasing the concentration of CA crosslinkers (10% to 16%) (figures 8A & 8B). It is due to the creation of more crosslinking points by increased CA between polymer chains resulting in enhanced crosslinking density and reduced pore sizes in the hydrogel network. The smaller pore sizes in the hydrogel network cause a reduction in the diffusion of water molecules into the network, reducing swelling capability.

Moreover, the swell ability of NaCMC/HEC- based hydrogels depends on the pH of the swelling medium. At higher pH (6.8) than the p*Ka* of the carboxylic groups (p*Ka* 4.5 – 5.5), the carboxylic acid (-COOH) groups get protonated to form carboxylate ions (COO^-) and the resulting electrostatic repulsion between negative charges cause increased swell ability of the hydrogel. However, further increasing the pH of the swelling medium, i.e., pH 9 and pH10, resulted in reduced water absorption (figure 8C). It is due to the increased concentration of ions in the medium, which acted against the electrostatic repulsion in the hydrogel. It is also responsible for the low osmotic pressure gradient between the hydrogel and the surrounding medium, resulting in reduced water absorption. At low pH (> p*Ka)*, i.e., pH 3, COO^- ions protonate to form -COOH causing a reduction in electrostatic repulsion leading to network shrinkage and lower water absorption.

The swelling ratios of CNCs-reinforced hydrogel composites with varying CNCs contents are shown in Figure 8D. It can be observed that the water absorption capabilities of hydrogel composite reduced with increasing CNC content. It may be due to the impenetrable crystalline structure of CNCs restricting the diffusion of water molecules into the network leading to lower water absorption.

