


# Eco-friendly smart hydrogels for soil conditioning and sustain release fertilizer

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**Abstract** In the agricultural industry, biomass waste generated along with the production of food, is transformed into value-added products. Also, the demand for the slow or control release fertilizer is increasing to reduce the cost of maintaining the agricultural land. These issues are tackled by converting biomass waste to a slow fertilizer release vehicle and biodegradable water retention material that could reduce the cost for fertilizer application and simultaneously preserved the soil from dryness. A series of carboxymethyl sago pulp (CMSP) hydrogels were prepared by electron beam irradiation. Slow release systems were evaluated by loading potassium nitrate ( $\text{KNO}_3$ ) and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) into the CMSP hydrogels. These CMSP hydrogels endow slow release property, biodegradability and a soil moisture preservation property that could find greener application in agricultural industries. The results indicate that CMSP hydrogels have a great potential as an agent for slow release of fertilizers.

**Keywords** Carboxymethyl sago pulp · Hydrogel · Soil preservation · Soil biodegradation · Slow release fertilizer

## Introduction

New arable lands are being developed to increase the production of commercial plantation crops such as oil palm, paddy, cocoa, natural rubber, pepper and sago starch. A study made on the soil characteristics under crop farming found that the biggest problems faced were soil erosion and the effects of slope terracing on soils which, led to significant fertilizer loss with concomitant water pollution in lower lying areas (Pincus et al. 2016; Smith and Siciliano 2015; Wei et al. 2016). The leachates from conventionally applied agrochemicals are recognized to be a significant contributor to ground water contamination (Islami et al. 2011; Quirós et al. 2015). Additionally, the leachates cause changes in soil microbiological properties and a shift in soil microbial communities, which indicates soil stress that adversely influences the productivity of the farm (Gupta et al. 2017; Huang et al. 2014). The presence of nutrients such as phosphorus and nitrogen in ground water may also adversely affect biological attributes due to their toxicity and ability to bio-accumulate in the food chain (Mahdy et al. 2017; Zeinali and Lenjannezhadian 2017). As such there is a need for a more controlled application of agrochemicals to reduce the amounts of active ingredients at any given time without diminishing efficiency (Pourjavadi et al. 2011). The replacement of conventional agrochemical formulations by controlled-release systems helps to avoid treatment with excess amounts of active substances by maintaining a local concentration of active ingredients in the soil and reducing runoff, thereby providing a pragmatic

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solution to the various environmental problems caused by traditional water-soluble fertilizers (Pincus et al. 2016).

There are many approaches to providing a controlled-release environment. One way that shows promise is to take advantage of the interwoven characteristics associated with polymeric hydrogels, which by definition trap aqueous solvent within their lattice to produce the hydrogel characteristics. In a recent example where agrochemicals were trapped in the hydrogel by including them in the feed mixture undergoing radiation-based polymerization, their findings suggest the amount of swelling controlled the agrochemical release, i.e., when the swelling percentage is high, the amount of fertilizer release will also be higher. Similarly, release studies on CMC-g-polyacrylamide hydrogels loaded with 63% w/v aqueous potassium nitrate ( $\text{KNO}_3$ ) solution showed the fertilizer to have been fully released within 7 days. This is not appealing for agriculture use as the fertilizer needs to be retained for longer periods of time (Bajpai and Giri 2003). CMC-based superabsorbent hydrogels are also finding increasing interest as a result of their high biodegradable characteristics and high swelling capacity (El-Mohdy 2007).

The composition of the hydrogel is also vital to its practical use in an agricultural environment. For example, the degradation of polyacrylamide leads to the formation of acrylamide that creates potential environmental hazards such as contamination of surface and ground water systems and health risks such as nerve toxins (Chadwick et al. 2015; Smith et al. 1997). The concerns of both government and public opinion regarding environmental conservation have diverted manufacturers toward producing more sustainable cellulose-based superabsorbent hydrogels from renewable organic resources, which biodegrade completely and safely (Marci et al. 2006).

Superabsorbent hydrogels can also be added as a soil conditioner, to reduce soil water loss and allowing a sustained release of water to the soil and the plant roots. Simultaneously, it promotes the formation of soil aggregates and enhances the soil microbial activity that increase crop yield (Li et al. 2014). The use of the hydrogel on a large scale might have a revolutionary impact on water resources management, particularly in arid areas (Demetri et al. 2013).

