



# Thermo and pH-responsive methylcellulose and hydroxypropyl methylcellulose hydrogels containing $K_2SO_4$ for water retention and a controlled-release water-soluble fertilizer

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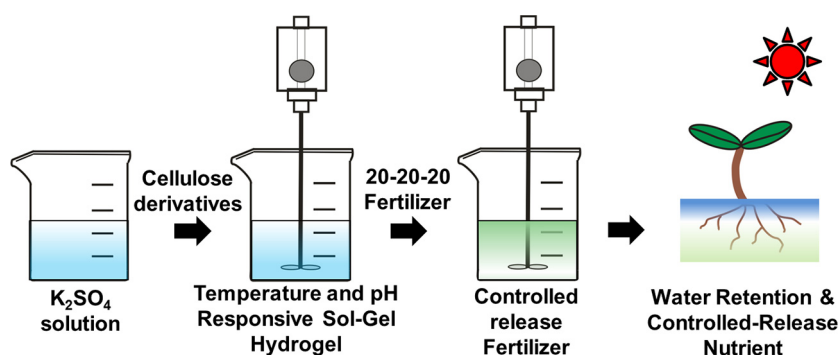
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## HIGHLIGHTS

- Gel temperature of cellulose-based hydrogel can be adjusted by concentration of  $K_2SO_4$ .
- Adding  $K_2SO_4$  can improve the initial swelling rate and mechanical properties of hydrogels.
- The hydrogels could effectively improve the water-retention capacities of sandy soil.
- The hydrogels can reduce the release rate of the fertilizer.
- The fertilizer release profiles reveal temperature- and pH-responsive behavior.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Hydrogel as commercial soil conditioner has the potential to improve soil properties and reduce water scarcity in growing plants. However, use of polyacrylamide-based hydrogel in agriculture pose potential human health hazards. Hydrogel systems were prepared from temperature-responsive methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) blended with potassium sulfate ( $K_2SO_4$ , K-containing fertilizer). Blended  $K_2SO_4$  in hydrogels affects the hydrophobic interaction of MC and HPMC, and hydrogels prepared in 0.25 M  $K_2SO_4$  decrease the gelation temperatures of MC and HPMC from 55.6 and 67.4 °C to 27.8 and 35.1 °C, respectively. The equilibrium swelling ratio ( $St$ ) of MC and HPMC hydrogels was increased 15 times and hydrogels maintained a steady appearance. The swelling kinetics of the MC and HPMC hydrogels followed Schott's second-order model and kinetic parameters indicated that adding  $K_2SO_4$  can improve the initial swelling rate.  $K_2SO_4$  decreases the pore size of the MC and HPMC hydrogel from 26.8 and 21.5  $\mu\text{m}$  to 14.7 and 14.2  $\mu\text{m}$ . A plant growth assessment indicated inhibition in plant growth occurred without the application of the hydrogels. Adding  $K_2SO_4$  increases mechanical properties of the hydrogels. Treatment with 0.5% hydrogel considerably improves the water-holding and water-retention capacities of sandy soil. The 20-20-20 fertilizer release results revealed that at 35 °C and a pH below 7, the hydrogel systems reduce the release rate of the fertilizer. The best result was observed with the Korsmeyer–Peppas model, indicating that the fertilizer transport mechanism involves Fickian diffusion and swelling-controlled release. This study discovered that environmentally responsive cellulose-based hydrogels have potential for use as soil conditioners and as controlled release devices in horticulture and agriculture.

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## 1. Introduction

Hydrogels can save water and fertilizer in agricultural application; hydrogels demonstrated considerable the potential to improve some soil properties and control the growth of some plants (Guilherme et al., 2015). Hydrogels are water-swollen and cross-linked network hydrophilic polymers (Ahmed, 2015). Polyacrylamide-based hydrogels were developed for possible use as soil conditioners and as carriers for the release of agricultural nutrients (Elbarbary et al., 2017; Pushpamalar et al., 2018). However, depolymerization of polyacrylamide is a noteworthy danger because it can release free acrylamide into the aqueous environment (Smith and Oehme, 1991). Neurotoxicity appears to be the only documented effect of acrylamide in human epidemiological studies. On the basis of animal studies of reproductive toxicity, genotoxicity, clastogenicity and carcinogenicity are potential human health risks associated with acrylamide (Friedman, 2003). Moreover, polyacrylamides are prepared from fossil-based raw materials.

Cellulose and its derivatives are well-known biodegradable resources that collapse in soil or under controlled conditions through enzymatic degradation (Pérez et al., 2002; Simon et al., 1998). Previous studies have demonstrated that MC and HPMC can be converted to carbon dioxide and water as end products (Rimdisut et al., 2008; Wach et al., 2003). MC and HPMC aqueous solutions are liquid at low temperatures, but gel upon heating at low concentrations (1–10 wt%) (Li et al., 2001; Sarkar and Walker, 1995; Silva et al., 2008). Blended salts usually have a higher affinity for water molecules than polymers do; therefore, in the removal of water from hydrated the polymers, results in dehydrating or “salting out” the polymeric molecules. Cellulose derivatives can be used as a soil conditioner and for the controlled release of fertilizer.

The main goal of this study is to develop a non-toxic, renewable and environmental responsive hydrogel system by using green processes in agriculture and horticulture applications. The ratios for the anions following a typical Hofmeister order are  $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$  (Zhang and Cremer, 2006).  $\text{K}_2\text{SO}_4$  was used to control the properties because  $\text{SO}_4^{2-}$  can salt out anions and enhance the hydrophobicity of the solution. Potassium is required by plants. From 1961 to 1999, the warming effect from greenhouse gases has raised global temperatures by 0.9–2.7 °C (Hsu and Chen, 2002). MC and HPMC hydrogels exist in a gel state and can be used as soil conditioners for water-retention in high temperatures. Hydrogels can be loaded with 20–20 water-soluble fertilizer for the controlled release of ions that nourish plants.

## 2. Materials and methods

### 2.1. Materials

MC (viscosity of 2% w/v solution at 20 °C is 3000–5600 cps) and HPMC (viscosity of 2% w/v solution at 20 °C 4000 cps) were reagent-grade chemicals obtained from Acros.  $\text{K}_2\text{SO}_4$  was purchased from Sigma. Sandy soil from Sin-Yi Inc., Taiwan, was used for the experiment. Seeds of Chinese cabbage [*Brassica rapa* L. (Chinensis Group)] and commercial soil conditioner (CS; polyacrylamide-based hydrogel) were obtained from Known-You Seed Co., Ltd. Soil (Jiffy substrates) was obtained from Jiffy products Ltd.