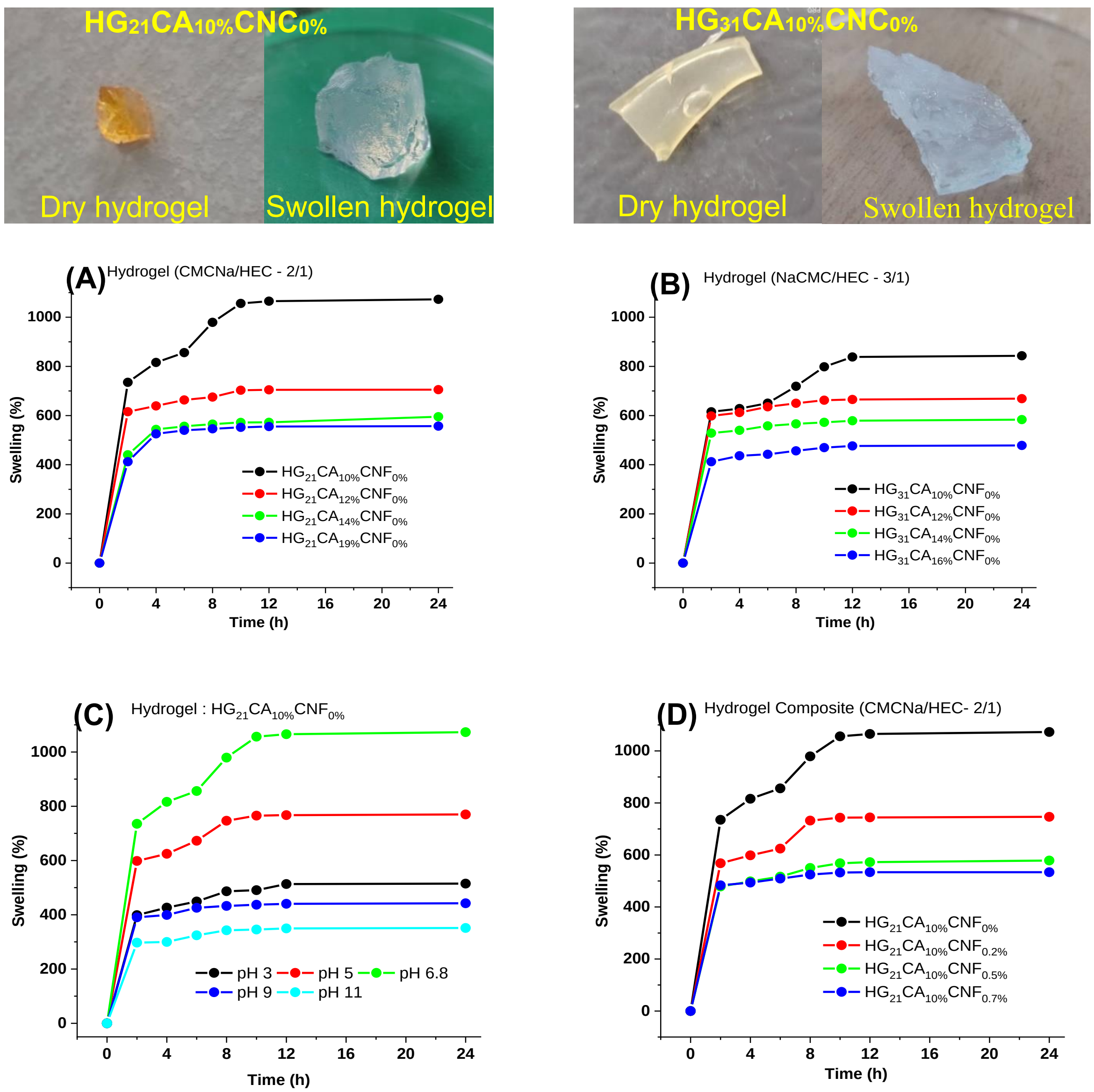


Fig. 8: swelling % of hydrogels (A) NaCMC/HEC :2/1, (B) NaCMC/HEC: 3/1, (C) in different pH mediums (pH: 3, 5, 6.8, 9, and 11), and (D) swelling % of hydrogel nanocomposites with 0%, 0.2%, 0.5%, and 0.7% CNCs.

4.8. Water Retention capability of hydrogels

It is crucial to evaluate the water retention behavior of NaCMC/HEC hydrogels for their agriculture applications. Hydrogels require to retain more water than the soil for such applications, where a hydrogel acts as a water reservoir that absorbs a significant amount of water and releases it to the ground and plants in a controlled and sustained manner. Water loss (evaporation) through hydrogels and soil was assessed periodically in open environmental conditions to evaluate water retention behavior. The water retention behaviors of the hydrogels (NaCMC/HEC – 2/1 and 3/1) and the soil are shown in Figures 9A and 9B. It can be observed from Figures 9A and 9B that the hydrogels needed thirteen (13) days to lose around 80% of water. In contrast, soil required nine (9) days for evaporation of 80% of water, suggesting better water holding capacity of the hydrogels than the soil. The hydrogel prepared with a 2/1 ratio of NaCMC/HEC and 16% of CA crosslinker shows relatively improved water retention capacity (75% water evaporation in 13 days) than the hydrogel prepared with a low concentration of CA crosslinker (~ 80% evaporation in 13 days) (figure 9A). It may be because of the formation of high crosslinking density and small pore size with a high concentration of CA crosslinker, which holds water molecules into the network and doesn't allow them to release out quickly. No significant distinction has been observed in the water retention capacity of the hydrogel prepared using a 3/1 ratio of NaCMC/HEC with different concentrations of CA crosslinker (figure 9B). Moreover, the photographs of water retention experiments for soil with and without hydrogel taken on days 1, 4, 8, and 13 are shown in Figure 10. The swollen hydrogel granules in the soil can be observed from the photographs, which confirm the hydrogels' water-holding and retaining capability. The soil with hydrogel seems more moist in visual appearance than the soil without hydrogel in the water retention experiment.

