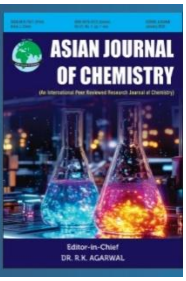
Asian Journal of Chemistry; Vol. 37, No. 9 (2025), 2183-2194

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2025.34270



Studies on the Slow Release of Urea and Water from Malonic Acid Crosslinked Sodium Carboxymethylcellullose–Hydroxyethyl Cellulose Superabsorbent Hydrogel for Potential Applications in Agriculture Sector

M. DAS*, B. KALITA and D.K. KAKATI

Department of Chemistry, Gauhati University, Guwahati-781014, India

*Corresponding author: E-mail: mitudas2603@gmail.com

Received: 16 June 2025 *Accepted*: 30 July 2025 *Published online*: 30 August 2025 AJC-22098

Superabsorbent hydrogels prepared from cellulose derivatives are gaining applications in the agricultural sector for controlled and slow release of nutrients and water to prevent nutrient loss and facilitate the prudent use of water. The present work reports the synthesis of superabsorbent hydrogel based on two cellulose derivatives, sodium carboxymethyl cellulose (CMCNa) and hydroxyl ethyl cellulose (HEC) with malonic acid (MA) as the crosslinker. The ratio of the two cellulose derivatives as well as the concentration of the crosslinker were varied to find out the most suitable ratio to yield the hydrogel with highest water retention capacity and most efficient encapsulation and slow release of urea. Hydrogel synthesized from HEC and CMCNa in the ratio 1:3 in the presence of 1% MA as the crosslinker had shown the best results. Further a comparative study with another crosslinker citric acid was also investigated and found that malonic acid crosslinked hydrogel showed better results.

Keywords: Superabsorbent hydrogels, Crosslinker, Water retention, Encapsulation, Slow release.

INTRODUCTION

Agriculture plays a dominant role in the economic well-being of a country. It has been estimated that by 2050, feeding a population of over nine billion people will require a 50% increase in agricultural productivity and a 15% increase in water demand [1]. To meet up the global food demand with concomitant minimization of adverse effects on the environment the agriculture sector needs innovations in the present practice of the use of fertilizers and irrigation [2]. The over use of chemical fertilizers to enhance food productivity is resulting in environmental problems arising out of nutrient leaching from soil and contaminating fresh water sources. However, slow release of fertilizers encapsulated in biodegradable polymers can address this issue by slowing down the nutrient release rate. Slow release of fertilizers can enhance the fertilizer usage efficiency, simultaneously delaying the nutrient release or even increasing the availability of nutrients over longer period of time, thereby mitigating the environmental issues associated with the fertilizer management [3-5]. For the production of various crops, nitrogen is one of the most essential macronutrients and urea is the most widely used fertilizer because it has high nitrogen content of 46%. But the efficiency of urea uptake by plants generally ranges under 50%. Due to the high solubility of the fertilizer, only a small percentage can be utilized by the plants paving the way for the loss of urea by leaching. This accounts for usage of high amount of urea which not only increases the cost but also creates environmental problems [6-8].

Agricultural sector is also highly dependent on the consumption of water and uses about 70% of fresh water all over the world. It has been estimated that by 2030, global water demand will increase by almost 50% putting a tremendous pressure on fresh water resources leading to severe water scarcity [9]. Hydrogels with ability to store and release water to soil at a slow rate may lead to better water management in agriculture. Environmental concerns and the need to conserve water have led to the search for biodegradable superabsorbent hydrogels for commercial agricultural applications. With the emergence of superabsorbent hydrogels as carriers of fertilizer and water, the challenges such as water scarcity, degradation in soil quality or the loss caused from excessive use of chemical fertilizers, has been controlled to a greater extent. Besides, the hydrophysical, physico-chemical or the biological environ-

---

ments of the soil, the soil water retention and release capacity, the nutrient use efficiencies or the quality of agricultural productivity can also be enhanced by the application of hydrogel as a soil conditioner [10-12]. In the agricultural sector, hydrogels can lead to a substantial reduction in water consumption, prevention of plant mortality and enhancement of soil water retention capacity [13].

Superabsorbent hydrogels consist of cross-linked hydrophilic networks, developed from both natural and synthetic polymers. Due to the presence of large number of hydrophilic groups (carboxyl, amino, amide, hydroxyl and sulfonic groups) on their polymer backbone, high polymer chain flexibility, extra ionic crosslinks, porous structure and the availability of large free volume between polymeric chains results in very high swelling capacity of superabsorbent hydrogels. They can imbibe more than 100 times their dry weight of water. Currently hydrogels have found wide applications in the different sectors including agriculture [14-17], pharmaceuticals and biomedical appliances [18-22], food industry [23-26], baby diapers [27,28], waste water treatment [29], *etc.* But most of the commercially available hydrogels are acrylate-based which are non-biodegradable or degrade very slowly leading to the possibility of environmental pollution. Furthermore, there is also concern about their toxicity [30]. Therefore, for applications in the agricultural sector the first choice is the hydrogel from biodegradable natural polymers. Cellulose based hydrogels are endowed with the properties of biocompatibility, biodegradability, water solubility and low cost. Several cellulose derivatives are used for the preparation of hydrogels. Two such cellulose derivatives are sodium carboxymethyl cellulose and hydroxyethyl cellulose. Sodium carboxymethyl cellulose has a large number of carboxymethyl groups on the cellulose backbone and to prevent intramolecular crosslinks within the sodium carboxymethylcellullose molecules, hydroxyethyl cellulose is used in combination to promote intermolecular crosslinking stabilizing the polymer structure [31,32].

The present work proposes to develop the superabsorbent hydrogels from CMCNa and HEC. To increase the number of crosslinks leading to strengthening of hydrogel, malonic acid and citric acid were used as the crosslinker. The crosslinking effect results from the formation of diester bridges between the two polymeric components of the hydrogel and the crosslinker molecules [33,34]. The synthesized hydrogels will be investigated to assess their swelling efficiency under different pH, water and urea uptake capability and slow release pattern of absorbed urea to assess its suitability as an effective material acting as water and urea reservoir for their controlled release to the soil. Hydrogels using citric acid as crosslinker was synthesized to identify the better crosslinker between malonic acid and citric acid.

EXPERIMENTAL

Sodium carboxymethyl cellulose (CMCNa, Merck) and hydroxyethyl cellulose (HEC, Sigma-Aldrich), malonic acid (MA, Loba Chemie), citric acid (CA, Rankem), hydrochloric acid (HCl, Qualigen) and sodium hydroxide (NaOH, SRL, India) were used as received. Urea used for loading and release study was procured from Emparta ACS. Double distilled water was used in all the experiments.

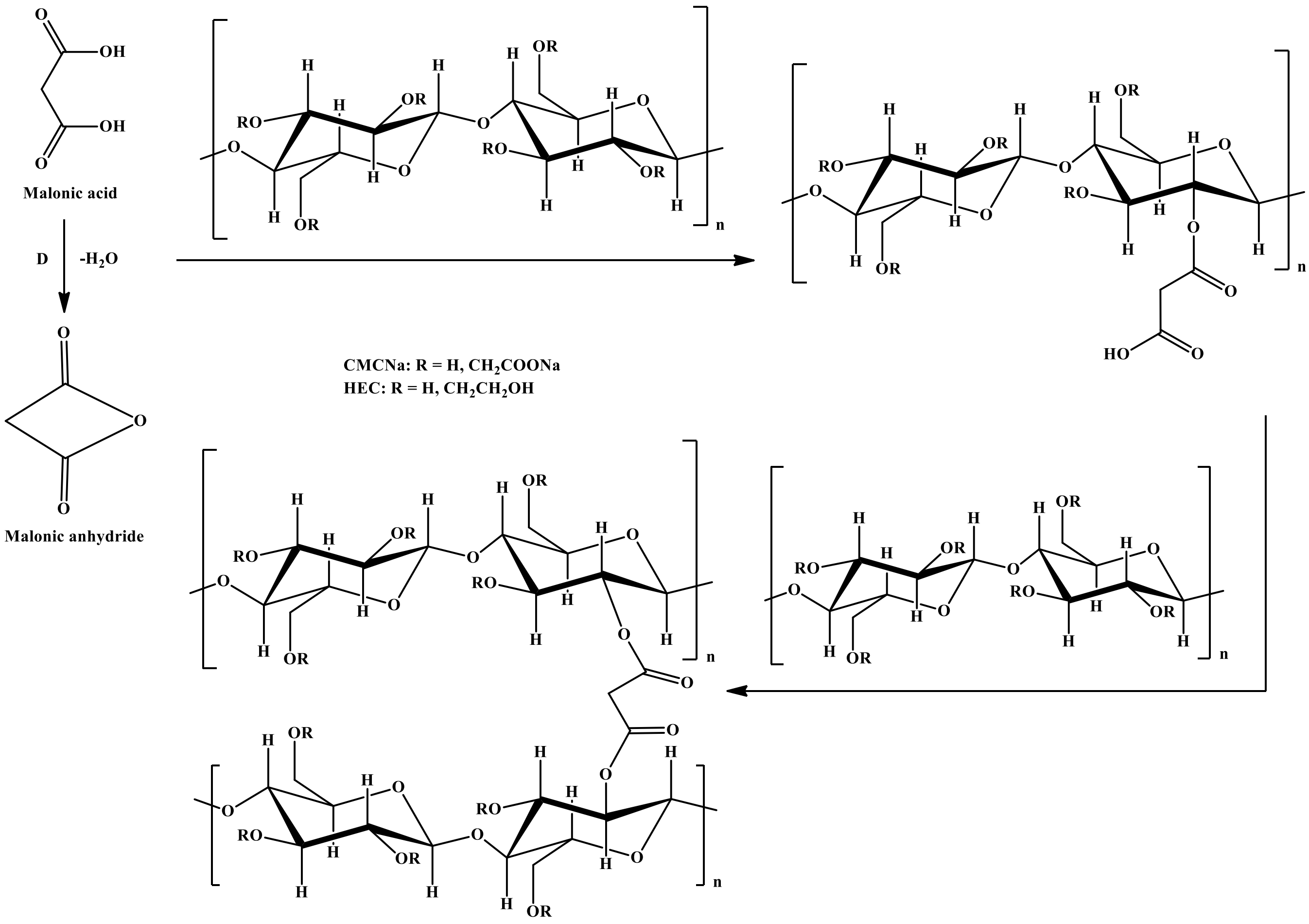
Fourier transform infrared (FTIR) spectra (4000-500 cm^{-1}) of the materials were recorded directly in a spectrophotometer (BRUKER ALPHA II), with attenuated total reflectance (ATR) crystal sampler. The thermogravimetric analyses (TGA) of the hydrogel samples were done with thermo gravimetric analyzer (TGA/DSC-1, Mettler Toledo and Mettler Toledo TGA-2) under N_2 atmosphere. The surface morphology of the hydrogel samples in the form of thin films were examined in a scanning electron microscope (ZEISS Sigma-300).