In 2015, the global fertilizers and agricultural chemicals market forecast a volume of 186.4 million metric tons, an increase of  $\sim 13\%$  since 2010 (Datamonitor June 2011). The slow release fertilizer (SRF)/control release fertilizer (CRF) annual growth rate in the period 2010–2015 was predicted to be 2.6%. Asia–Pacific accounts for 53.5% of the global fertilizers and agricultural chemicals market value followed by Americas (26.3%), Europe (16.5%),

Middle East and Africa (3.7%). Coated CRFs have the highest demand in these countries. The interest in using CRFs in developing countries such as Malaysia, India and China is also increasing (Rahman 2004; Smith and Siciliano 2015). In 2012, China produced 1.35 million tons of SRF/CRF for its agricultural markets in corn, wheat and rice (Liu 2013). Chinese SRF/CRF consumption has been growing significantly in recent years and projected to grow 12.8% annually during 2014–2019 (Handbook February 2015).

The drive to use SRFs/CRFs in agricultural markets is to reduce labor costs, environmental concerns and maintaining high nutrient use efficiency (NUE). Increased usage could be achieved by producing new, less expensive technologies which could be derived using cheaper starting material, such as plant waste, and developing efficient application method unique to market needs (Carlos et al. 2009; Shaviv and Mikkelsen 1993). This approach to producing CMSP hydrogels from natural resources, such as sago pulp from sago waste, shows promise in our laboratory (Pushpamalar 2010). In this study, the hydrogels demonstrated SRF, water absorbing, soil conditioner properties and biodegradability.

Our current research is focusing on CMSP hydrogels that are prepared by using CMSP from sago pulp and irradiated under electron beam irradiation without the use of cross-linking agents. In this paper, we are reporting on the investigations of slow release properties, swelling and soil biodegradability of our CMSP hydrogels.

## Materials and methods

### Biodegradation of CMC hydrogels in garden soil

Sago pulp was isolated from sago waste (PPES Sago Industries (Mukah) Sdn Bhd., Sarawak) and converted to CMSP with different degrees of substitution (DS), and the CMSP solutions were irradiated using EB radiation to form the CMSP hydrogels as mentioned in our earlier published work (Pushpamalar et al. 2006, 2013b). The biodegradation behavior of the CMSP hydrogels of DS 0.4, 0.6 and 0.8 with %GFs of 25, 35 and  $\geq 40\%$  in garden soil (Plant Lover brand, Selangor) was studied. Perforated transparent plastic cups were prepared by drilling holes in the wall of the plastic cups (holes are 1 cm apart from each other) to allow water movement, and the labels were sealed separately to avoid water penetration. The black garden soil (pH 6–7) used in this study is a six-in-one commercial organic potting mix (supplied by Plant Lover, Selangor) with the reported the properties of promoting plant growth.



The black garden soil contained coco peat, burnt soil, river sand, burnt husk, rich humus and charcoal powder which reduced the acidity of soil and prevented pests. Half of the cups were filled with black garden soil, and the label was inserted near the inner wall of the cup to allow the label to be seen from outer part of the cup. The pre-weighed hydrogel samples were then inserted, and the cups filled fully with the black garden soil and pressed. A land area of 4 m<sup>2</sup> was dug to a depth of 30 cm and filled to a 5 cm height with black garden soil. The cups were then arranged to open downwards in the plot area, and the plot was filled with black garden soil to bury the plastic cups. After a period of 1–16 weeks, plastic cups were taken out at regular intervals, and the samples were washed carefully with water, dried in the oven at 70 °C and then weighed. All the periodically weighed hydrogel samples were averages of three replicates. Percentage of biodegradation (BP) of the hydrogel was calculated using the following Eq. (1):

$$BP = ((W_0 - W_1)/W_1) \times 100 \quad (1)$$

where  $W_0$  and  $W_1$  were the weights of the hydrogel in the plastic cups before and after degradation (Nie et al. 2004).