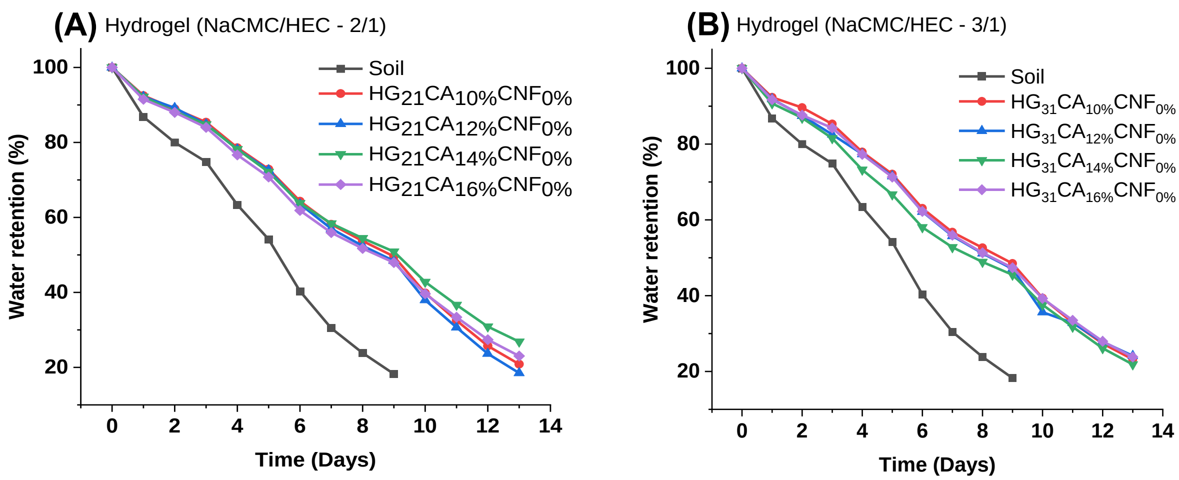


Fig. 9: water retention capacity of hydrogel prepared with (A) NaCMC/HEC: 2/1, and (B) NaCMC/HEC: 3/1.

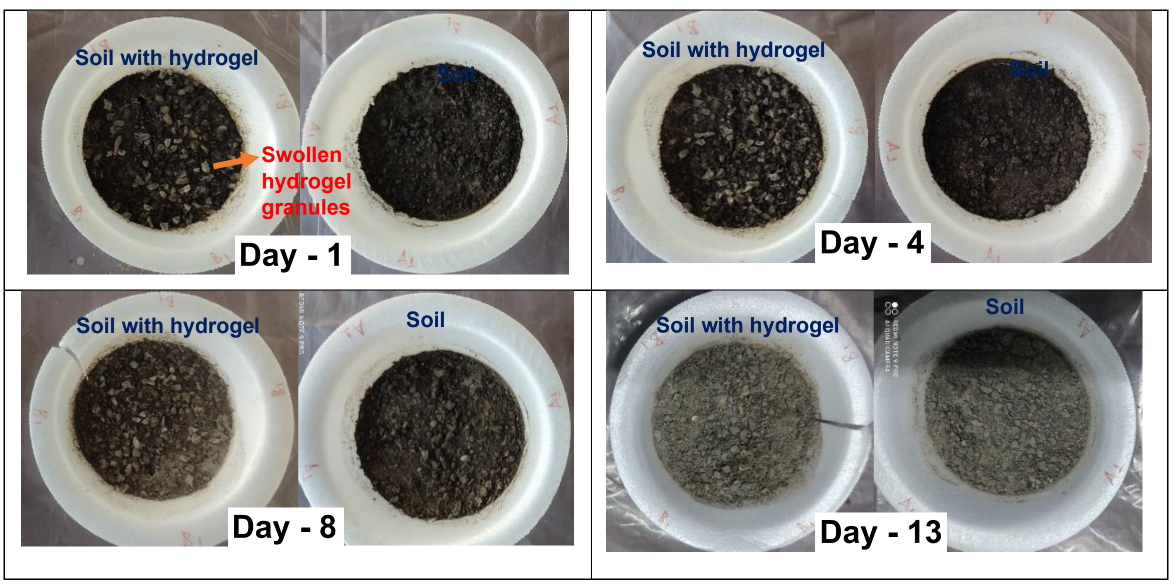


Fig. 10: photographs show water retention test of soil with and without hydrogel on day 1, day 4, day 8, and day 13.

4.9. Mechanical properties

Figure 11 demonstrates the mechanical strength of CNCs (0.2%, 0.5%, and 0.7%) reinforced hydrogel composites compared to the hydrogel without reinforcement. The mechanical analyses were performed for the hydrogel samples, demonstrating better-swelling properties, i.e., hydrogels with a 2:1 ratio of NaCMC/HEC and 10% CA. The mechanical analysis revealed improved tensile strength of hydrogel composites than the hydrogel without reinforcement (without CNCs). Increasing the CNC concentration from 0.2% to 0.7% in the hydrogel improved the mechanical strength of the hydrogel composite, indicating the reinforcing effect of crystalline CNCs. Moreover, the elongation property has also improved for hydrogel composites compared to hydrogel, pointing to the fragile and brittle nature of the hydrogel. The tensile strength, elongation, and modulus data are given in Table 2.