Synthesis of hydrogel: For the preparation of samples of hydrogel, the total concentration of the two components CMCNa and HEC was maintained at 2% (w/v), with a variation in their ratio as shown in Table-1. The procedure followed is a partially modified process of Demitri *et al.* [35]. The required amount of HEC was added to distilled water under stirring at 300 rpm at room temperature followed by addition of calculated amount of CMCNa after 15 min. The mixture was stirred for about 28 h to get a clear solution. It was followed by the addition of crosslinking agent MA to the viscous solution and stirring continued for about 0.5 h. The resultant product was transferred to a thick glass mould and dried under vacuum at 40 ºC for 24 h. Then the temperature was increased to 80 ºC and maintained at that temperature for 24 h for completion of the crosslinking process. After that the hydrogel was stored in a vacuum desiccator for further analysis. By following the same procedure hydrogel samples crosslinked with CA were also prepared (**Scheme Ia-b**). The hydrogel samples prepared were designated as $H(x:y)_{C_z}$ and $H(x:y)_{M_z}$ where x, y in the parenthesis denotes the ratio of HEC:CMCNa and C_z, M_z denote the amount of crosslinker used.

TABLE-1
COMPOSITION OF HEC-CMCNA BASED HYDROGELS

Sample	HEC/CMCNa ratio	Concentration of cross-linker (%)
$H(1:3)_0$	1:3	0
$H(1:3)_{M_1}$	1:3	1
$H(1:3)_{M_2}$	1:3	2
$H(1:3)_{M_5}$	1:3	5
$H(1:3)_{M_{10}}$	1:3	10
$H(1:3)_{M_{20}}$	1:3	20
$H(1:1)_{C_1}$	1:1	1
$H(1:2)_{C_1}$	1:2	1
$H(2:1)_{C_1}$	2:1	1
$H(1:3)_{C_1}$	1:3	1
$H(3:1)_{C_1}$	3:1	1
$H(1:1)_{M_1}$	1:1	1
$H(1:2)_{M_1}$	1:2	1
$H(2:1)_{M_1}$	2:1	1
$H(3:1)_{M_1}$	3:1	1

Preparation of urea-loaded hydrogel: For loading of urea, a concentrated (2% w/v) aqueous solution of urea was prepared in distilled water and a pre-weighed hydrogel sample was immersed in the above solution for 72 h at room temperature without stirring. Thereafter the hydrogel sample was washed with distilled water to remove urea adhered to the surface if any and dried at 40 ºC. The urea loaded sample was



Scheme-Ia: Cross-linking by malonic acid

then kept in a vacuum desiccator and weighed accurately till constant weight was obtained. The loading capacity of the hydrogel was calculated using the following expression:

$$\text{Loading capacity (\%)} = \frac{W}{W'} \times 100 \tag{1}$$

where W′ the weight of dry hydrogel before loading; W is the weight of net urea loaded obtained by subtracting the weight of dry hydrogel from the weight of the urea loaded hydrogel.

Swelling index studies: Swelling index of hydrogel was evaluated in three different mediums *viz.*, neutral (distilled water), acidic (0.1 M HCl) and basic (0.1 M NaOH). A completely dried pre-weighed hydrogel sample was immersed in a certain known volume of the respective solution at room temperature. The sample was taken out periodically and excess surface adhered water was wiped using a tissue paper. The sample was thereafter weighed accurately using an electronic balance WENSAR, HPB310, followed by immersing it again in the respective swelling medium. The swelling index of the hydrogel was determined using the following equation:

$$\text{Swelling index (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \tag{2}$$

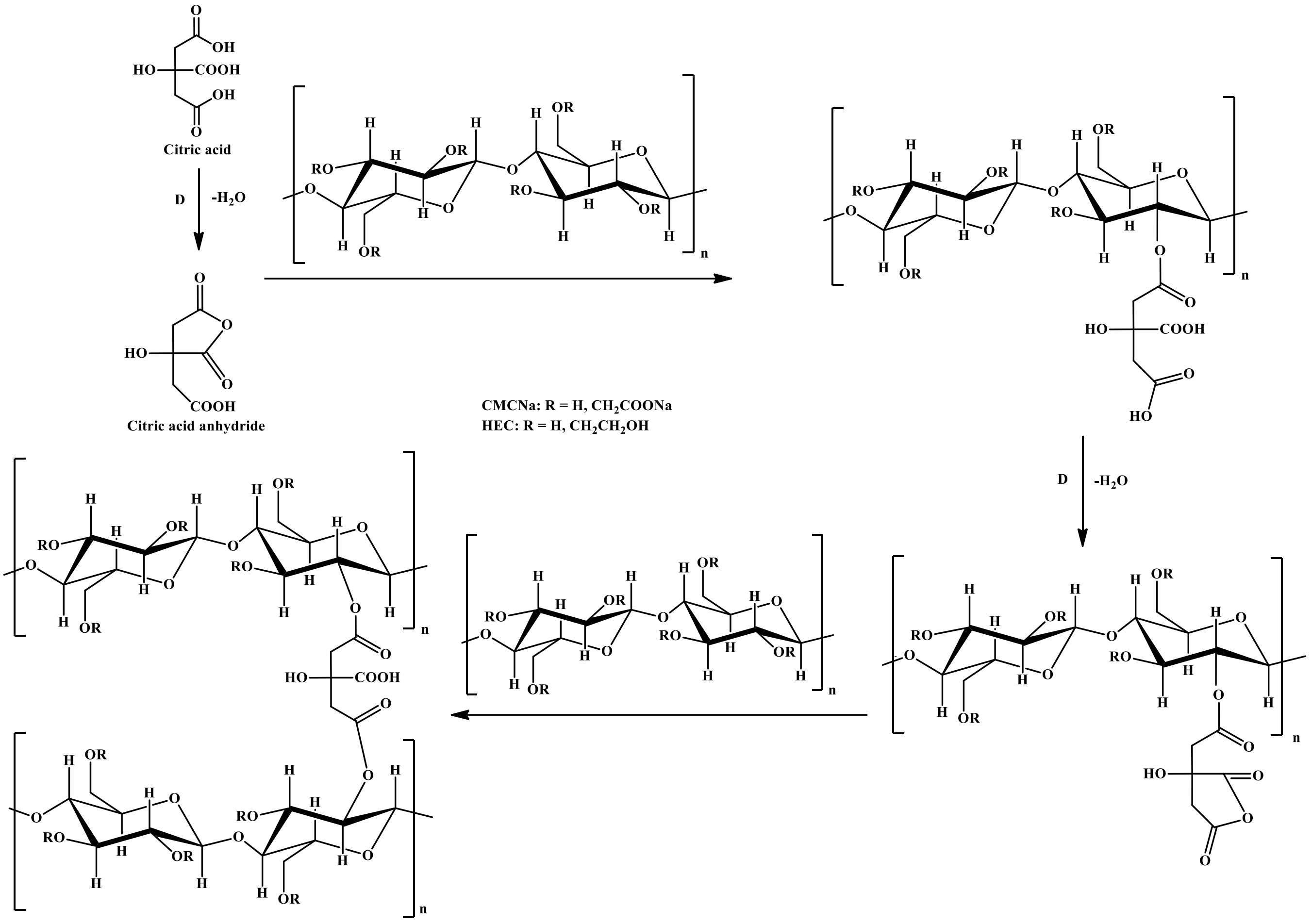
where W_0 is the weight of dry hydrogel and W_1 is the weight of swollen hydrogel.

Water holding capacity (WH): The water holding capacity of hydrogel in soil was studied to ascertain its efficiency to retain and slow release of water in soil for its potential application as water reservoir in soil [36,37]. In order to carry out the experiment, soil sample was collected from the lawn of Department of Chemistry, Gauhati University and also from a local hillside area of Kamrup Metropolitan district. The soil samples collected from both the sites were sandy soils. For this study, three beakers were taken, each filled up with a known amount of soil (10 g). A known amount of pre-weighed hydrogel sample was mixed with soil samples in two of the beakers separately. No hydrogel was added to the third beaker which acts as the blank. The three soil samples were carefully poured in three different glass tubes of diameter 2 cm sealed with filter paper at one end. Water was slowly poured from the top of the tube until the filter paper at the bottom just got wet and the glass tube was weighed again. The water holding percentage (%WH) was then calculated using the following equation:

$$\text{Water holding (\%)} = \frac{W_2 - W_1}{W_0} \times 100 \tag{3}$$

where W_0 is the weight of pure soil; W_1 is the weight of soil sample mixed with hydrogel and and W_2 is the weight of soil sample mixed with hydrogel after addition of water.