### 2.2. Preparation of MC and HPMC hydrogel, xerogels and the controlled release fertilizer

Aqueous MC and HPMC solutions of different concentrations (1%, 2% and 4% by w/v) were prepared by dispensing weighed MC and HPMC powders with the addition of  $\text{K}_2\text{SO}_4$  at varying known concentrations [0, 0.1, 0.125, 0.15, 0.2, and 0.25 M, in double distilled (DD) water] in a cold water bath. The controlled release fertilizer was prepared by the

same process that the solution was 0.25 M  $\text{K}_2\text{SO}_4$  and 0.1% of 20–20–20 fertilizer. After thorough stirring for 2 h, the aqueous MC and HPMC solutions were kept overnight in a refrigerator at 4 °C. Supplementary material indicates the properties and codes of the solutions. M2 and H2 hydrogels were blended with 0 to 0.25 M  $\text{K}_2\text{SO}_4$  and the gelation temperatures of these solutions were 55.6 to 27.8 °C and 72.3 to 35.1 °C (Fig. S1). For the swelling characteristics experiment, 5 mL of test MC and HPMC solutions were poured into a glass dish (diameter 10 cm) at room temperature. Subsequently, the dish was heated at 40 °C overnight and a layer of 1.5–2 mm-thick xerogels formed on the dish (diameter 10 cm). Then, the xerogels were grinded and screened between 10 and 20 meshes for the water-holding and water-retention experiments. For the mechanical experiment of the hydrogel, the specimen was prepared by dispensing 10% (w/v) xerogels powders in water at 4 °C. Subsequently, the hydrogel was cast in a cylindrical aluminum mold measuring 3 cm in diameter and 1.2 cm in height at 4 °C overnight. Before compression tests, the hydrogel with the mold was moved in a water bath at 25 or 35 °C.

### 2.3. Morphological studies

For observation of swelling morphology, 5% dry hydrogel was swollen in deionized water for 24 h. The morphology of the obtained lyophilized solution and hydrogel was observed using a scanning electron microscope (SEM) (Hitachi TM-1000, Japan). The pore sizes of the scaffolds were measured based on the SEM images using image visualization software U-IMAGE (2013). The average pore size was determined from about 30 measurements on an SEM image.

### 2.4. Swelling characteristics of xerogels

A certain amount of xerogel was immersed in deionized water at 25 °C. The samples were removed from the water at pre-determined time intervals and the surface water was removed using paper. The swollen hydrogels were weighed and the  $St$  (g/g) was measured by the following equation:

$$\text{Swelling ratio } (St; \text{g/g}) = \frac{W_b - W_a}{W_a}$$

where  $W_b$  and  $W_a$  are the weights of the swollen hydrogel at time  $t$  and dry hydrogel, respectively.

Previous research demonstrated that the swelling kinetics of hydrophilic polymers are compatible with Schott's second-order swelling kinetics (Quintana et al., 1999; Yin et al., 2008). This kinetics model was used to calculate the swelling kinetics of cellulose-based hydrogels in previous studies (Fekete et al., 2014; Li et al., 2016). The kinetic model is described by the following equation (Schott, 1992):

$$\frac{dS_t}{dt} = K(S_t - S_\infty)$$

where  $S_\infty$  is the theoretical equilibrium  $St$  (g/g) for second-order kinetic;  $K$  is the specific rate constant of the initial swelling rate.

The equation on integration between the limits  $S_t = 0$  when  $t = 0$  and  $S_t$  for  $t$  yield:

$$S_t = \frac{KS_\infty^2 t}{1 + S_\infty}$$

Rearrangement yields Schott's equation for second-order swelling:

$$\frac{t}{S_t} = \frac{1}{KS_\infty^2} + \frac{t}{S_\infty}$$

OriginPro8 was used for the calculation of  $K$  and determination of correlation coefficients ( $R^2$ ).

## 2.5. Plant growth assessment

Considering the composition of hydrogel consisted of MC, HPMC, and  $K_2SO_4$ , the tested samples were assumed to be nontoxic. Plant growth testing was undertaken according to the Organisation of Economic Cooperation and Development (OECD, 2006) 208 method, using concentrations of 1000 mg of dry hydrogel per kg of dry weight soil (Rychter et al., 2016). The OECD 208 method is used to confirm that biodegraded and composted materials do not introduce toxic components into the compost. Chinese cabbage was used for the assessment of toxicity.

Plant growth testing (20 replicates for every sample) was carried out in a growth chamber at  $25 \pm 2$  °C, and lighting was maintained for 16 h. Approximately 200 g of soil samples with a moisture content of 60%–70% water-holding capacity were placed in plastic pots (length and width: 8.8 cm [top], height: 9.5 cm) and distilled water was added every two days to continuously maintain available water as required. Plants were harvested after 30 days of exposure when 80% of the seeds had germinated in the control soils. The biomass was then harvested and fresh weight was immediately determined to the nearest 0.001 g. The dry biomass was weighed after drying at 70 °C, until constant weight was obtained.

## 2.6. Compression testing

The compression tests of the hydrogels were measured according to a previous study (Darnell et al., 2013). The dimensions of the hydrogels were measured using calipers and the hydrogels were subjected to compression tests using universal testing machines (Shimadzu EZ TEST-500N). The crosshead speed of compression was set at 1 mm/min. Elastic modulus was calculated from the slope of the linear region of the resulting stress-strain curve. For testing the compressive properties of the gels outside of culture conditions, cylindrical gels 30 mm in diameter and 12 mm high were cast and tested as mentioned previously, but the strain was terminated at 50%.

## 2.7. Measurement of water-holding and water-retention capacities of sandy soil using cellulose hydrogel

Water-holding and water-retention capacities of soil were determined using a modified protocol from a previous investigation (Wang et al., 2014). The experiment was conducted at a relative humidity ranging from 72% to 78% at  $25 \pm 3$  °C. The water-holding capacity of the sandy soil was measured for four different treatments: a control, 40 g of dry sandy soil and 40 g of dry sandy soil mixed with 0.2, 0.4 or 0.8 g dry hydrogel. Each sample was placed into a poly(vinyl chloride) tube of 4.5 cm diameter. The bottom of the tube was sealed with two layers of nylon fabric and weighed ( $W_0$ ). The soil samples were slowly drenched from the top of the tube using tap water until the water seeped out from the bottom. After water seepage stopped from the tube bottom, the tube was weighed again ( $W_2$ ). The water-holding capacity (%) of the soil was calculated from the following equation:

$$\text{Water-holding capacity (\%)} = \frac{W_2 - W_0}{40} \times 100\%$$

The water-retention capacity of dry hydrogel was measured for the previously mentioned conditions. Soil samples were placed into a poly(vinyl chloride) tube of 4.5 cm diameter. The bottom of the tube was sealed using two layers of nylon fabric and weighed ( $W_0$ ). The soil samples were slowly drenched by tap water from the top of the tube until the water seeped out the bottom. After no further leakage of water was observed from the tube bottom, the tube was weighed again ( $W_3$ ). The columns were kept under identical conditions at room temperature and weighed every day ( $W_i$ ). A measurement was obtained after a period of 30 days. The water-retention ratio of the soil was

calculated from the following equation:

$$\text{Water-retention ratio (\%)} = \frac{W_i - W_0}{W_3 - W_0} \times 100\%$$

## 2.8. Fertilizer release assay

Release studies were performed by monitoring diffusion from a cellulose membrane dialysis bag (molecular weight cutoff of 3500; Orange Scientific). The systems were added to 50 mL deionized water or 0.006 mol/L simulated soil solution (Ureña-Amate et al., 2011) containing NaCl,  $Na_2SO_4$ , and  $Na_2CO_3$ . The pH of simulated soil solutions was adjusted to 5, 7, and 9 using 0.1 M  $HCl_{(aq)}$  and  $NaOH_{(aq)}$ . The time course of the controlled fertilizer released from the controlled release fertilizer (50 mg/L) at 25 °C and 35 °C was assessed over a range of pH values. A 2 mL media was observed on a regular basis and analyzed using UV-Vis spectrometry (U-2900, HITACHI) at 198 nm, corresponding to the absorbance peak of the fertilizer. The release media removed for sampling were returned to the original solution after determination.