#### Loading of the model fertilizers potassium nitrate (KNO<sub>3</sub>) and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>)

Loading of CMSP hydrogels of DS 0.4, 0.6 and 0.8 with %GFs of 25, 35 and  $\geq 40\%$  was achieved by allowing the dry hydrogel (0.1–0.2 g) to swell in aqueous KNO<sub>3</sub> solutions of 10 and 20% w/v concentration and aqueous NH<sub>4</sub>NO<sub>3</sub> solutions of 20 and 40% w/v concentration. The swollen hydrogels were washed with distilled water, dried at 40 °C for 3 days and stored under vacuum at 27 °C in polyethylene bags. The percentage loading of KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> in the hydrogel was calculated by the following Eq. (2) (Bajpai and Giri 2002):

$$\% \text{Fertilizer loading} = \frac{\text{Weight of fertilizer loaded}}{\text{Weight of unloaded hydrogel}} \times 100 \quad (2)$$

#### Assay on KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> release

In a typical release experiment, KNO<sub>3</sub>- and NH<sub>4</sub>NO<sub>3</sub>-loaded CMSP hydrogels of DS 0.4, 0.6 and 0.8 with %GFs of 25, 35 and  $\geq 40\%$  of known weight and percentage loading were placed in distilled water (50 ml) as a release medium under diffusion (unstirred) conditions. The concentration of released KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> was estimated by measuring the conductivity of the release medium using a

conductivity meter (Bajpai and Giri 2002). A HANNA model HI9635 conductivity meter was used to measure the conductivity of the fertilizers. The concentration of KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> released was quantified using calibration curves of  $R^2 = 0.9906$  and  $0.9933$ , respectively. The equilibrium concentration ( $M_\infty$ ) of released KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> was determined by measuring the conductivity of the release medium after 9 days. Kinetic analysis of the release data was made using the following Eq. (3); moreover, the diffusional release kinetic mechanism exponent ( $n$ ) was evaluated graphically (Bajpai and Giri 2002).

$$F = W_t/W_\infty = kt^n \quad (3)$$

where  $F$  denotes the fraction of model fertilizer diffused out of the hydrogel at time  $t$ ,  $k$  is the diffusion ratio factor,  $n$  is diffusional release kinetic mechanism exponent, and  $W_t$  and  $W_\infty$  are the amounts of accumulation release of model fertilizer at time  $t$  and equilibrium time, respectively.

These hydrogels were characterized to study the surface morphology, crystallinity and the biodegradation in garden soil.

#### Scanning electron microscopy (SEM) observation

Observation of exterior/surface and interior morphology of CMC hydrogels of DS 0.4, 0.6 and 0.8 with % GFs of 25, 35 and  $\geq 40\%$  were investigated using SEM model Quanta 400 ESEM. For preparation of dried hydrogel, the swollen hydrogel was dried in the oven 2 days at 70 °C and transferred to a freezer for a day and freeze-dried for 2 days until all the non-bound water was removed. The dried hydrogel was mounted onto an aluminum stud and sputter-coated with gold.

#### X-ray diffractometry analysis

Powder X-ray diffraction patterns of sago pulp and CMCs with DS 0.4, 0.6 and 0.8 were obtained by using diffractometer PHILIPS 1729 model in the scanning range of  $\theta = 1^\circ$  to  $60^\circ$  with the following operating conditions: 40 kV and 25 mA with CuK $\alpha$  radiation at 1.54059 Å. The  $K_\beta$  radiation can be eliminated by using a nickel foil as the filter. The diffractometer is equipped with  $1^\circ$  divergence,  $1^\circ$  receiving,  $1^\circ$  scatter, a graphite monochromator and proportional detector. The sample for analysis was prepared by using a quartz plate applied with Vaseline, and the sample was sprinkled on to it (Pushpamalar 2010).