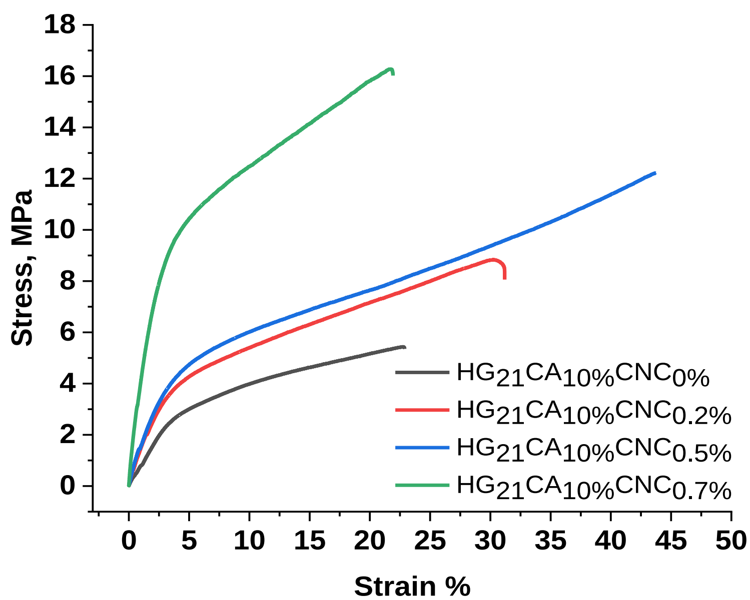


Fig. 11: stress-strain curve for the hydrogel and hydrogel nanocomposites.

Table 2: mechanical properties of hydrogel and hydrogel composites

Hydrogel	Thickness (mm)	Tensile Strength (MPa)	Elongation at break (%)	Modulus (MPa)
$HG_{21}CA_{10\%}CNF_{0\%}$	0.30	5.35	23	0.23
$HG_{21}CA_{10\%}CNF_{0.2\%}$	0.29	8.81	30	0.29
$HG_{21}CA_{10\%}CNF_{0.5\%}$	0.31	12.21	44	0.27

$HG_{21}CA_{10\%}CNF_{0.7\%}$	0.30	16.27	22	0.74

4.10. Biodegradation analysis

FTIR spectra in Figure 12A show the chemical structure changes (biodegradation) of NaCMC/HEC hydrogel during the soil burial test for 60 days. The intensity of peaks at 3432 cm^{-1} for -OH stretching and 2929 cm^{-1} for C-H aliphatic stretching, respectively, have reduced due to biodegradation. It indicates microorganisms' cleavage of OH and CH_2 bonds during the test. The carbonyl peak (C=O) of ester linkage at 1749 cm^{-1}, formed during crosslinking of CA and cellulose chains for the hydrogel, has also disappeared for degraded hydrogel. It reveals that biodegradation has destructed crosslinked ester linkages and formed simple molecules. Moreover, C-O stretching at 1085 cm^{-1} has also decreased as a result of degradation during the soil burial test. Figure 12B demonstrates hydrogel's appearance (photographs) before and after soil degradation. The color change and structural decomposition can be observed for a hydrogel sample after 15 days of the burial test. The notable change in structure morphology has been recorded after 60 days of the test, where the hydrogel sample's noticeable degradation and damaged integrity are observed.