## 2.9. Statistical analyses

Results for gelation temperatures,  $St$ , pore size, water-holding capacities, water-retention capacities, and fertilizer release profiles are presented as mean and standard deviation. Statistical analysis was performed using SPSS software version 20 (SPSS Inc., Chicago, IL, USA). Tukey's multiple range test was used to determine the statistical significance ( $p = 0.05$ ) between pairs.

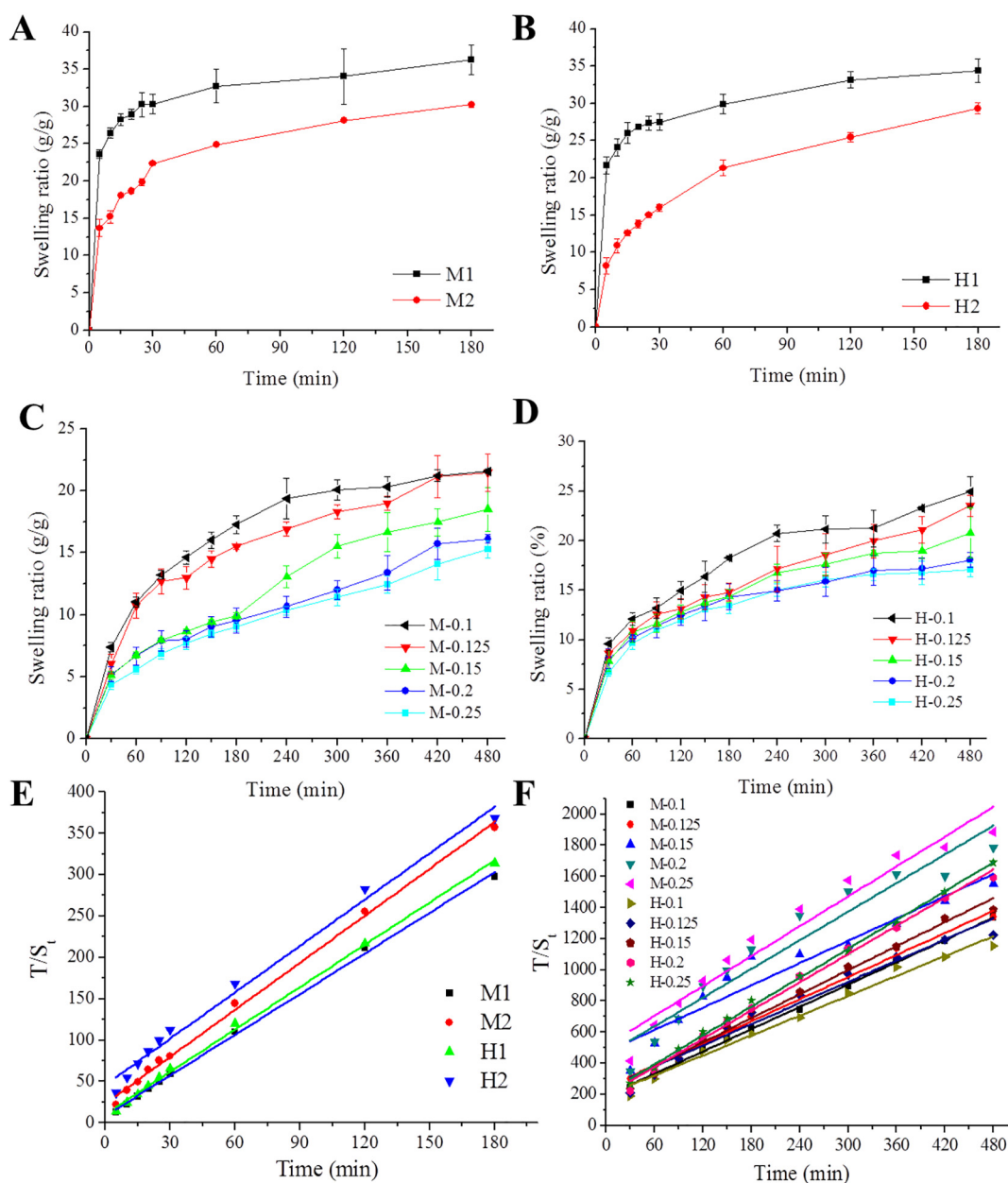
## 3. Results and discussion

### 3.1. Swelling kinetics of MC and HPMC hydrogels

The  $St$  of MC and HPMC hydrogels are illustrated in Fig. 1A and B. The results indicated the  $St$  of M1, M2, H1, and H2 hydrogels were 29.9, 21.4, 32.7, and 24.9 g/g at 60 min, respectively. The swelling ratios of the hydrogels decreased with the increase in the concentration of cellulose derivative. MC and HPMC hydrogels rapidly swelled for 30 min, and then the structure of raw MC and HPMC hydrogels was destroyed. Therefore, raw cellulose derivative hydrogels exhibited rapid swelling in water. This is not desirable because rapid release of the entrapped water in the soils may occur.

To investigate the influence of  $K_2SO_4$  concentration on water absorption, the swelling behaviors of hydrogels were studied at various  $K_2SO_4$  concentrations ranging from 0.1 to 0.25 M. The  $St$  of MC and HPMC hydrogels blended with  $K_2SO_4$  are illustrated in Fig. 1C and D. The results indicated that the  $St$  of M-0.1, M-0.15, M-0.25, H-0.1, H-0.15, and H-0.25 hydrogels were 20.32, 16.67, 12.45, 21.24, 18.75 and 16.58 g/g respectively, at 300 min. Increasing concentrations of  $K_2SO_4$  slightly reduced and considerably delayed the water uptake of the hydrogels. The MC and HPMC hydrogels-blended salts affect the structures of the entangled network and their swelling characteristics (Liang et al., 2004). A stable hydrophobic interaction could be formed in MC and HPMC hydrogels blended with  $K_2SO_4$ . A hydrophobic interaction occurred among the substituent group of cellulose chains, hydrogen-bond formation in the hydrogel, and hydrophobic interactions between the methoxy and hydroxypropyl methyl-substituted segments within the hydrogels. All the MC and HPMC hydrogels blended with  $K_2SO_4$  exhibited a swelling ratio higher than 15 g/g after 8 h and maintained their shape. The swelling ratio results were similar to cellulose hydrogels prepared from NaOH and urea solution (Chang et al., 2010), but lower than polyacrylamide-based hydrogel (Elbarbary et al., 2017).