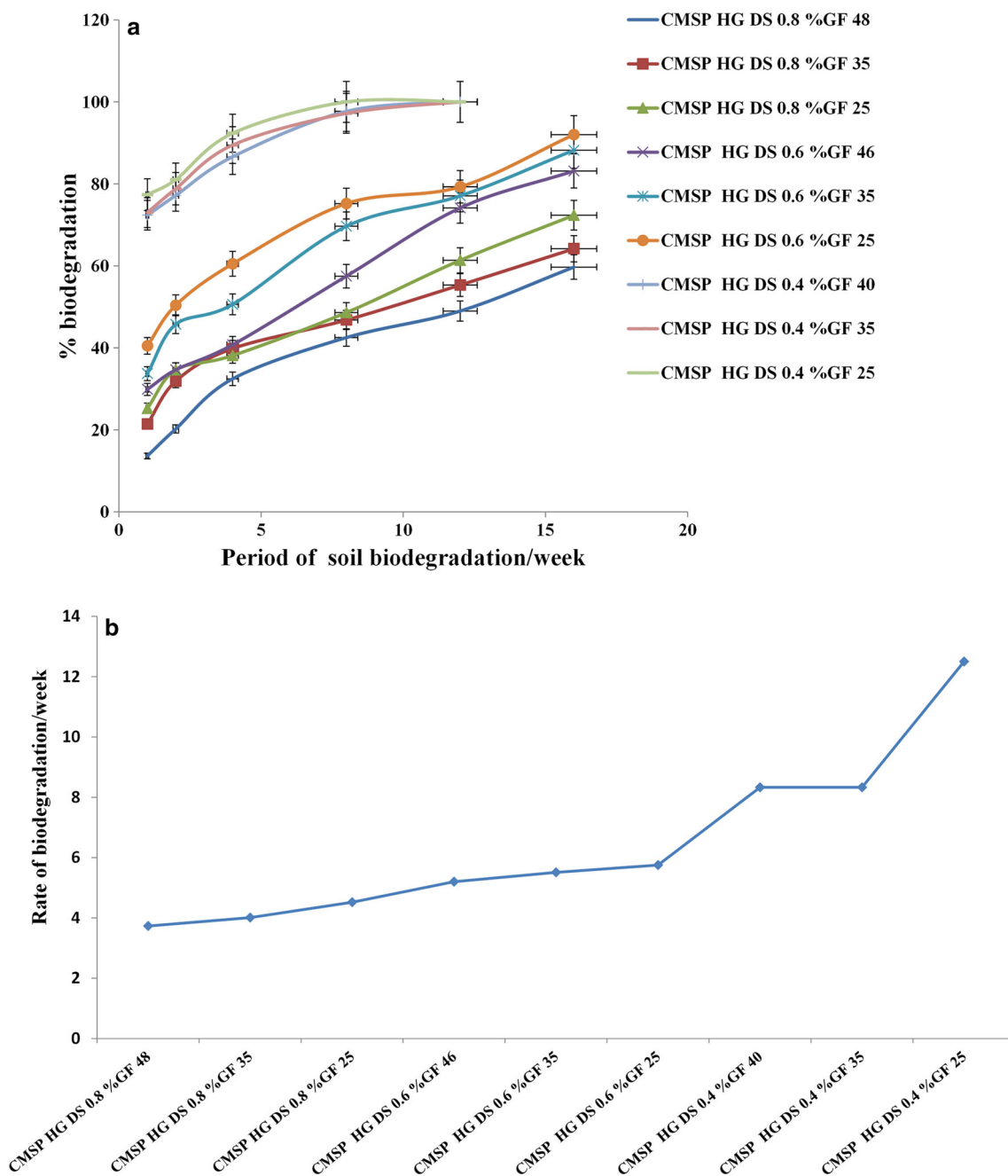


## Results and discussion

### Biodegradation test

The series of CMSP hydrogels were tested for biodegradability in the black garden soil, the loading of the model fertilizer was determined, and the release kinetic characteristics of the model fertilizers were studied.

Dried CMSP hydrogels of DS 0.4, 0.6 and 0.8 with %GF 25, 35 and  $\geq 40$  were buried in a perforated cup to allow the samples to be exposed to microorganisms and moisture within the soil. The hydrogels were swollen by the soil humidity, and the soils loosely adhered to the gels. Interestingly, the hydrogels taken out after 2 months were covered with soil and grass roots that grew into the remnant network of the hydrogels.