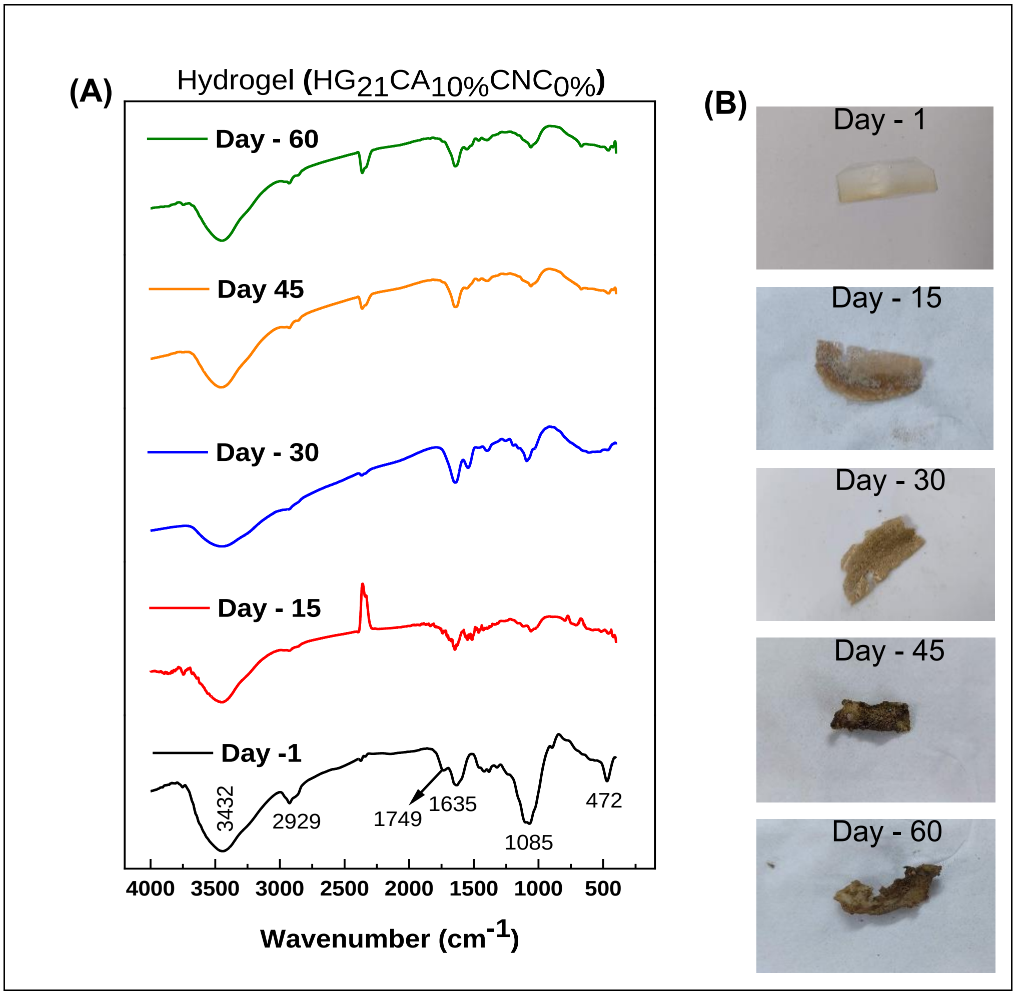


Fig. 12: FTIR spectra of NaCMC/HEC hydrogel (A) during soil burial test (day-1, day-15, day-30, day-45, and day-60), and (B) photographs of hydrogel during burial test.

5. Plant Growth study using hydrogel-modified soil and unmodified soil (control)

For this study, black clay soil (available in Tripura state) was used and modified with 2% (w% of total soil) of hydrogel granules (> 2mm). Healthy seeds of cucumber were planted in different pots of modified soil and unmodified soil (control) and observe the plant growth for 30 days. Different pots were watered (irrigated) in regular intervals, i.e., every 48 hr. As shown in Figures 13, 14, and 15.