Fig. 1G and H indicated  $t/St$  versus  $t$  are straight lines with favorable linear correlation coefficients, which confirmed that Schott's second-order swelling kinetics model is suitable to assess the kinetic swelling



**Fig. 1.** (A) Swelling ratio of MC, (B) HPMC, (C) MC blended with  $K_2SO_4$  and (D) HPMC blended with  $K_2SO_4$  hydrogels in deionized water at 25 °C. (E) Variation of the reciprocal rate of swelling  $T/S_t$  as a function of the swelling time for MC, HPMC, (F) MC blended with  $K_2SO_4$  and HPMC blended with  $K_2SO_4$  hydrogels in deionized water at 25 °C.

behaviors of the MC and HPMC based hydrogels. Swelling kinetic parameters  $S_\infty$ ,  $K$  and the  $R^2$  are listed in Table 1. The results indicated that  $S_\infty$  and  $K$  decrease and increase, respectively, with the increase in concentration of MC, HPMC and  $K_2SO_4$ , respectively. The results indicated that the initial swelling rate is favorable to improve the swelling rate of the hydrogel and might reflect complexity between cations and methyl and hydroxypropyl methyl groups (Zhou et al., 2018). Therefore, MC and HPMC hydrogels blended with  $K_2SO_4$  are sufficient to be applied as a soil conditioner for water uptake.

### 3.2. Morphology of MC and HPMC hydrogels

SEM was used to study and identify the differences in the surface morphology, size, shape and porosity between the solution and hydrogel of MC and HPMC blended with  $K_2SO_4$ . Fig. 2 depicts the micrographs of solutions (top) and hydrogel (bottom) of M2, M-0.25, H2 and H-0.25 in the freeze-dried state. The results indicate homogeneous random micro-scale opened pores with similar pore sizes and salt penetrating

**Table 1**

Results of swelling kinetic analysis of the hydrogels according to the second-order kinetic model.

Code	$^aQ_\infty$ (g/g)	$^aK \times 10^3$ (g/g/min)	$^aR^2$
M1	36.6300	27.3	0.9986
M2	31.6456	31.6	0.9971
H1	35.2113	28.4	0.9985
H2	32.1543	31.1	0.9893
M-0.1	25.1256	39.8	0.9989
M-0.125	25.3807	39.4	0.9896
M-0.15	25.1889	39.7	0.9230
M-0.2	19.5695	51.1	0.9294
M-0.25	18.7617	53.3	0.9518
H-0.1	28.1690	35.5	0.9848
H-0.125	26.4550	37.8	0.9678
H-0.15	23.3100	42.9	0.9865
H-0.2	19.8413	50.4	0.9945
H-0.25	19.4553	51.4	0.9979

<sup>a</sup> Theoretical equilibrium swelling ratio ( $Q_\infty$ ), specific rate constant ( $K$ ) and correlation coefficients ( $R^2$ ) are presented.



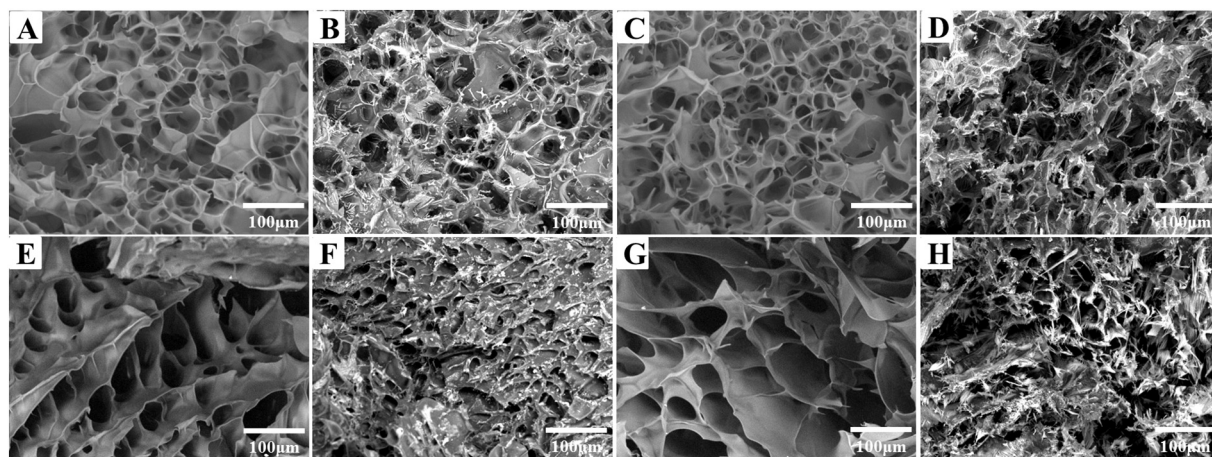


Fig. 2. SEM images of the cellulose ether solution (top) and hydrogels (bottom) at 100× magnification: (A and D) M2, (B and F) M-0.25, (C and G) H2 and (D and H) H-0.25.

into the porous microstructure. Because of the many interconnected pores in the hydrogel structure, water can easily diffuse in and out (da Silva and Ganzarolli de Oliveira, 2007). The average pore sizes of solution and hydrogel ranged from 21.1 to 24.6  $\mu\text{m}$  and 14.2 to 35.6  $\mu\text{m}$  (Fig. 3A). The results indicated the average pore sizes of the hydrogel forms of M2 and H2 were bigger than the pore sizes of their solutions, whereas, the average pore sizes of solutions of M-0.25 and H-0.25 were bigger than pore sizes of their hydrogels. Interestingly, adding  $\text{K}_2\text{SO}_4$  can decrease the pore size of xerogel. The phenomenon may be caused by the effect of anion  $\text{SO}_4^{2-}$  on salting-out polymers and inducing the hydrophobic property (Hribar et al., 2002). The porous microstructure was helpful for water penetration into the network of hydrogels, aiding to improvement of the controlled release of fertilizer.

### 3.3. Phytotoxicity of MC and HPMC hydrogels

Previous studies have demonstrated that MC and HPMC are non-toxic and possess excellent biocompatibility through *in vitro* cytotoxicity assay (Jyoti et al., 2010; Tate et al., 2001; Zhang et al., 2014). To assess the phytotoxicity of the hydrogels, visual assessment of was conducted to detect any damage to the Chinese cabbage mainly the degree growth inhibition, necrosis or chlorosis was reflected in the photographs. Phytotoxicity testing was performed according to the standard guidelines (OECD 208) or negative control. Fig. 3B displays the digital photographs of a Chinese cabbage on the 30th day after introduction to the M-0.25 and H-0.25. The Chinese cabbage did not exhibit any damage. The average heights of the plants of the negative control and soil treated with M-0.25 and H-0.25 are  $21.98 \pm 1.64$ ,  $21.55 \pm 1.46$ , and  $21.86 \pm 1.58$  cm. Fig. 3C depicts the average fresh weight and average dry weight of the plants of the negative control, soil treated with M-0.25 and H-0.25 hydrogels. Negligible decrease ( $p > 0.05$ ) was observed in the average heights, average fresh weight and average dry weight of plants for M-0.25 and H-0.25 hydrogels. These plant growth assessments indicate that M-0.25 and H-0.25 do not present a considerable toxicity problem.