Urea release study: The slow release of urea from the loaded hydrogel was determined as previously reported work by Teodorescu *et al.* [38]. For the urea release study, a known



Scheme-Ib: Cross-linking by citric acid

amount of the loaded hydrogel sample was taken and immersed in 100 mL of distilled water at room temperature without stirring. An amount of exactly 2 mL was taken out at different time interval, transferred to a pre-weighed petri dish and dried in an oven at 60 ºC. The volume was made up by adding 2 mL of distilled water each time. After complete drying, the petri dish was reweighed until constant weight was obtained and the amount of fertilizer released was determined gravimetrically. The percentage of urea released (UR) was determined using the following equation:

$$\text{UR }(\%) = \frac{(\Delta W)_n \times \frac{[100-(n-1)\times 2]}{2} + \sum_{i-1}^{n=1}(\Delta W)_i}{W_0} \qquad (4)$$

where (ΔW) is the weight of the fertilizer released in the ith 2 mL sample solution; W_0 is the initial amount of fertilizer present in the urea loaded sample determined by subtracting initial weight of the hydrogel before loading from the urea loaded hydrogel.

RESULTS AND DISCUSSION

Synthesis of hydrogel: Hydrogel samples were prepared from two cellulose derivatives, CMCNa and HEC, mixed in varying proportions to find out the best composition leading to formation of hydrogel with the desired properties. The two crosslinking agents MA and CA were also evaluated to choose the one leading to better products. The compositions of synthesized samples are shown in Table-1.

FTIR studies: The FTIR spectra of citric acid (CA), malonic acid (MA), hydroxyethyl cellulose (HEC) and carboxymethyl cellulose sodium salt (CMCNa) are shown in Fig. 1a, while the spectra of non-crosslinked and citric acid (CA) crosslinked hydrogel films are displayed in Fig. 1b. The FTIR spectra of malonic acid (MA) crosslinked hydrogel films are shown in Fig. 1c. The broad peak at 3371 cm^{-1} and the peaks at 2918 cm^{-1}, 1584 cm^{-1} can be attributed to the stretching vibration of –OH, CH$_2$ asymmetric stretching and carboxylate, C=O stretching, respectively in the spectrum of CMCNa. The absorption peaks observed at 1412 cm^{-1}, 1324 cm^{-1} and 1028 cm^{-1} correspond to the symmetrical stretching of -COO$^-$ groups, CH-O-CH$_2$ stretching and C-O-C stretching on the polysaccharide skeleton respectively. The spectrum of HEC displays a broad peak at 3360 cm^{-1} corresponding to –OH stretching vibration. The peaks at 2880 cm^{-1}, 1640 cm^{-1}, 1330 cm^{-1} and 1032 cm^{-1} can be attributed to the C-H stretching vibrations of methylene group, asymmetric COO$^-$ stretching, C-H deformations and C-O stretching vibrations respectively. The IR peaks of MA are observed at 2916 cm^{-1}, 1703 cm^{-1}, 1419 cm^{-1}, 1188 cm^{-1} and 906 cm^{-1} which correspond to C-H stretching vibrations of methylene group, C=O stretching, symmetric COO$^-$ stretching, C-O-C stretching and bending vibration of

–OH in the acid, respectively. The IR peaks of CA are observed at 3297 cm^{-1}, 2866 cm^{-1}, 1703 cm^{-1}, 1416 cm^{-1}, 1223 cm^{-1} and 1095 cm^{-1} respectively, which can be attributed to the stretching vibration of –OH, C-H stretching vibrations of methylene group, carboxylate, C=O stretching, symmetric COO^{-} stretching, C-O stretching and C-O-C stretching, respectively. Comparing the non-crosslinked hydrogel with that of the crosslinked samples, a displacement in the peak for –OH stretching was observed which indicates the involvement of -OH group in the crosslinking process. Further it was observed that the extent of change observed in the shape and absorption frequency of the OH peak is dependent on the amount of the crosslinking agents. Moreover, a change was observed in the peak due to C=O of the carboxyl group in the crosslinker, after formation of the hydrogel indicating formation of ester crosslinks [32,33,39-44].

TGA studies: The thermal behaviour of CMCNa, HEC and non-crosslinked hydrogel sample (NC) are shown in Fig. 2a, while the MA crosslinked hydrogel samples are shown in Fig. 2b, respectively. The thermogram of CMCNa and HEC displayed two stages of mass loss. The first stage was observed between 40-144 ºC with a 16% weight loss and 40-90 ºC with 10% mass loss for CMCNa and HEC respectively, which can be attributed to the dehydration of weakly adsorbed water molecules in the samples. The second stage of degradation was observed between 233-312 ºC with 42.2% weight loss and 256-376 ºC with 82% weight loss for CMCNa and HEC. From the major weight loss pattern, it can be stated that CMCNa is thermally more stable than HEC. The major weight loss for the non-crosslinked hydrogel sample was observed between 254-310 ºC with 40% weight loss. From the thermogram of 1% MA, 2% MA, 5% MA, 10% MA and 20% MA crosslinked hydrogel samples, the major weight loss was observed between 270.8-324.7 ºC, 204-327 ºC, 181.2-327 ºC, 182-329 ºC and 37-343 ºC with a weight loss of 40.7%, 42%, 44.7%, 42.7% and 58% respectively. The thermal stability of the prepared hydrogel films was improved compared to the non-crosslinked hydrogel film due to the formation of crosslinks within the polymeric networks [39,41,42,45].

Morphology studies: The surface morphology of the hydrogel was studied by the scanning electron microscopy to investigate if any, the effect of amount of crosslinker in the surface morphology. Fig. 3 displays the SEM images of (a) non-crosslinked hydrogel and (b), (c), (d), (e) and (f) crosslinked hydrogel with 1%, 2%, 5%, 10% and 20% MA respectively. The hydrogel used had HEC-CMCNa in the 1:3 ratios.

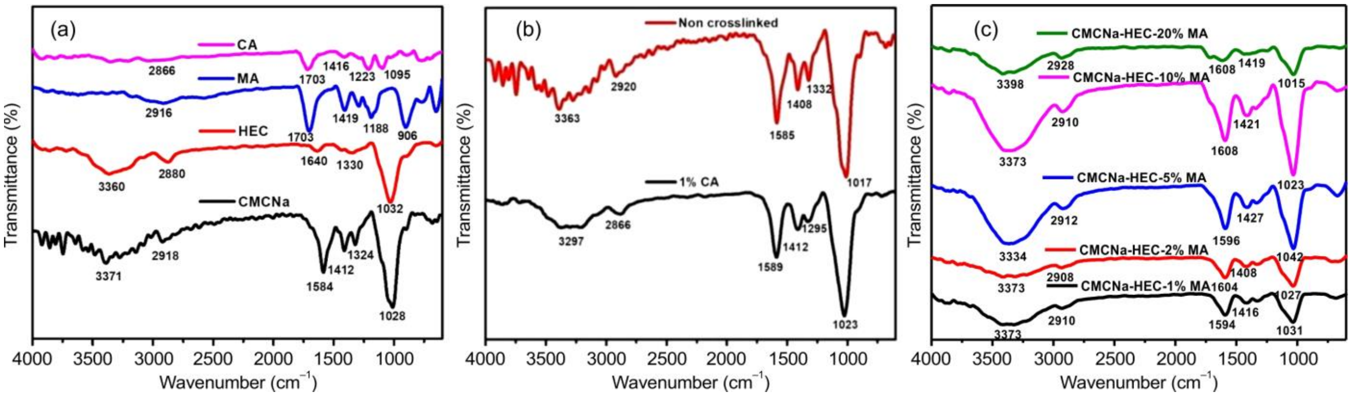


Fig. 1. FTIR spectra of (a) CA, MA, HEC, CMCNa (b) non-crosslinked and CA cross-linked hydrogel (c) MA crosslinked hydrogel