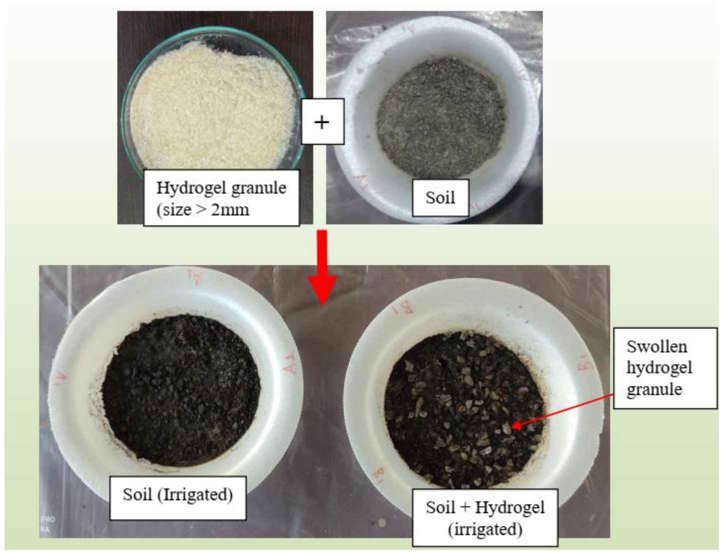


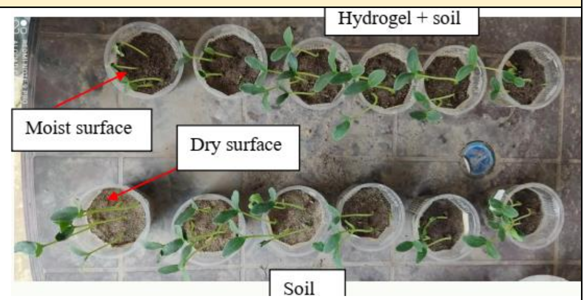
Fig. 13: 2% of hydrogel mixed with black clay soil (hydrogel-modified soil)

Figure 14 demonstrates the cucumber plant growths for the 4th, 6th, 10th, 20th, and 30th days in hydrogel-modified and controlled soil. Pictures are taken right before adding water to the plants at regular intervals. It can be observed that the surface of modified soil visually appears moist compared to controlled soil, indicating the water-holding capacity of hydrogel-modified soil. Moreover, on the 30th day, plants grown in modified soil seem greener and healthier.

After allowing the plants to grow for 30 days, plants growth was analyzed by performance indicators such as fresh weight (FW) and dry weight (DW) of the plants, total moisture content (MC) of the plants, root-to-shoot ratio (R/S) ratio, crop growth rate (CGR), total chlorophyll production (chlorophyll A and chlorophyll B), and net assimilation rate (NAR). Results demonstrate that the growth parameters for the plants grown in hydrogel-modified soil appear promising. The FW, MC, CGR, and NAR values are higher for modified soil than the controlled soil, indicating hydrogel has a positive impact on plant growth. The R/S ratio in modified soil is lower than in controlled one, which means root length in controlled soil is more than in modified soil. In contrast, shoot length for modified soil is more than for controlled soil. This is primarily because of the deeper growth of roots in controlled soil in search of water due to the unavailability of water on the upper part of the soil, hence longer roots but smaller shoots. Whereas, in modified soil, plant roots get enough water to grow (due to the water-holding capacity of the soil) in the upper part of the soil, resulting in smaller roots and longer shoots.