### 3.4. Mechanical properties of MC and HPMC hydrogels

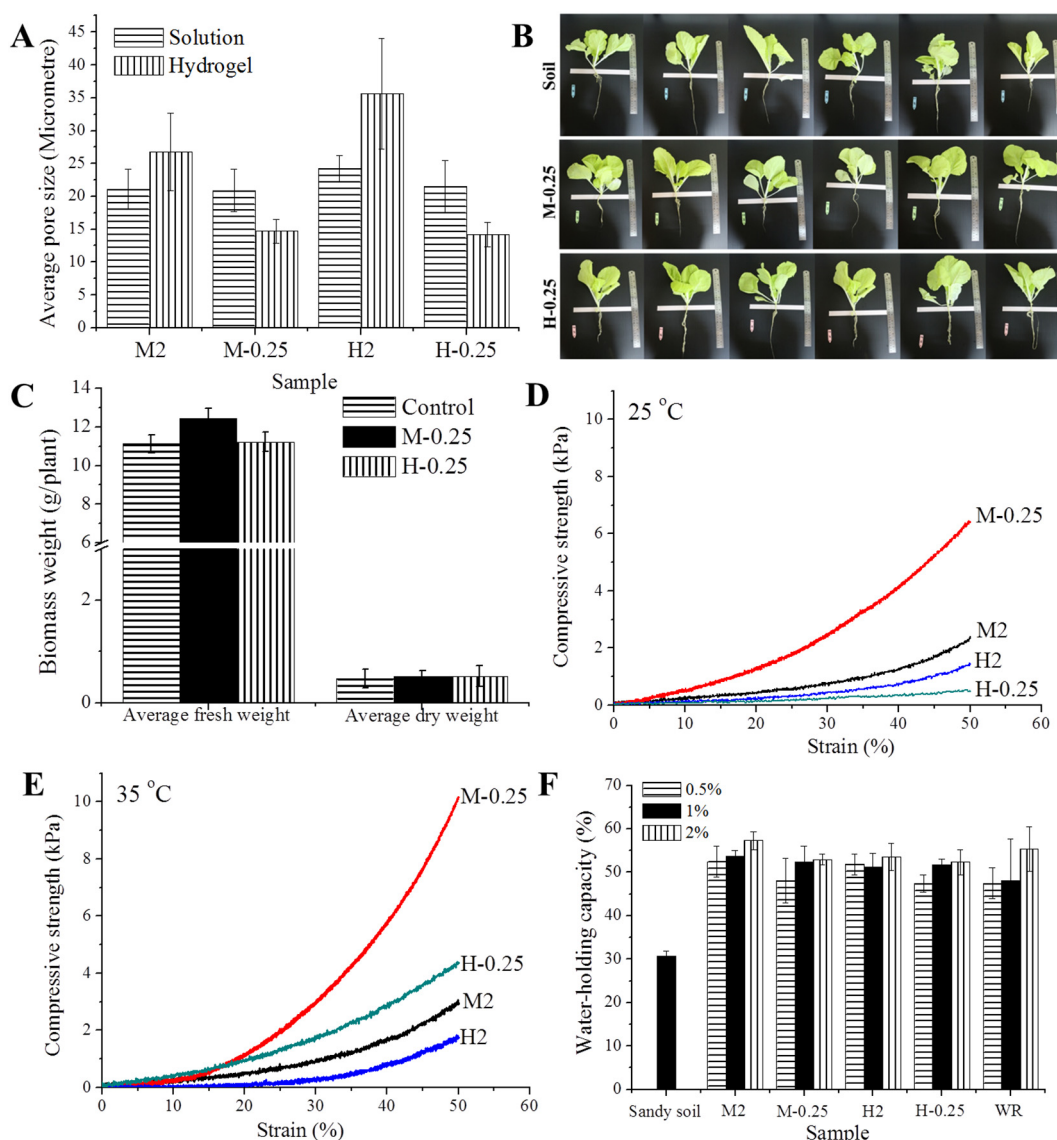
Fig. 3D and E illustrate the stress-strain curves obtained through compression testing of the M2, M-0.25, H2, and H-0.25 hydrogels at 25 and 35  $^{\circ}\text{C}$ . The area under compressive stress curves is associated with toughness of the hydrogels. The toughness of the hydrogels at 35  $^{\circ}\text{C}$  is higher than that at 25  $^{\circ}\text{C}$  because of the temperature response. M-0.25 exhibits the highest toughness and strength among four kinds of hydrogels at 25 and 35  $^{\circ}\text{C}$ . Mechanical properties of M-0.25 were

attributed to low gel temperature (27.8  $^{\circ}\text{C}$ ). At 50% strain, the MC-based hydrogels exhibited a considerably higher compressive modulus and strength than those of the HPMC-based hydrogels (Table 2). At 35  $^{\circ}\text{C}$ , both compressive modulus and strength of M-0.25 and H-0.25 were significantly higher than those of M2 and H2. Compressive modulus and strength of the H2 hydrogel were very low because gel temperature was 67.4  $^{\circ}\text{C}$ , whereas compressive modulus and strength of H-0.25 were significantly higher than M2 and H2 at 35  $^{\circ}\text{C}$  because its gel temperature was 35.1  $^{\circ}\text{C}$ . Improvement in mechanical properties with the addition  $\text{K}_2\text{SO}_4$  was attributed to the increase in hydrophobic interaction of MC and HPMC and the decrease in gel temperature. High mechanical properties of hydrogels can maintain their shape in or on soil and aid physical property of the soil.

### 3.5. Water-holding and water-retention capacity of sandy soil with hydrogels

Increasing the water-holding capacity of sandy soils can help increase the yield of crops and reduce the drainage overflow water below the root zone (Reynolds et al., 2000). In recent years, studies have demonstrated that hydrogels enhance soil water-holding capacity (Coello et al., 2018; Guilherme et al., 2015; Savi et al., 2014). Fig. 3F depicts the water-holding capacity of the soil treated with the different types of hydrogels, and the CS is considerably higher than that of the untreated soil. Water-holding capacities of soil treated with 0.5% dosage treatments of hydrogels were higher than or equal to CS. In addition, increasing the dosage from 0.5% to 2% of hydrogels slightly increased the water-holding capacity. Adding 0.5% of M2, M-0.25, H2, H-0.25, and CS increased the water retention of sandy soil by 71.2%, 57.0%, 69.2%, 54.9%, and 54.9% relative to the control. Thus, only a 0.5% dosage of hydrogels could effectively improve the water-holding capacity of sandy soil. These results, similar to the previous investigation, indicate that hydrogel could effectively improve the water-holding capacity of sandy soil (Ni et al., 2011).