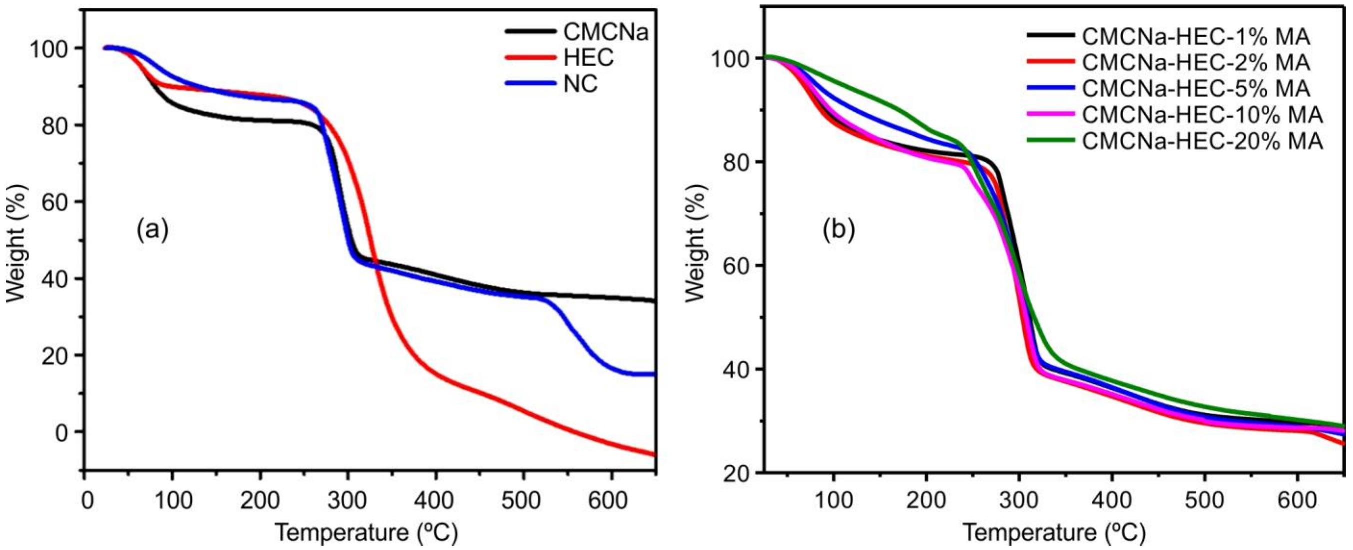


Fig. 2. (a) TGA curve of CMCNa, HEC and non-crosslinked (NC) hydrogel film (b) TGA curve of MA crosslinked hydrogel films with 1:3 HEC-CMCNa ratios

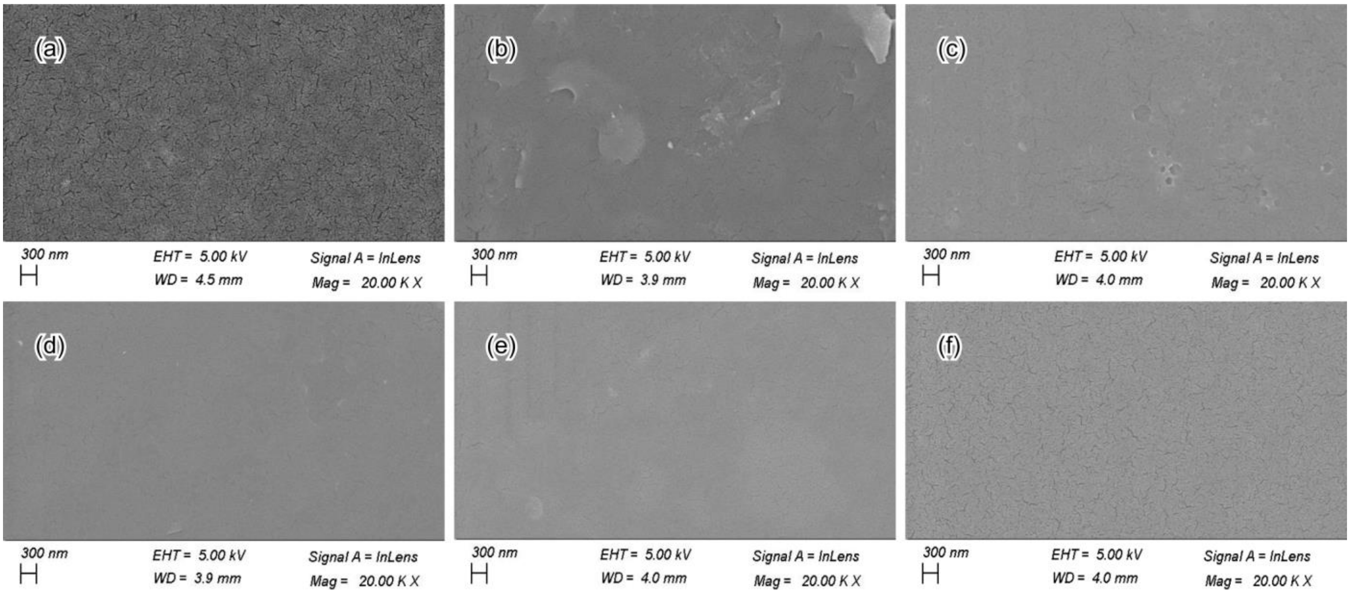


Fig. 3. SEM images of (a) non-cross linked hydrogel and cross linked (b) H(1:3)$_{M_1}$, (c) H(1:3)$_{M_2}$, (d) H(1:3)$_{M_5}$, (e) H(1:3)$_{M_{10}}$, (f) H(1:3)$_{M_{20}}$, hydrogel samples

Bulk density and the number of cavities present in the hydrogel are the two main factors which affect its absorption capacity. Greater the bulk density, smaller will be the absorption capacity and higher the number of cavities; greater will be the absorption capacity. As can be seen from the SEM-images, the non-crosslinked hydrogel has a homogenous surface whereas a rough and porous structure can be clearly seen at for 1% MA and 2% MA crosslinked hydrogel films which is not regularly shaped. Pore structure plays an important role in diffusion of water molecules and the pore structures observed for the hydrogel with lower concentration of the crosslinker are in accordance with the swelling degree, which decreased significantly as the percentage of crosslinker was increased. With increase in concentration of the crosslinker, the surface of the hydrogel film gradually becomes smoother and shows more rigid and compact surface morphology as MA forms covalent and intermolecular hydrogen bonds between the polymeric networks *via* crosslinking [40,46].

Swelling studies of hydrogels: The swelling behaviour of the hydrogels was studied in neutral (distilled water), acidic (0.1M HCl) and basic (0.1 M NaOH) medium. The values of swelling index in neutral and acidic medium are presented in Tables 2 and 3, respectively. Swelling behaviour of the hydrogel in basic medium could not be studied as the hydrogel attained maximum swelling with attended degradation immediately on immersion. With an increase in pH of the external solution, the swelling ratio was observed to increase. This can be attributed to dissociation of the carboxylic groups present on the CMCNa polymeric network, which is dependent on the pH of surrounding medium [30].

Swelling behaviour of hydrogel is affected by the pore size present within the polymeric network which is related to

TABLE-2
SWELLING INDEX OF DIFFERENT COMPOSITIONS OF HEC-CMCNA BASED HYDROGELS

Sample	HEC/CMCNa ratio	Concentration of crosslinker (%)	Swelling index (%) (neutral medium)				
			5 min	10 min	15 min	20 min	25 min
H(1:1)$_{C_1}$	1:1	1	338	1175	2748	3883	–
H(1:2)$_{C_1}$	1:2	1	1067	3167	4775	6285	–
H(2:1)$_{C_1}$	2:1	1	271	485	775	1117	1885
H(1:3)$_{C_1}$	1:3	1	1552	3419	5131	7044	–
H(3:1)$_{C_1}$	3:1	1	254	530	1061	1381	–
H(1:1)$_{M_1}$	1:1	1	384	272	5587	7700	–
H(1:2)$_{M_1}$	1:2	1	1364	3741	6197	8129	–
H(2:1)$_{M_1}$	2:1	1	400	1208	2720	4376	5816
H(3:1)$_{M_1}$	3:1	1	172	362	655	1134	1903
H(1:3)$_{M_1}$	1:3	1	6120	8317	10460	11277	–
H(1:3)$_{M_2}$	1:3	2	2058	2550	2608	2727	2880
H(1:3)$_{M_5}$	1:3	5	244	251	256	261	268
H(1:3)$_{M_{10}}$	1:3	10	140	156	180	200	224
H(1:3)$_{M_{20}}$	1:3	20	73	93	120	133	160

TABLE-3
SWELLING INDEX OF THE DIFFERENT COMPOSITIONS OF HEC-CMCNA IN ACIDIC MEDIUM

Sample	HEC/CMCNa ratio	Concentration of crosslinker (%)	Swelling index (%)				
			5 min	10 min	15 min	20 min	25 min
H(1:1)$_{M_1}$	1:1	1	237	507	673	710	797
H(1:2)$_{M_1}$	1:2	1	326	531	689	720	732
H(2:1)$_{M_1}$	2:1	1	316	658	867	983	1204
H(3:1)$_{M_1}$	3:1	1	225	442	668	832	1028
H(1:3)$_{M_1}$	1:3	1	607	943	1143	1321	1414
H(1:3)$_{M_2}$	1:3	2	347	416	437	458	500
H(1:3)$_{M_5}$	1:3	5	169	177	188	208	238
H(1:3)$_{M_{10}}$	1:3	10	94	100	112	124	141
H(1:3)$_{M_{20}}$	1:3	20	59	62	69	79	90

the density, type, rigidity of the crosslinker used and also the nature of the hydrogel. It also depends on the kind, charge, concentration of ions and ionic strength of the solution [37]. The swelling studies were done in detail by changing the crosslinker, as well as the concentration of the crosslinker, time of immersion and also the HEC:CMCNa ratio. The concentration of crosslinker played a significant role in swelling ability of the hydrogels. It forms 3D polymeric network connecting the polymer chains leading to the formation of pores within the matrix. Experimental data revealed that for the hydrogel with 1:3 ratio of HEC:CMCNa, the swelling index changed with concentration of crosslinking agent MA (by weight of the polymer), in the order 20% < 10% < 5% < 2% < 1%, respectively in the aqueous medium, which is shown in Fig. 4a. The swelling index was found to be the highest, 11277%, at a crosslinker concentration of 1% for MA at about 20 min after which the material started to degrade. The results observed were in accordance with Flory's Network theory. On increasing the crosslinker concentration, crosslinking density between the polymeric network increases leading to a rigid structure that cannot be expanded to hold large quantity of water [47,48].