**Fig. 1** a Percentage of soil biodegradation and b rate of biodegradation per week of CMSP hydrogel of DS 0.4, 0.6 and 0.8 with %GF 25, 35 and above 40

The soil burial test was conducted over for 4 months with the average daily temperature around 29–32 °C, falling to 20–25 °C with heavy rain over the winter months. Figure 1a shows the percentage biodegradation of the hydrogel with DS 0.4, 0.6 and 0.8 with %GF 25, 35 and  $\geq 40$  against time of exposure. The degradation of CMSP hydrogel of DS 0.4 was the fastest of all CMSP hydrogels to degrade by this measure with each %GF completely degraded within 3 months. Within experimental error, there appear to be differences in the rates of degradation for hydrogels of different GF and DS values. The deterioration of the hydrogels, however, was proportional to the DS with DS 0.6 (88% w/w) more prone to degradation than DS 0.8 (72% w/w). Here, too, the %GF did trend with 25% GF > 35% GF > 46–48% GF. Figure 1b shows the rate of degradation of the hydrogel with DS 0.4, 0.6 and 0.8 with %GF 25, 35 and  $\geq 40$ . The rate of biodegradation of CMSP hydrogels with DS 0.8 is about 3–4% (w/w)/week, DS 0.6 is about 5% (w/w)/week, and DS 0.4 is 8–12% (w/w)/week. What we can conclude is that CMSP hydrogels with higher DS are more resistant to microbial attack. It also appears that CMSP hydrogels with higher %GF, with their higher cross-linking density, degrade slower. The biodegradability of the CMSP hydrogel in the soil is an essential requirement to use the CMSP hydrogels as a carrier for slow release fertilizer and it is an effective polymer for environmental conservation. A complementary study on enzymatic degradation on CMC hydrogel formed using gamma irradiation also showed cross-linked CMC hydrogels degraded by the action of *cellulase* and thereby was classified as an environmentally friendly polymer (Wach et al. 2001). In other work, the rate of biodegradation the CMC hydrogel was enhanced by the addition of nutrient element, especially by the addition of urea. The results of biodegradation in different soils indicated sand soil was favorable for hydrogel degradation (Nagasawa et al. 2004; Nie et al. 2004).

### Loading and release of fertilizers

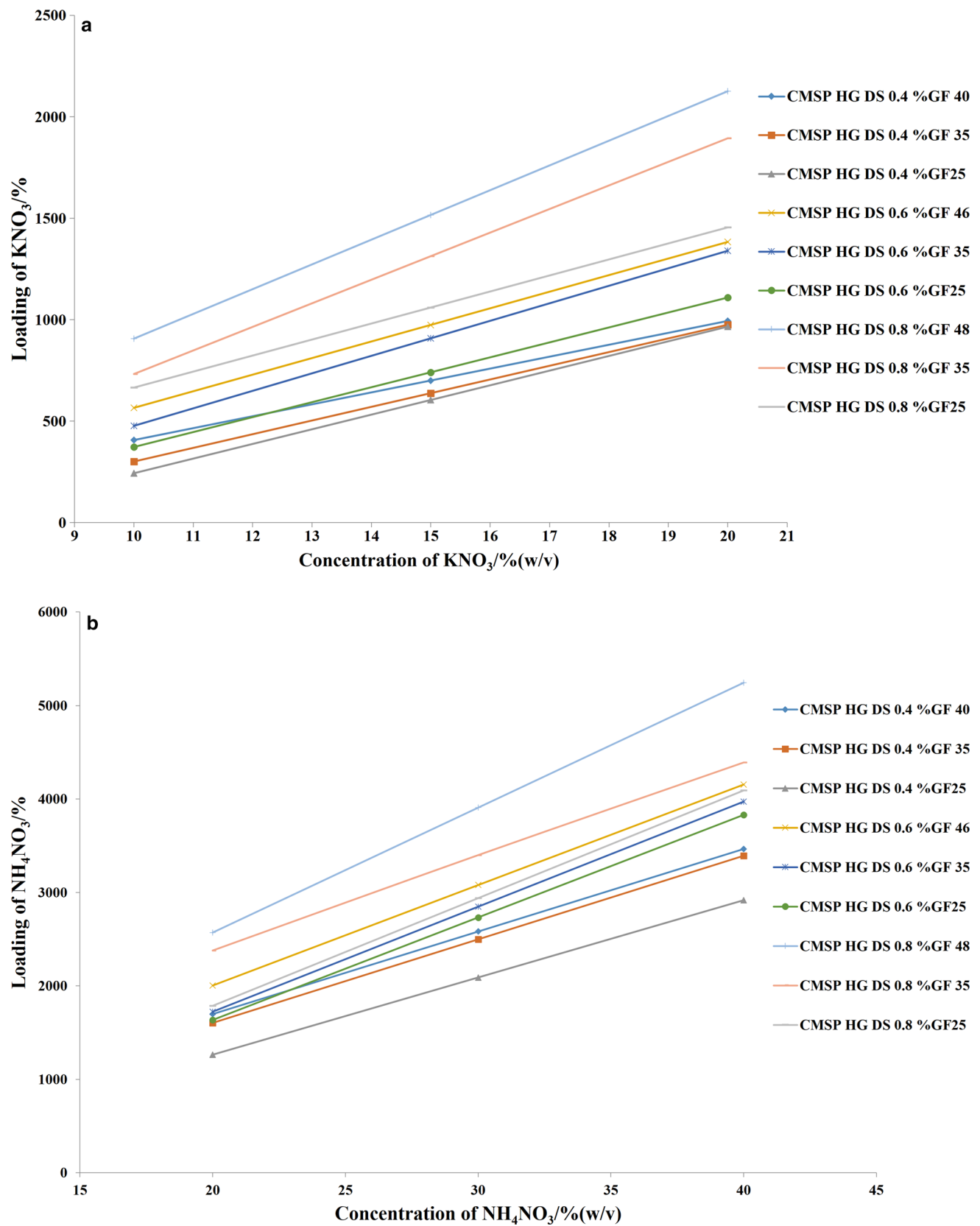
In this study, we investigated CMSP hydrogels entrapped with model fertilizers ( $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$ ). It is expected that when the fertilizer-loaded CMSP hydrogel is allowed to contact an aqueous release medium, the water would penetrate the surface of hydrogel releasing the  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$ . The effect of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  concentration on the CMSP hydrogels loading is shown in Fig. 2. It indicates that the percentage of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  loading (w/w %) on CMSP hydrogel increased with increasing  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  concentration. This is a result of increasing of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  diffusion rate inside the