Water-retention capacities of sandy soil with various dosages of hydrogels and CS are depicted in Fig. 4. Fig. 4A illustrates the water-retention capacity of the control sample (sandy soil) was 0% at 11 days. Fig. 4B–F demonstrates that the water-retention capacity of sandy soil mixed hydrogel and CS is much higher than that of the control sample and rises with an increasing dosage of hydrogel. In the 15-day test, the water-retention capacities of 0.5%, 1%, and 2% dosages of CS resulted in 32.5%, 53.3%, and 59.3%. The water-retention capacities of 0.5%, 1%, and 2% dosages of M2 were 32.5%, 53.3%, and 59.3%. 0.5%, 1% and 2% dosages of CS reported the water-retention capacities of



**Fig. 3.** (A) Average pore size of cellulose ether solutions and hydrogels. (C) Digital photographs of the Chinese cabbage on the 30th day after introduction to the M-0.25 and H-0.25 hydrogel. (D) Average fresh weight and average dry weight for the Chinese cabbage exposed to soil and mixed with M-0.25 and H-0.25. (E) Compressive strength and modulus of the hydrogels. (F) Water-holding capacities of sandy soils mixed with various dosages of cellulose ether hydrogels and commercial soil conditioner (CS).

were <8, 9.7 and 18.8%, respectively, whereas, the water-retention capacities of soil with 0.5%, 1%, and 2% of M2 dosage were 10.4%, 11.5%, and 31.3% on the 30th day. Therefore, the experimental studies

demonstrated the water-retention capacity of MC hydrogel is better than that of the current commercial production.

**Table 2**

Compressive strength and modulus of the hydrogels.

Temperature (°C)	Code	Compressive strength at 50% strain (kPa)	Compressive modulus (kPa)
25	M2	2.56 ± 0.33 <sup>cd</sup>	3.46 ± 0.31 <sup>bc</sup>
	M-0.25	6.51 ± 0.56 <sup>f</sup>	10.32 ± 0.45 <sup>d</sup>
	H2	1.45 ± 0.24 <sup>ab</sup>	2.03 ± 0.05 <sup>ab</sup>
	H-0.25	0.47 ± 0.03 <sup>a</sup>	1.36 ± 0.04 <sup>a</sup>
35	M2	3.07 ± 0.23 <sup>d</sup>	4.54 ± 0.33 <sup>c</sup>
	M-0.25	10.52 ± 0.33 <sup>g</sup>	14.90 ± 1.41 <sup>e</sup>
	H2	1.64 ± 0.36 <sup>bc</sup>	2.06 ± 0.12 <sup>ab</sup>
	H-0.25	5.06 ± 0.60 <sup>e</sup>	9.90 ± 0.52 <sup>d</sup>

\*Mean ± standard deviation with different capital letters indicates significant differences between bamboo charcoal composites using Tukey's multiple range tests at p < 0.05.

**3.6. Temperature- and pH-responsive fertilizer release kinetics and mechanism**

As mentioned previously, M2, M-0.25, H2, and H-0.25 exhibit temperature-response and stable water-retention capacity. To illustrate the temperature-responsive fertilizer release profile, a controlled release fertilizer was applied under DD water at 25 and 35 °C. The fertilizer release profiles of the 20-20-20 fertilizer are presented in Fig. 5A–B. The release rates of the fertilizer are high in deionized water. Proportions of 84.0% and 89.0% of the total fertilizer were released in deionized water at 25 and 35 °C within 60 min. The 20-20-20 fertilizer was released in an initial burst and displayed negligible temperature-responsiveness. The fertilizer release profiles of M2, M-0.25, H2 and H-0.25 in deionized water at 25 and 35 °C are illustrated in Fig. 5C–D. The results indicated that the fertilizer release profiles of the controlled release fertilizers