The dependence of swelling behaviour of the hydrogel on the ratio of the two constituent cellulose derivatives, CMCNa and HEC and the two crosslinking agents MA and CA was also investigated and results are shown in Fig. 4b-d. While maintaining the ratio of HEC and CMCNa as 3:1, 2:1, 1:1, 1:2, 1:3, the effect of crosslinker MA and CA on the swelling was investigated. It was observed that in every case hydrogel with MA as the crosslinker exhibited higher swelling index, as shown in Fig. 4a-b. The maximum swelling was observed with 1% MA in the hydrogel with the ratio of HEC to CMCNa at 1:3, as shown in Fig. 4c. The increasing order of swelling index follows the trend in the order 3:1 < 2:1 < 1:1 < 1:2 < 1:3 of the HEC:CMCNa ratio in the hydrogel. Swelling index increased with increase in the concentration of CMCNa and decrease in the concentration of HEC in the mixture. Although the presence of HEC is an important to avoid the formation of intramolecular crosslinks among CMCNa molecules, it was observed that there is an optimum concentration of HEC in a HEC-CMCNa mixture ensuring enough stability to the material while giving the maximum swelling index [43].

Study of swelling index in acidic medium: In acidic medium, two aspects were investigated. The ratios of HEC to CMCNa were varied keeping the amount of crosslinker MA constant. It was observed that even in acidic medium, the maximum swelling was observed in the hydrogel with 1:3 ratios of HEC and CMCNa (Fig. 5a). Then keeping the ratio of HEC to CMCNa at 1:3, the amount of MA was varied and the results are presented in Fig. 5b. The highest swelling was observed at 1% MA. However, the extent of swelling was lower in acidic medium than in neutral medium (Table-3), since at low pH, Na^+ ions of carboxymethyl group are replaced by hydrogen ion decreasing ionization with resultant decrease of negative charges on the polymeric backbone. This will reduce the ionic "Donnan type" contribution to the corresponding hydrogel equilibrium swelling capacity; thereby lower the swelling index of the hydrogel [30]. Further, the chloride ions will also compete with water molecules for the voids in the hydrogel network (WH).

Water holding capacity of hydrogel in soil: To evaluate the possibility of the hydrogel as the slow release source of water, it is necessary to understand the water holding capacity of the soil containing the hydrogel. All together five samples with MA as the crosslinker [H(1:3)$_{M_1}$, H(1:3)$_{M_2}$, H(1:3)$_{M_5}$, H(1:3)$_{M_{10}}$, H(1:3)$_{M_{20}}$] and one sample with CA as the crosslinker H(1:3)$_{C_1}$ were investigated. The water holding capacities were studied in detail by considering different factors like effect of change in crosslinker concentration, effect of change in amount of the hydrogel and effect of crosslinker in two different soil samples (Fig. 6a-d).

To study the effect of change in crosslinker concentration, effect of crosslinker and effect of change in amount of added hydrogel on WH capacity, the soil sample was collected from the lawn of Department of Chemistry, Gauhati University. The WH capacity of the untreated soil was 36.05% but increased on addition of 0.3% (w/w) hydrogel to 10g of the soil sample. The WH values were found to be 47.54%, 40.83%, 39.41%, 38.66%, 38.18% for samples H(1:3)$_{M_1}$, H(1:3)$_{M_2}$, H(1:3)$_{M_5}$, H(1:3)$_{M_{10}}$, H(1:3)$_{M_{20}}$ and 41.29% for sample H(1:3)$_{C_1}$, respectively. The WH capacity of the soil was found to decrease with increase in concentration of the crosslinker. With rise in crosslinker concentration, there will be a rise in crosslinking density and this will lower the water holding capacity [8]. From Fig. 6a-b, it is evident that hydrogel with 1% MA as the crosslinker showed better WH capacity in comparison to that with 1% CA crosslinked hydrogel. The rise in WH for

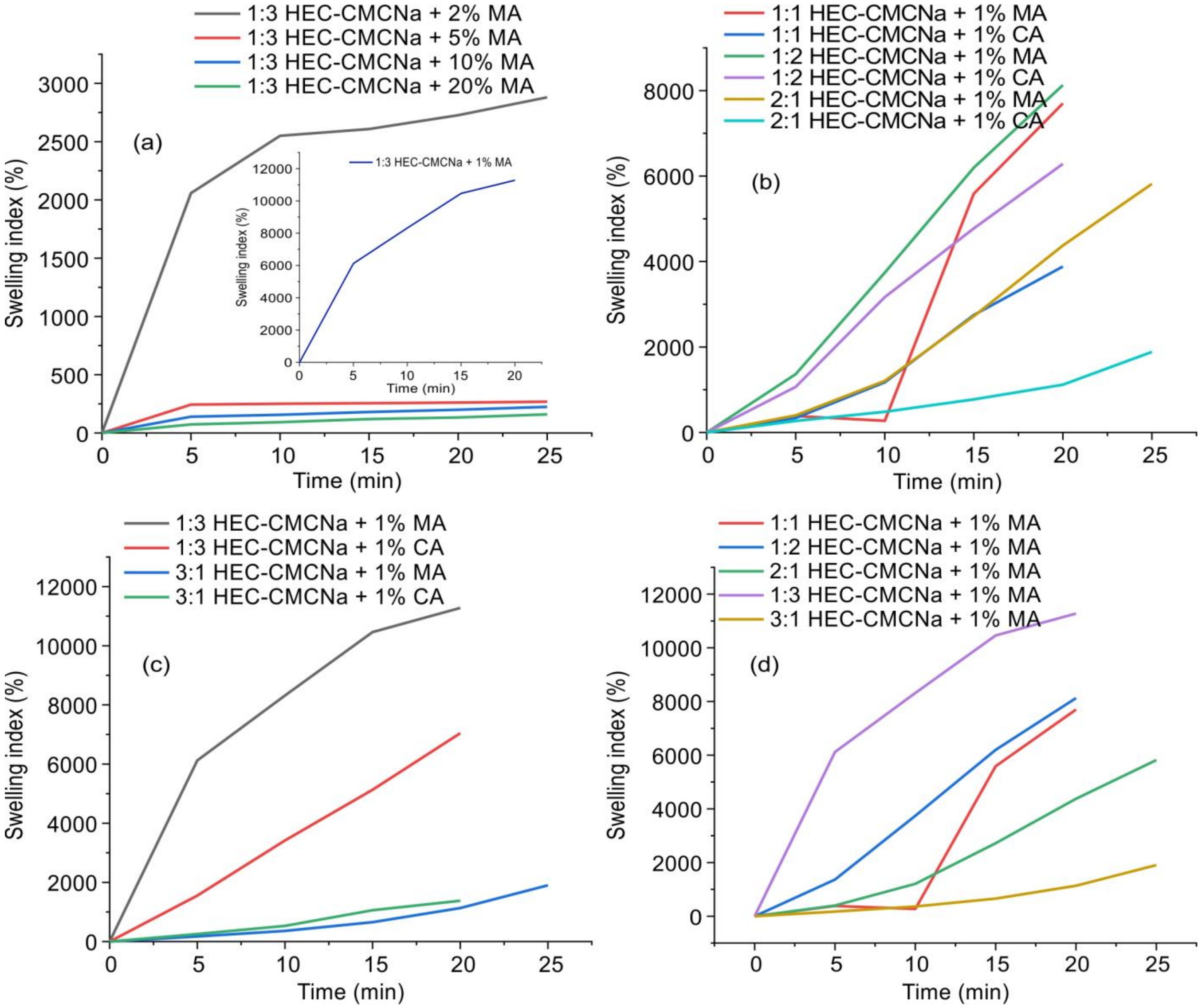


Fig. 4. Variation of swelling index with (a) change in concentration of crosslinker (MA) (b)-(c) change in crosslinker (d) change in HEC:CMCNa ratio

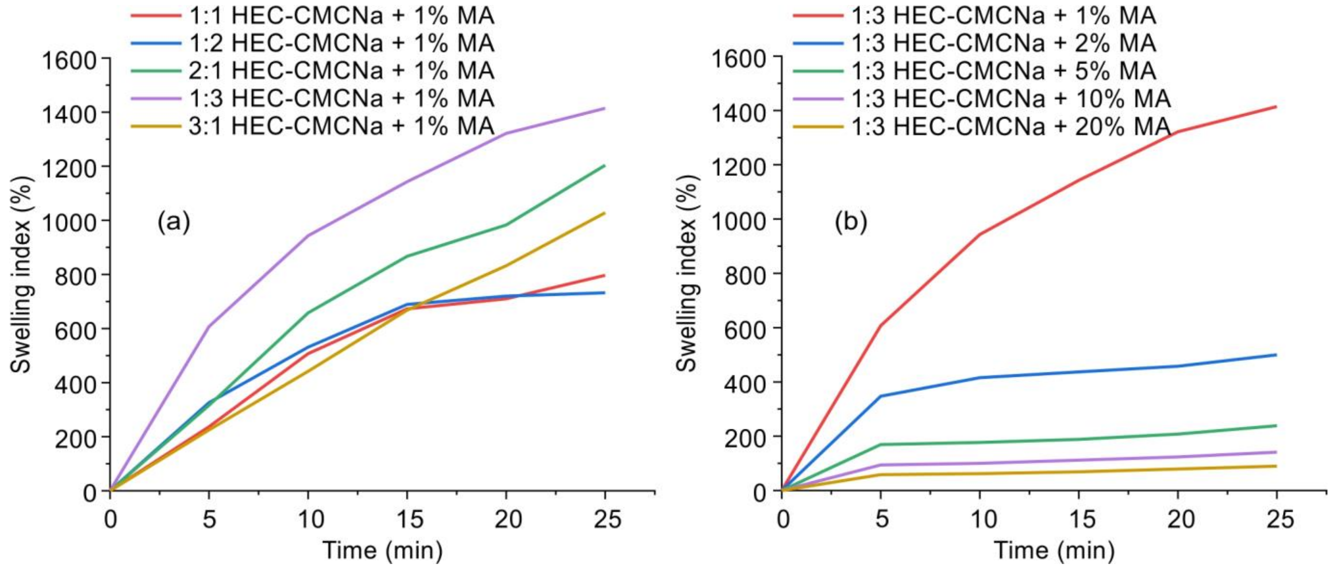


Fig. 5. Variation of swelling index with (a) change in HEC:CMCNa ratio (b) change in concentration of cross linker