CMSP hydrogel matrix (El-Mohdy 2007). From Fig. 2a, the CMSP hydrogels of DS 0.8 with %GF of 25, 35 and 48 (w/w %) were immersed in aqueous 10% w/v  $\text{KNO}_3$  solution resulting in a  $\text{KNO}_3$  loading of 660, 730 and 900% (w/w %), respectively. CMSP hydrogels treated with an aqueous 20% w/v  $\text{KNO}_3$  resulted in 1450, 1900 and 2100% (w/w %), respectively. The CMSP hydrogels of DS 0.6 with %GF of 25, 35 and 46 (w/w %) immersed in aqueous 10% w/v  $\text{KNO}_3$  resulted in lower percentages of  $\text{KNO}_3$  loading and even lower with DS 0.4. Overall, the loading of  $\text{KNO}_3$  increased with increasing DS and %GF. It is to be noted that the percentage of  $\text{KNO}_3$  loading obtained in swelling in aqueous 10–20% w/v  $\text{KNO}_3$  is much higher (600–2100% w/w) for different CMC hydrogels prepared than the percentage of  $\text{KNO}_3$  loading with 3% (w/v)  $\text{KNO}_3$  into CMC/polyacrylamide hydrogels (El-Mohdy 2007). The high  $\text{KNO}_3$  loading property is critical in slow release fertilizer as the highly  $\text{KNO}_3$ -loaded hydrogel will release higher amounts of  $\text{KNO}_3$  where more  $\text{KNO}_3$  nutrient will be supplied to the plants and the CMC hydrogel could be subjected for more days in the soil as the biodegradation period for the different CMC hydrogels are from 1–4 months as reported in the biodegradation study.

The effect of  $\text{NH}_4\text{NO}_3$  concentration on the CMSP hydrogel loading is shown in Fig. 2b. Here, the percentage of  $\text{NH}_4\text{NO}_3$  loading (w/w %) within the CMSP hydrogel increases with increasing  $\text{NH}_4\text{NO}_3$  concentration, a trend similarly observed for the potassium nitrate loading. The CMSP hydrogels of DS 0.8 with %GF of 25, 35 and 48 (w/w %) were immersed in aqueous 20% w/v  $\text{NH}_4\text{NO}_3$  solutions resulted in a percentage of  $\text{NH}_4\text{NO}_3$  loading of 1800, 2400 and 2600% (w/w %), respectively, and with aqueous 40% w/v  $\text{NH}_4\text{NO}_3$  resulted in 4100, 4400 and 5200% (w/w %), respectively. The CMSP hydrogels of DS 0.6 and 0.4 absorbed proportionately less with %GF of 25, 35 and 40–46 (w/w %) showing the general trend of loading 25 < 35 < 40–46%.