4th Day of Growth

6th Day of Growth



10th Day of Growth

20th Day of Growth

30th Day of Growth

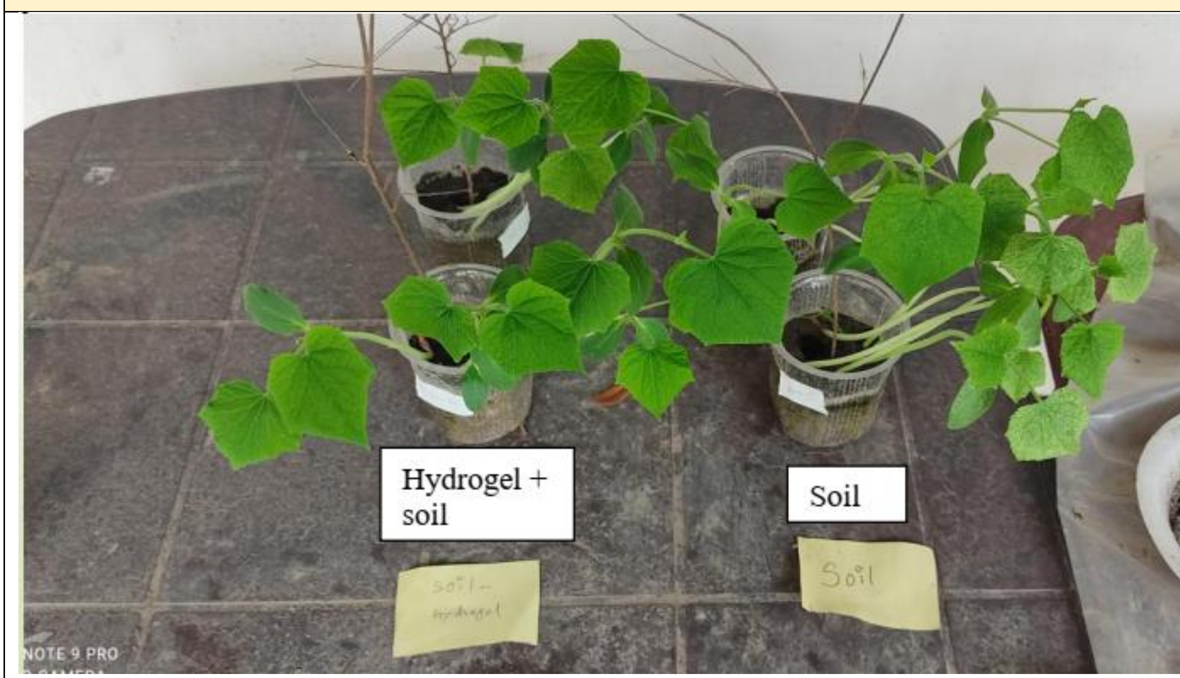


Fig. 14: cucumber plant growth in modified and unmodified soil for 4th, 6th, 10th, 20th, and 30th days

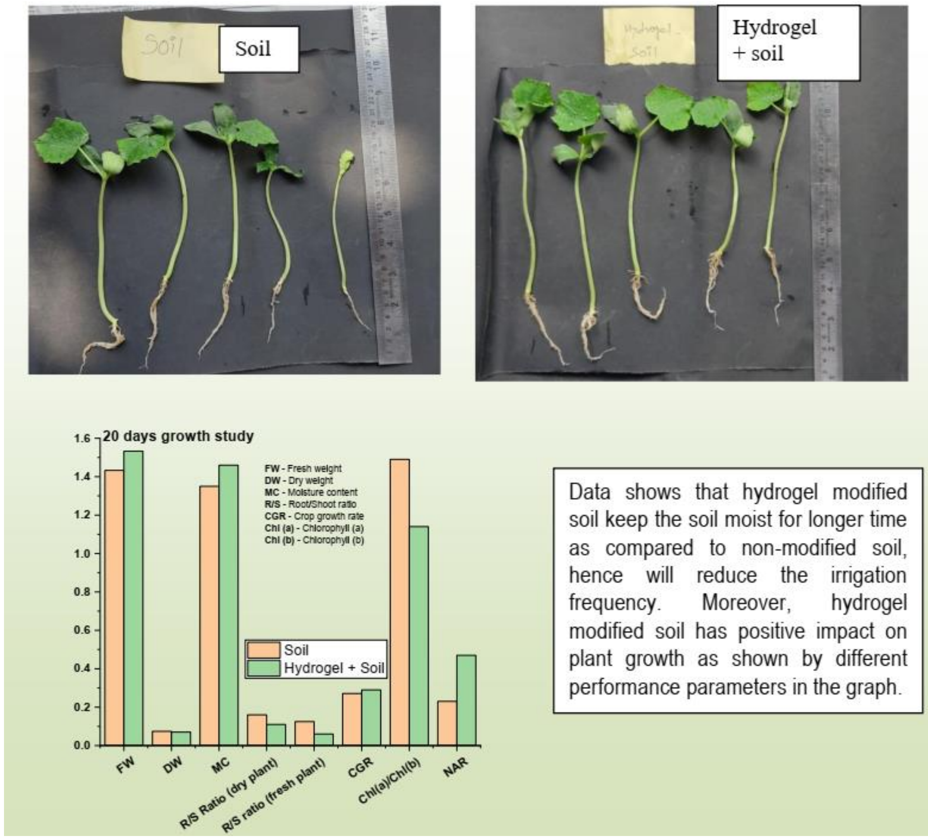


Fig. 15: plant growth parameters in modified and unmodified soil after 30^{th} days of growth