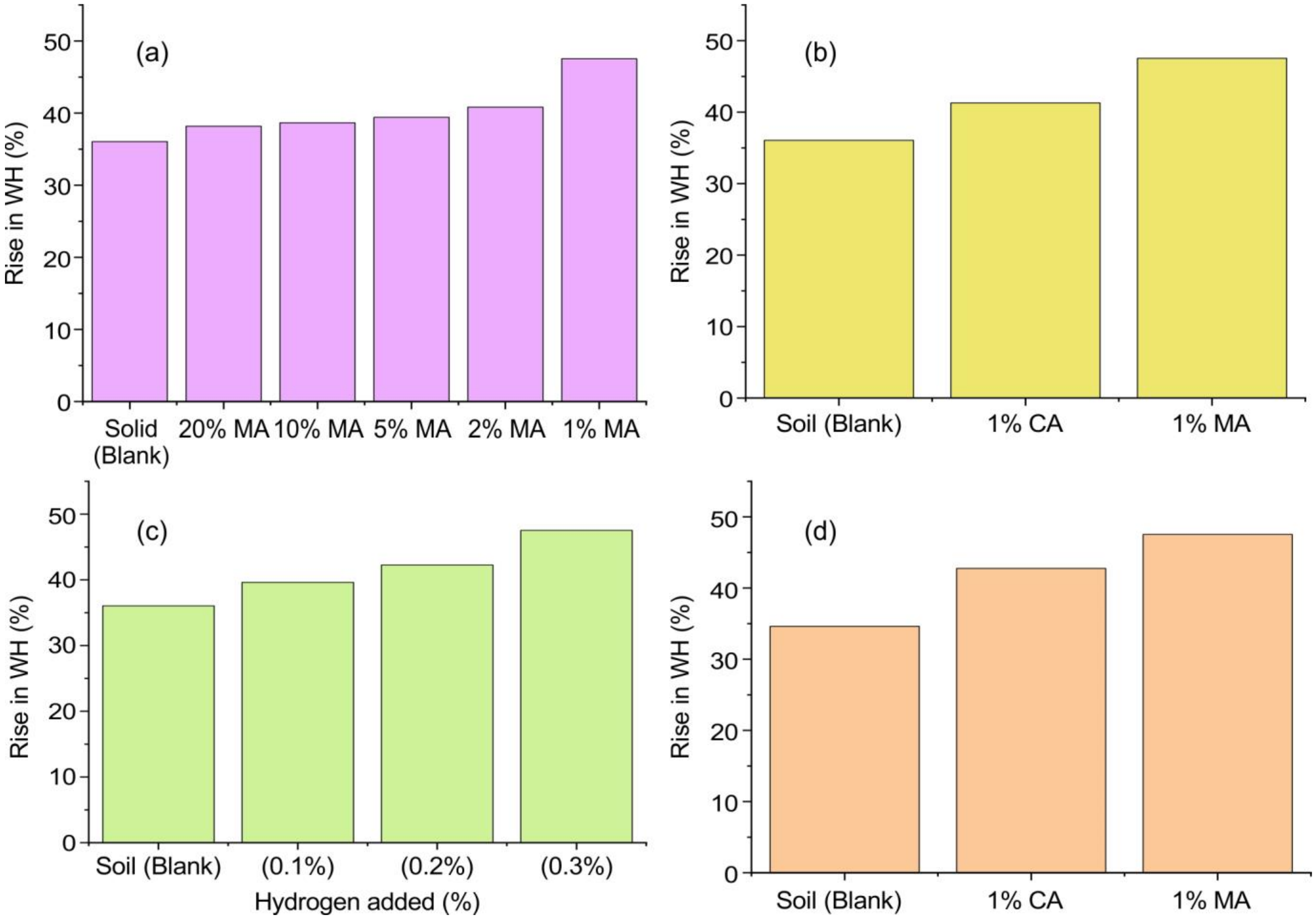


Fig. 6. (a)-(c) Effect of cross-linker concentration, effect of crosslinker, effect of change in hydrogel amount added on WH capacity in soil sample collected from lawn of Department of Chemistry, Gauhati University (d) effect of crosslinker on WH capacity in soil sample collected from local hillside area of Guwahati, Assam, India

the sample $H(1:3)_{M_1}$ was investigated by varying the amount of hydrogel loading to the soil from 0.1-0.3% (w/w). The values obtained for WH showed a rise with values 39.61%, 42.26% and 47.54% respectively as shown in Fig. 6c. WH capacity was also tested on another sandy soil sample collected from a local hillside area of Guwahati, Assam and the samples $H(1:3)_{M_1}$ and $H(1:3)_{C_1}$ was used for investigation. The WH capacity of the untreated sandy soil collected from local hillside area of Guwahati, was 34.63% but increased on addition of 1% (w/w) hydrogel to 10 g of the soil sample and attained 47.53% and 42.76% for samples $H(1:3)_{M_1}$ and $H(1:3)_{C_1}$, respectively (Fig. 6d). 1% MA crosslinked hydrogel showed higher WH capacity compared to 1% CA crosslinked hydrogel. The WH factor of the two different soil samples showed similar trend in the rise of WH values in the presence of hydrogel in the soil samples. Further superabsorbent hydrogel prepared with malonic acid as crosslinker was better in increasing the WH capacity [49].

Urea loading and release study: The urea loading capacity of the hydrogel was examined for the samples $H(1:3)_{M_1}$ and $H(1:3)_{M_2}$. To calculate the loading capacity, 0.095 g of dried sample $H(1:3)_{M_1}$ and 0.106 g of dried sample $H(1:3)_{M_2}$ were taken. After loading of urea and complete drying, the loaded hydrogels were weighed properly and found to be 0.501 g and 0.337 g, respectively. The loading capacity was calculated using eqn. 1 and found to be 427.37% for sample $H(1:3)_{M_1}$ and 217.92% for sample $H(1:3)_{M_2}$, respectively. With increase in concentration of the crosslinker, the loading capacity considerably decreased which can be attributed to the fact that as the crosslinker concentration increased, more of the hydroxyl groups in cellulose were involved in the crosslinking and the polymer network became denser and more compact. This resulted in the lowering of the amount of urea absorbed [50]. The FTIR spectra of urea and urea loaded hydrogel films are shown in Fig. 7.

The characteristic bands of pure urea observed at 3385 cm^{-1}, 1674 cm^{-1}, 1562 cm^{-1} and 1412 cm^{-1}, which can be attributed to the stretching vibration of –NH in $–CONH_2$, stretching vibration of –C=O in $–CONH_2$, N-H deformation C-N stretching respectively. Similar peaks were observed for the hydrogel samples $H(1:3)_{M_1}$ and $H(1:3)_{M_2}$, respectively, which implies the loading of urea into the polymeric network [51].

Urea loaded hydrogel film for study of the surface morphology was prepared by soaking the samples $H(1:3)_{M_1}$ and $H(1:3)_{M_2}$ in a urea solution, wiping the surface with tissue paper to remove surface adhered urea and then drying it. The SEM images for the loaded and unloaded hydrogel samples are shown in Fig. 8a-d and Fig. 8e is the EDS spectra of the urea

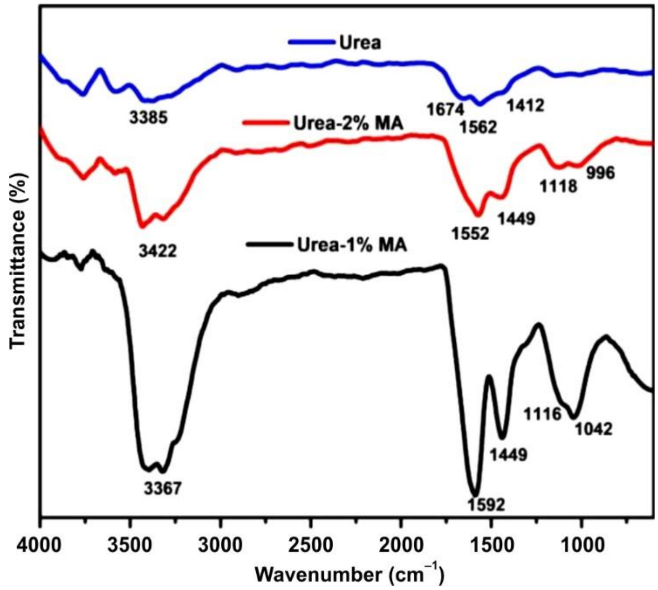


Fig. 7. FTIR spectra of urea, urea loaded $H(1:3)_{M_1}$ and $H(1:3)_{M_2}$ hydrogel samples

loaded sample. The SEM-images of the urea loaded hydrogels were found to have different morphological features in comparison to the unloaded samples, indicating the successful loading of urea in the hydrogels. The corrugated surface morphology increases the surface area for urea absorption [52]. The presence of elements C, O, N was confirmed from the EDS spectrum of the urea loaded sample.