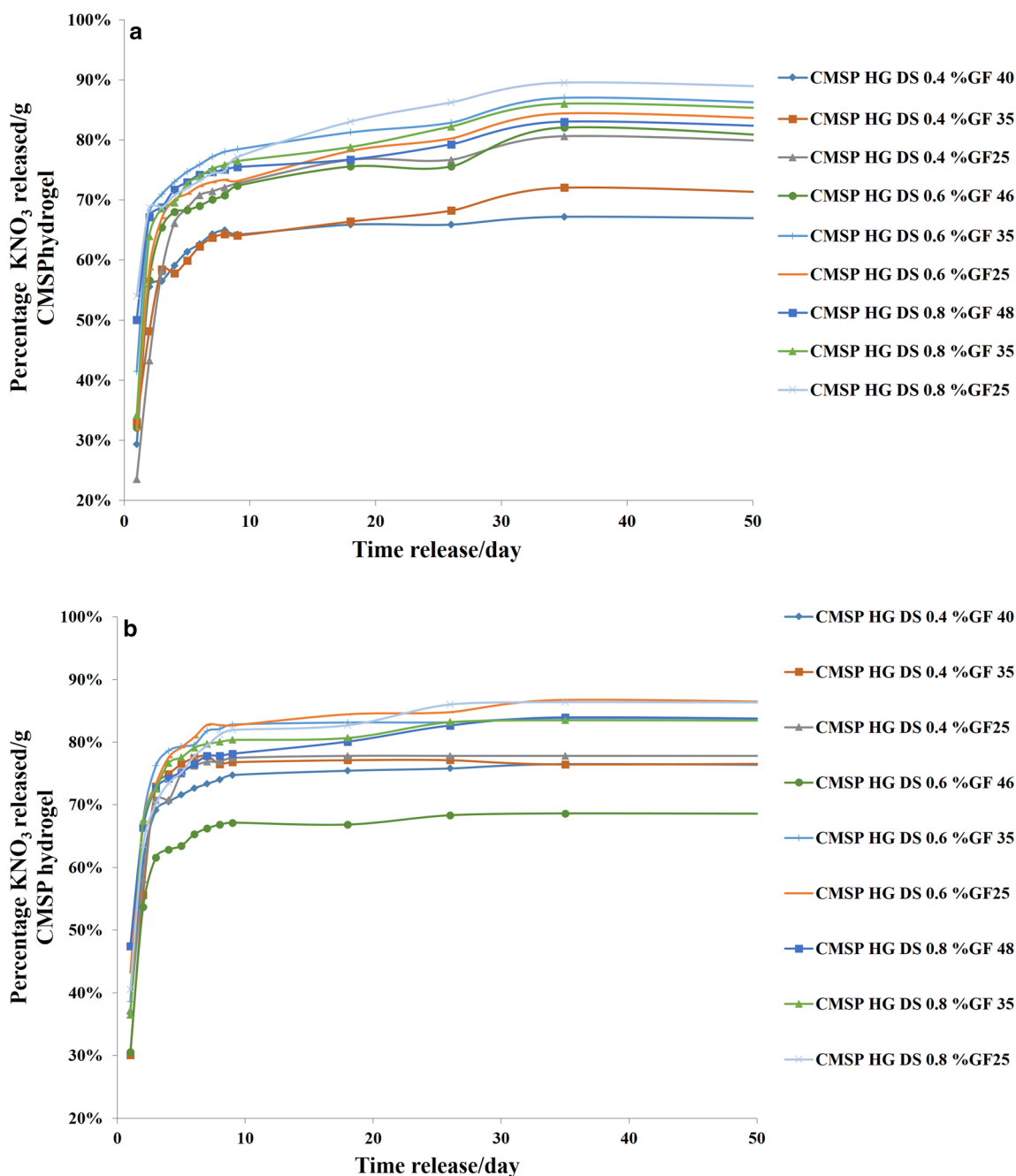
In related work, a new synthetic hydrogel formed by free radical copolymerization of acrylamide, acrylic acid, hydroxypropyl acrylate and glycidyl methacrylate was studied for its  $\text{NH}_4\text{NO}_3$  release. (Wang et al. 2007) This hydrogel was loaded with  $\text{NH}_4\text{NO}_3$  solutions (20 and 40% w/v) and resulted in 180 and 360 wt%  $\text{NH}_4\text{NO}_3$  loading, respectively. The release rate of the higher loaded hydrogel was faster than that of the lower loaded hydrogel. It indicates that the release rate of  $\text{NH}_4\text{NO}_3$  is influenced substantially by the difference in loading concentration. Encouragingly, the 20 and 40%  $\text{NH}_4\text{NO}_3$  solutions subjected to the different CMC hydrogels prepared in this study resulted in 1000–2500% w/v  $\text{NH}_4\text{NO}_3$  and 4000–5200% w/v  $\text{NH}_4\text{NO}_3$  loading, respectively. This is