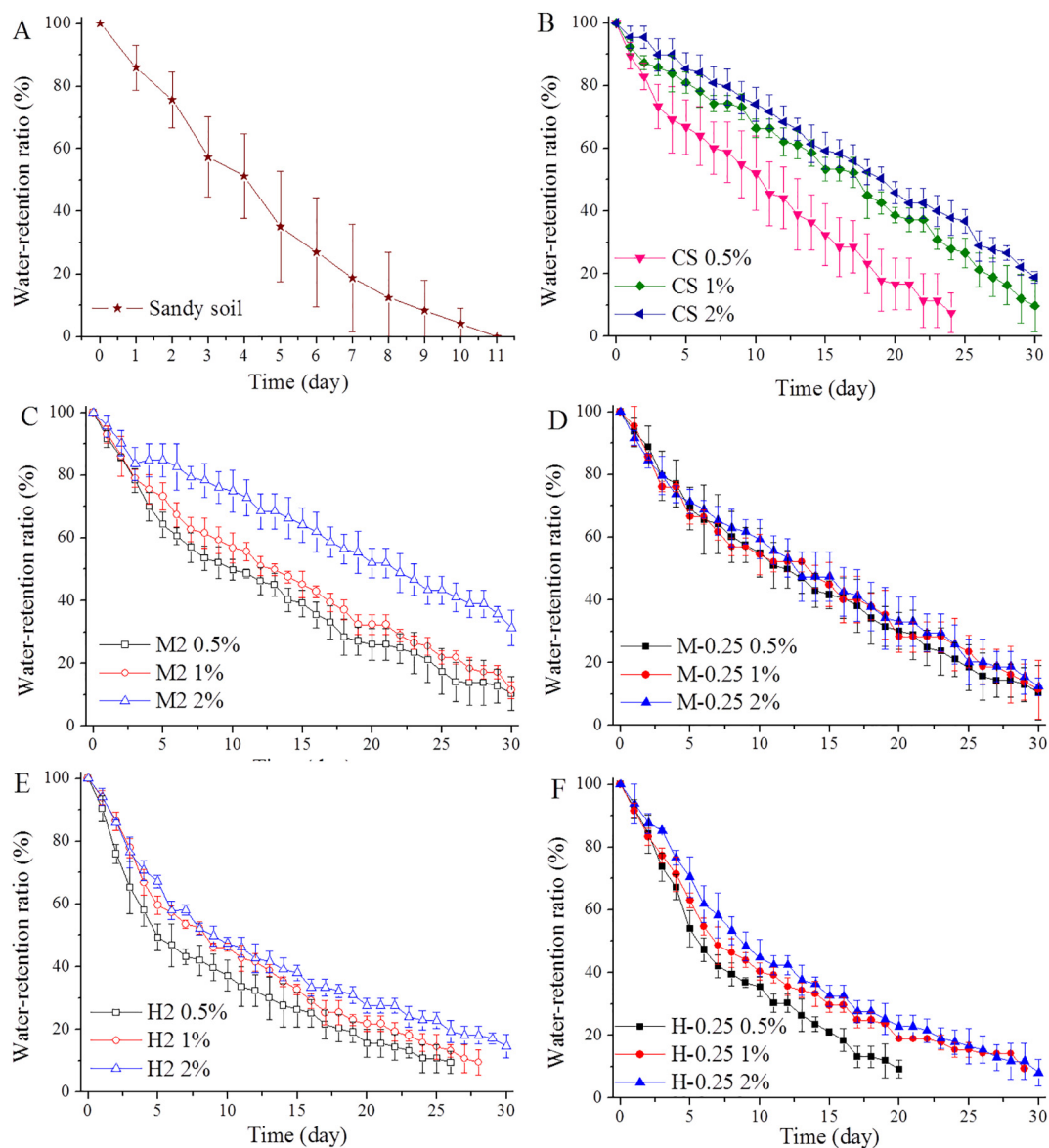


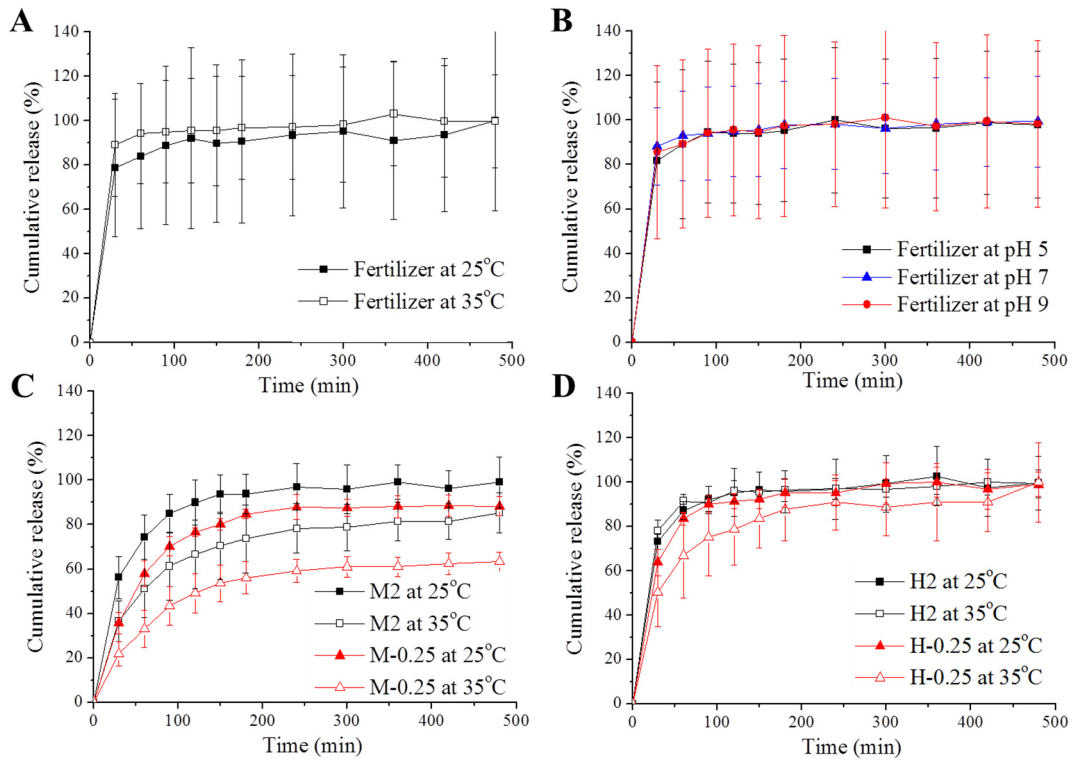
Fig. 4. Water-retention capacities of sandy soils mixed with various dosages of cellulose ether hydrogels and commercial soil conditioner (CS).

were lower than that of free fertilizer. After 60 min, M2, M-0.25, H2, and H-0.25 released fertilizer at 25 °C were 74.3%, 58.0%, 87.3%, and 83.6%. At 35 °C, the released fertilizer from M2, M-0.25, H2, and H-0.25 was approximately 51.1%, 33.1%, 91.4%, and 66.9% within 60 min. The results indicated that the fertilizer release of M2 and H2 were higher than that of M-0.25 and H-0.25, respectively. These findings demonstrate that decreasing the pore size of dry hydrogel with  $K_2SO_4$  can slow the release rate. The fertilizer release rates of M2, M-0.25, and H-0.25 at 35 °C are lower than that at 25 °C. The fertilizer release profiles of M2, M-0.25 and H-0.25 considerably differed between 25 °C and 35 °C. The temperature-responsive fertilizer release can be attributed to the temperature-sensitive segment and salt-out effect of the hydrogels.

For comparing soil characteristics, acidic (pH 5), neutral (pH 7), and alkaline (pH 9) simulated soil solutions were used to observe the pH-responsive release of fertilizer. The fertilizer was rapidly released under simulated soil solutions of pH 5, pH 7, and pH 9 (Fig. 5B). A total of 89.1%, 93.0% and 89.2% of total fertilizer was released under simulated soil solutions of pH 5, pH 7, and pH 9 within 60 min. The results indicated that the released fertilizer has an initial burst without a pH-

dependent change. The fertilizer release profiles of M2, M-0.25, H2, and H-0.25 under simulated soil of various pH values at 25 °C are shown in Fig. 6. At pH of 5, 7, and 9, 58.9, 74.7 and 81.8%, respectively, of the fertilizer was released from M2 within 60 min. M-0.25 released fertilizer of pH 5, 7 and 9 were observed to be 51.2%, 47.5%, and 69.8%. The release rate of M2 and M-0.25 at pH 9 was lower than that at pH 5 and 7, whereas, 81.9%, 76.5%, and 81.7% of fertilizer was released from H2 at pH of 5, 7, and 9 after 60 min. The result indicated H2 has negligible pH-responsiveness. The released fertilizer from H-0.25 at pH of 5, 7, and 9 was approximately 62.4%, 64.9%, and 70.5% within 60 min. These results indicated that the fertilizer release profiles of M2, M-0.25, and H-0.25 were influenced by altering the pH value. The release rates of M2, M-0.25, and H-0.25 at pH 9 were slightly higher than that at pH 7 and 5, which could be ascribed to hydroxide ion exclusion and hydrogel salt-out in the alkaline environment (Pegram and Record, 2008). Moreover, the anion parameter is a major deciding factor of the Hofmeister series (Xu and Li, 2005). The temperature- and pH-dependent controlled release fertilizer likely results from the temperature-sensitive segment of MC and HPMC and the Hofmeister effect of the hydrogels. The pH range of typical