The hydrogel sample $H(1:3)_{M_1}$ with higher swelling capacity was taken to examine the urea release in aqueous medium at room temperature. Highly swelled hydrogels can release a greater amount of the fertilizer trapped within the polymeric network [53]. The urea release profile from the loaded hydrogel is presented as a function of time and is shown in Fig. 9. The release of urea after 1, 5, 9 and 17 days were found as 24.6%, 60.8%, 72.7% and 95.8%, respectively. At the initial stage, the 3D-polymeric network of the hydrogel remains strong enough to hold the urea molecules but with time, the network weakens leading to the increased release rate of urea [54]. A burst release was observed at the initial stage, which can be attributed to the high concentration gradient of loaded urea within the hydrogel matrix [37]. But with time, the release rate decreased with

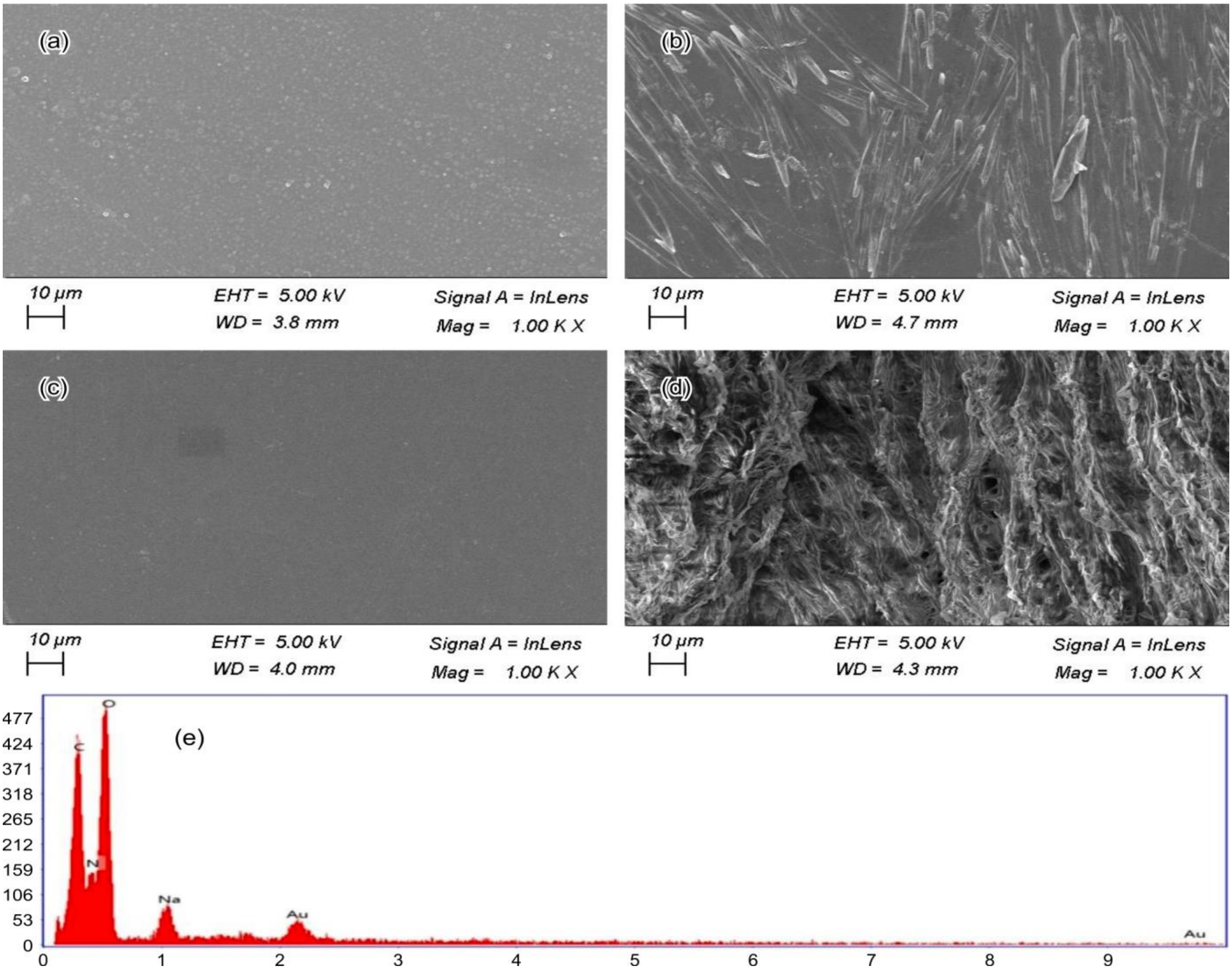


Fig. 8. SEM images of (a)-(b) unloaded and urea loaded hydrogel sample $H(1:3)_{M_1}$ (c)-(d) unloaded and urea loaded sample $H(1:3)_{M_2}$ (e) EDS spectra of urea loaded sample

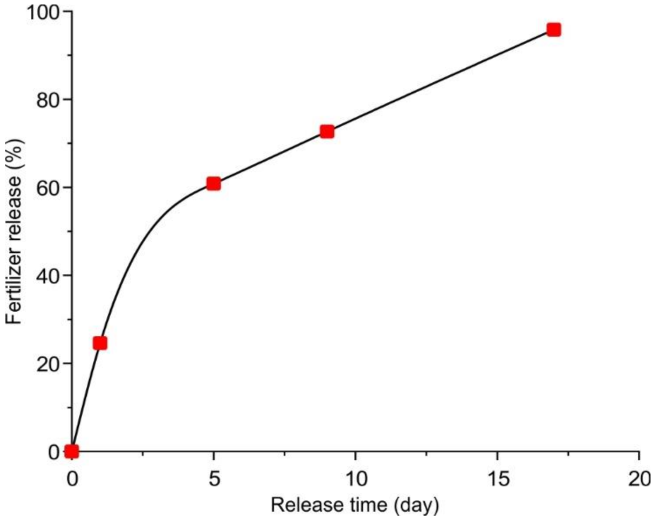


Fig. 9. Urea release profile

a complete release after 17 h. The urea absorption by the hydrogel diffused through the 3D-polymeric network is due to the difference in osmotic pressure inside and outside the hydrogel sample [36].

Conclusion

Superabsorbent hydrogels from two cellulose derivatives, sodium carboxymethyl cellulose and hydroxyl ethyl cellulose were synthesized by varying the ratio of the two components. Two different crosslinker malonic acid and citric acid were used. The hydrogel with the ratio of HEC:CMCNa as 1:3 with 1% MA as the crosslinker was found to have the highest water absorption capacity. A swelling index as high as 11277% in the neutral medium was observed. The water holding capacity in soil significantly increased on addition of the hydrogel samples into it which was higher for the hydrogel with MA crosslinker. The urea was successfully loaded and maximum loading capacity attained was 427.37% for 1% MA crosslinked hydrogel with 1:3 HEC-CMCNa ratios. The urea loaded in the hydrogel showed a burst release of 24.6% at the initial phase which thereafter showed a slow release behaviour attaining a maximum release of 95.8% in 17 days. Thus, the urea loaded hydrogel can act as a source of urea for at least a period of 17 days.