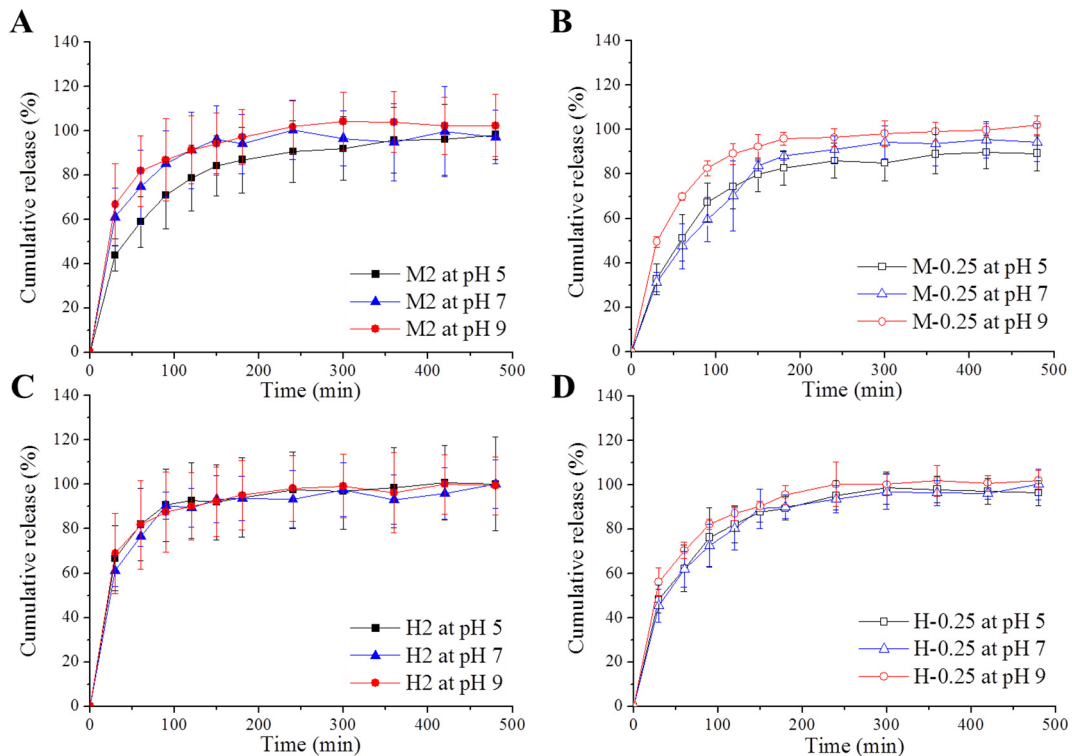




**Fig. 5.** Fertilizer release profiles of the 20-20-20 fertilizer in deionized water (A) and in simulated soil solutions at 25 °C (B). Fertilizer release profiles of controlled release fertilizer (C and D) in deionized water at 25 and 35 °C.

sandy soils under citrus production in Florida, USA is 5.2–7.8 (Yu et al., 2006). Consequently, sandy soil temperature at 35 °C and pH below 7 slowed the fertilizer release from the M-0.25 hydrogel.

The fertilizer release data were analyzed kinetically using zero order, first order, Higuchi, and Korsmeyer–Peppas model (Dash et al., 2010). The equations of models can be simplified (Treenate and Monvisade,



**Fig. 6.** Fertilizer release profiles of the controlled release fertilizer (A) M2, (B) M-0.25, (C) H2 and (D) H-0.25 in simulated soil solutions at 25 °C.



**Table 3**  
Results of curve fitting analysis using the different mathematical models for fertilizer release of 180 min.

Code	Medium	Temp. (°C)	<sup>a</sup> R <sup>2</sup>				<sup>a</sup> n
			Zero order	First order	Higuchi	Korsmeyer-Peppas	
M2	Water	25	0.8012	0.8012	0.9002	0.9443	0.2930
	Water	35	0.8908	0.8908	0.9614	0.9767	0.3930
	PBS at pH 5	25	0.9160	0.9160	0.9751	0.9882	0.3917
	PBS at pH 7	25	0.8342	0.8342	0.9199	0.9625	0.2585
	PBS at pH 9	25	0.8514	0.8514	0.9322	0.9660	0.2038
M-0.25	Water	25	0.8459	0.8459	0.9314	0.9420	0.4766
	Water	35	0.9214	0.9214	0.9772	0.9828	0.5398
	PBS at pH 5	25	0.8795	0.8795	0.9529	0.9642	0.5293
	PBS at pH 7	25	0.9778	0.9778	0.9939	0.9972	0.5876
	PBS at pH 9	25	0.8448	0.8448	0.9311	0.9566	0.3713
H2	Water	25	0.6793	0.6793	0.8030	0.8876	0.1524
	Water	35	0.6310	0.6310	0.7428	0.8273	0.1124
	PBS at pH 5	25	0.6722	0.6722	0.7950	0.8788	0.1901
	PBS at pH 7	25	0.7169	0.7169	0.8277	0.8981	0.2439
	PBS at pH 9	25	0.8275	0.8275	0.9161	0.9603	0.1747
H-0.25	Water	25	0.6574	0.6574	0.7787	0.8540	0.2111
	Water	35	0.8782	0.8782	0.9500	0.9699	0.3006
	PBS at pH 5	25	0.8938	0.8938	0.9600	0.9801	0.3573
	PBS at pH 7	25	0.9225	0.9225	0.9762	0.9887	0.3924
	PBS at pH 9	25	0.8971	0.8971	0.9630	0.9834	0.2963

<sup>a</sup> Correlation coefficients ( $R^2$ ) and release exponent ( $n$ ) are presented.

2017) as follows:

$$\text{Zero order model: } \frac{R_t}{R_\infty} = kT - R_0$$

$$\text{First order model: } \frac{R_t}{R_\infty} = R_0 e^{kT}$$

$$\text{Higuchi model: } \frac{R_t}{R_\infty} = R_0 T^{0.5}$$

$$\text{Korsmeyer-Peppas model: } \frac{R_t}{R_\infty} = kT^n$$

where  $R_t$  represents the fertilizer released amount in time  $T$ ,  $R_\infty$  is the total percentage of fertilizer released,  $R_0$  is the fertilizer concentration at beginning time,  $k$  is the rate constant, and  $n$  is the release exponent of fertilizer release mechanism. OriginPro8 was used for the calculation of  $n$  and the resolution of the  $R^2$ . The release kinetic models of  $R^2$  and  $n$  are listed in Table 3. M2, M-0.25, H2 and H-0.25 were suited for the Korsmeyer-Peppas model compared with the Higuchi, zero order, and first order models. In this study,  $n$  is the release exponent characterizing the different release mechanisms:  $n \leq 0.50$  (Fickian diffusion) and  $0.50 < n < 0.87$  (non-Fickian transport) (Dash et al., 2010). For M2 and M-0.25,  $n$  ranged from 0.2930 to 0.5876 and 0.3713 to 0.5876, respectively. The results obtained with the Korsmeyer-Peppas equation indicate release of 20-20-20 fertilizer from M2 was through Fickian diffusion at different temperatures and pH values. At 35 °C and pH 5 and 7, fertilizer release from the M2, H2, and H-0.25 was through diffusion, whereas, the release from M-0.25 was through non-Fickian transport ( $n > 0.50$ ). Both swelling and diffusion controlled release of M-0.25 play major roles in the fertilizer transport mechanism (Jana et al., 2014). Moreover, these findings also demonstrate temperature- and pH- responsiveness of M-0.25 hydrogels. M-0.25 not only has superior water retention properties with high initial swelling rate but also can control fertilizer release.

#### 4. Conclusions

To encapsulate the water soluble fertilizer, temperature-responsive hydrogels of MC and HPMC with  $K_2SO_4$  were prepared. Toxic solvents were not required to stabilize the hydrophilic fertilizer. The salt concentration affects the temperature-responsive behavior of the solutions and

can change the sol-gel temperature. The swelling time of the hydrogels with  $K_2SO_4$  was longer than that for the raw MC and HPMC hydrogels. Behaviors of the MC and HPMC based hydrogels followed Schott's second-order swelling kinetics model and the parameters indicated that adding  $K_2SO_4$  can improve the initial swelling rate. Adding hydrogels could considerably enhance the water-holding and water-retention capacity of sandy soil. The fertilizer-release profiles demonstrated transport mechanism of the M-0.25 hydrogel is swelling and diffusion that retards the release rate of fertilizer, and reveals temperature- and pH-responsive behavior. The temperature-sensitive segment, Hofmeister effect, and porous microstructure were used in controlling the water penetration into the network of hydrogels, thus, improving the controlled release fertilizer. This study indicated that hydrogels can be used to prepare soil conditioner and nutrient carriers for sandy soil under high temperatures, which may find agricultural and horticultural application in arid and semi-arid regions.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.11.264>.

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