ACKNOWLEDGEMENTS

The authors express their gratitude to Department of SAIF Guwahati, Gauhati University, Gauhati, India for providing the support in TGA facilities.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. Y. Oladosu, M.Y. Rafii, F. Arolu, S.C. Chukwu, M.A. Salisu, I.K. Fagbohun, T.K. Muftaudeen, S. Swaray and B.S. Haliru, *Horticulturae*, **8**, 605 (2022); https://doi.org/10.3390/horticulturae8070605
2. C. Dingley, P. Cass, B. Adhikari and F. Daver, *Polym. Renew. Resour.*, **15**, 210 (2024); https://doi.org/10.1177/20412479231226166
3. E. Priya, S. Sarkar and P.K. Maji, *J. Environ. Chem. Eng.*, **12**, 113211 (2024); https://doi.org/10.1016/j.jece.2024.113211
4. E. Hidayat, N.M.M. Sarbani, S. Samitsu, F.A.A. Nugroho, S.K. Lahiri, M. Aoyagi, S. Yonemura and H. Harada, *Arab. J. Chem.*, **17**, 105877 (2024); https://doi.org/10.1016/j.arabjc.2024.105877
5. B. Azeem, K. Kushaari, Z.B. Man, A. Basit and T.H. Thanh, *J. Control. Rel.*, **181**, 11 (2014); https://doi.org/10.1016/j.jconrel.2014.02.020
6. S.K. Bajpai, M.P. Swarnkar and S. Ahuja, *J. Macromol. Sci. Part A Pure Appl. Chem.*, **52**, 779 (2015); https://doi.org/10.1080/10601325.2015.1067020
7. S. Muharam, A. Fitri, L.M. Yuningsih, Y.M.T.A. Putri and I. Rahmawati, *Indones. J. Chem.*, **20**, 616 (2020); https://doi.org/10.22146/ijc.44230
8. B. Ni, M. Liu and S. Lü, *Chem. Eng. J.*, **155**, 892 (2009); https://doi.org/10.1016/j.cej.2009.08.025
9. N. Singh, S. Agarwal, A. Jain and S. Khan, *Agric. Water Manage.*, **253**, 106939 (2021); https://doi.org/10.1016/j.agwat.2021.106939
10. A. Nirmala and T. Guvvali, *Int. J. Chem. Stud.*, **7**, 787 (2019).
11. S.K. Patra, R. Poddar, M. Brestic, P.U. Acharjee, P. Bhattacharya, S. Sengupta, P. Pal, N. Bam, B. Biswas, V. Barek, P. Ondrisik, M. Skalicky and A. Hossain, *Int. J. Polym. Sci.*, **2022**, 4914836 (2022); https://doi.org/10.1155/2022/4914836
12. B. Song, H. Liang, R. Sun, P. Peng, Y. Jiang and D. She, *Int. J. Biol. Macromol.*, **144**, 219 (2020); https://doi.org/10.1016/j.ijbiomac.2019.12.082
13. H. Tiwari and R. Kumar, *Int. J. Res. Publ. Rev.*, **5**, 202 (2024).
14. P. Calcagnile, T. Sibillano, C. Giannini, A. Sannino and C. Demitri, *J. Appl. Polym. Sci.*, **136**, 47546 (2019); https://doi.org/10.1002/app.47546
15. X. Zhang, Y. Liu, P. Lu and M. Zhang, *Green Process Synth.*, **9**, 139 (2020); https://doi.org/10.1515/gps-2020-0015
16. T.M. Neethu, P.K. Dubey and A.R. Kaswala, *Int. J. Curr. Microbiol. Appl. Sci.*, **7**, 3155 (2018); https://doi.org/10.20546/ijcmas.2018.705.369
17. M.M. Ibrahim, M. Abd-Eladl and N.H. Abou-Baker, *J. Appl. Polym. Sci.*, **132**, 42652 (2015); https://doi.org/10.1002/app.42652
18. N. Weerawan, J. Chalitangkoon and P. Monvisade, *Biointerface Res. Appl. Chem.*, **12**, 4770 (2022); https://doi.org/10.33263/BRIAC124.47704779
19. J. Chalitangkoon, M. Wongkittisin and P. Monvisade, *Int. J. Biol. Macromol.*, **159**, 194 (2020); https://doi.org/10.1016/j.ijbiomac.2020.05.061
20. B. Ye, R. Xiang and F. Luo, *Chem. Eng. J.*, **497**, 154436 (2024); https://doi.org/10.1016/j.cej.2024.154436
21. S. Wang, Q. Zhang, B. Tan, L. Liu and L. Shi, *J. Macromol. Sci. Part B Phys.*, **50**, 2307 (2011); https://doi.org/10.1080/00222348.2011.563196
22. C. Alvarez-Lorenzo, V.Y. Grinberg, T.V. Burova and A. Concheiro, *Int. J. Pharm.*, **579**, 119157 (2020); https://doi.org/10.1016/j.ijpharm.2020.119157
23. N. Kaur, P. Hamid, P. Choudhary and A.K. Jaiswal, *J. Agric. Food Res.*, **20**, 101756 (2025); https://doi.org/10.1016/j.jafr.2025.101756
24. J. Li, X. Jia and L. Yin, *Food Rev. Int.*, **37**, 313 (2021); https://doi.org/10.1080/87559129.2020.1858313
25. A.K. Singh, P. Itkor and Y.S. Lee, *Gels*, **9**, 433 (2023); https://doi.org/10.3390/gels9060433
26. Y. Liu, S. Ahmed, D.E. Sameen, Y. Wang, R. Lu, J. Dai, S. Li and W. Qin, *Trends Food Sci. Technol.*, **112**, 532 (2021); https://doi.org/10.1016/j.tifs.2021.04.016
27. L. Wang, P.Y. Mok, D. Shou, S. Xu and J. Fan, *Mater. Des.*, **244**, 113231 (2024); https://doi.org/10.1016/j.matdes.2024.113231
28. Y. Bachra, A. Grouli, F. Damiri, A. Bennamara and M. Berrada, *Results Mater.*, **8**, 100156 (2020); https://doi.org/10.1016/j.rinma.2020.100156

29. R. Mu, B. Liu, X. Chen, N. Wang and J. Yang, *Environ. Technol. Innov.*, **20**, 101107 (2020); https://doi.org/10.1016/j.eti.2020.101107
30. C. Demitri, F. Scalera, M. Madaghiele, A. Sannino and A. Maffezzoli, *Int. J. Polym. Sci.*, **2013**, 435073 (2013); https://doi.org/10.1155/2013/435073
31. N.S.V. Capanema, A.A.P. Mansur, A.C. de Jesus, S.M. Carvalho, L.C. de Oliveira and H.S. Mansur, *Int. J. Biol. Macromol.*, **106**, 1218 (2018); https://doi.org/10.1016/j.ijbiomac.2017.08.124
32. S. Durpekova, K. Filatova, J. Cisar, A. Ronzova, E. Kutalkova and V. Sedlarik, *Int. J. Polym. Sci.*, **2020**, 8363418 (2020); https://doi.org/10.1155/2020/8363418
33. V.R. Dhongde, B.S. De and K.L. Wasewar, *J. Chem. Eng. Data*, **64**, 1072 (2019); https://doi.org/10.1021/acs.jced.8b00972
34. T.G. Dastidar and A.N. Netravali, *Carbohydr. Polym.*, **90**, 1620 (2012); https://doi.org/10.1016/j.carbpol.2012.07.041
35. C. Demitri, R. Del Sole, F. Scalera, A. Sannino, G. Vasapollo, A. Maffezzoli, L. Ambrosio and L. Nicolais, *J. Appl. Polym. Sci.*, **110**, 2453 (2008); https://doi.org/10.1002/app.28660
36. D. Sarmah and N. Karak, *J. Appl. Polym. Sci.*, **136**, 48495 (2019); https://doi.org/10.1002/app.48495
37. S. Mohammadi-Khoo, P.N. Moghadam, N. Movagharnezhad and A.R. Fareghi, *J. Appl. Polym. Sci.*, **133**, 42935 (2016); https://doi.org/10.1002/app.42935
38. M. Teodorescu, A. Lungu, P.O. Stanescu and C. Neamtu, *Ind. Eng. Chem. Res.*, **48**, 6527 (2009); https://doi.org/10.1021/ie900254b
39. V.S. Ghorpade, R.J. Dias, K.K. Mali and S.I. Mulla, *J. Drug Deliv. Sci. Technol.*, **52**, 421 (2019); https://doi.org/10.1016/j.jddst.2019.05.013
40. K. Dharmalingam and R. Anandalakshmi, *Int. J. Biol. Macromol.*, **134**, 815 (2019); https://doi.org/10.1016/j.ijbiomac.2019.05.027
41. I. Ayouch, I. Kassem, Z. Kassab, I. Barrak, A. Barhoun, J. Jacquemin, K. Draoui and M.E. Achaby, *Surf. Interfaces*, **24**, 101124 (2021); https://doi.org/10.1016/j.surfin.2021.101124
42. K.K. Mali, S.C. Dhawale, R.J. Dias, N.S. Dhane and V.S. Ghorpade, *Indian J. Pharm. Sci.*, **80**, 657 (2018); https://doi.org/10.4172/pharmaceutical-sciences.1000405
43. V.S. Ghorpade, A.V. Yadav and R.J. Dias, *Carbohydr. Polym.*, **164**, 339 (2017); https://doi.org/10.1016/j.carbpol.2017.02.005
44. T. Liu, X. Peng, Y. Chen, J. Zhang, C. Jiao and H. Wang, *Polym. Chem.*, **11**, 4787 (2020); https://doi.org/10.1039/D0PY00023J
45. A. Isreb, M.A. Alhnan, A. Mkia, K. Al-Jammal, A. Yaghi, E.F. Oga, P. Timmins, M. Bonner and R.T. Forbes, *Methods Protoc.*, **8**, 4 (2025); https://doi.org/10.3390/mps8010004
46. H. Ritonga, M. Nurdin, L.O.A.N. Ramadhan, W.S. Salsabila, S. Si and F.S. Rembon, *Macromol. Symp.*, **391**, 1900159 (2020); https://doi.org/10.1002/masy.201900159
47. Y. Seki, A. Altinisik, B. Demircioglu and C. Tetik, *Cellulose*, **21**, 1689 (2014); https://doi.org/10.1007/s10570-014-0204-8
48. Y. Wang, M. Liu, B. Ni and L. Xie, *Ind. Eng. Chem. Res.*, **51**, 1413 (2012); https://doi.org/10.1021/ie2020526
49. F.F. Montesano, A. Parente, P. Santamaria, A. Sannino and F. Serio, *Agric. Agric. Sci. Procedia*, **4**, 451 (2015); https://doi.org/10.1016/j.aaspro.2015.03.052
50. H.V. Chavda and C.N. Patel, *Int. J. Pharm. Investig.*, **1**, 17 (2011); https://doi.org/10.4103/2230-973X.76724
51. K. Lu, R. Abouzeid, Q. Wu, Q. Chen and S. Liu, *Giant*, **18**, 100270 (2024); https://doi.org/10.1016/j.giant.2024.100270
52. P. Laddawan, S. Auecharoenrat and C. Tongsook, *ACS Omega*, **10**, 17296 (2025); https://doi.org/10.1021/acsomega.4c09928
53. Kiran, R. Tiwari, S. Krishnamoorthi and K. Kumar, *J. Environ. Chem. Eng.*, **7**, 103162 (2019); https://doi.org/10.1016/j.jece.2019.103162
54. Z. Mohammadbagheri, A. Rahmati and P. Hoshyarmanesh, *Int. J. Biol. Macromol.*, **182**, 1893 (2021); https://doi.org/10.1016/j.ijbiomac.2021.05.191