**Fig. 2** Effect of concentration of **a**  $\text{KNO}_3$  and **b**  $\text{NH}_4\text{NO}_3$  on the loading of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  into the CMSP hydrogels





**Fig. 3** KNO<sub>3</sub> release kinetics of **a** 10% and **b** 20% w/v KNO<sub>3</sub>-loaded CMSP hydrogels in distilled water at 25 °C, respectively

much higher than that of acrylamide, acrylic acid, hydroxypropyl acrylate and glycidyl methacrylate hydrogels, all synthetic hydrogels, in 20–40% NH<sub>4</sub>NO<sub>3</sub> immersion solution. Similar to the KNO<sub>3</sub> case, the high KNO<sub>3</sub> loading property is vital in slow release fertilizer where the highly KNO<sub>3</sub>-loaded hydrogel will increase the release rate and the amounts of KNO<sub>3</sub> nutrient to the plants.

**Assay of released KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub>**

An important factor in the use of CMSP hydrogels as the carrier of fertilizer is the effect of percent loading on the rate of fertilizer release. Aqueous 10 and 20% w/v loaded KNO<sub>3</sub> CMSP hydrogels release profiles are shown in Fig. 3. At a superficial level, the amount of KNO<sub>3</sub> released

increases with time and then levels off after 50 days. The profile appears to have three phases.  $\text{KNO}_3$  released increases significantly for the first 10 days (6.5–8.5%/day) and gradually increases for the next 50 days (1.5–2.5%/day) and then levels off up to 200 days. About 50%  $\text{KNO}_3$  release was achieved in 2 days under our conditions, 60–70%  $\text{KNO}_3$  release made in less than 10 days, and 80–90%  $\text{KNO}_3$  release achieved in 50 days, with no further release of  $\text{KNO}_3$  release beyond 90%. These results are not optimal as the major release over 10 days could lead to an accumulation of  $\text{KNO}_3$  in the soils, which could lead to  $\text{KNO}_3$  release exceeding the crop demand and the point of crop response, and when crop recovery of the applied  $\text{KNO}_3$  is low.

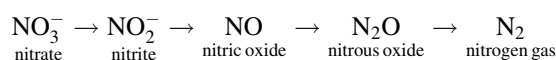
Interestingly, on the 18th day of the release study, there is a sudden high release of  $\text{KNO}_3$  from the 10%  $\text{KNO}_3$ -loaded CMSP hydrogels with DS 0.4 %GF 25, CMSP HG DS 0.6 %GF 25 and %GF 35 and CMSP HG DS 0.8 %GF 35. The same type of significant  $\text{KNO}_3$  release was also observed from 20%  $\text{KNO}_3$ -loaded of the CMSP HG DS 0.4 %GF25, CMSP HG DS 0.6 %GF25 and CMSP HG DS 0.8 %GF35 and 48. In these cases, the fertilizer release is due to the molecules (water and fertilizer) diffusion and polymer network degradation (Klinger and Landfester 2012). The degradation could occur due to the cleavage of the backbones or cross-linking points of the network-forming CMSP. The cleavage of cross-linking points leads to decreasing cross-linking density and increasing pore size. The diffusivity of the fertilizer is no more constant but increases with propagating polymer network degradation. This propagation of polymer network degradation increases with time and to a certain point where the network collapses and releases the fertilizer in an uncontrolled manner.

The aqueous 20 and 40% w/v  $\text{NH}_4\text{NO}_3$ -loaded CMSP hydrogel release profiles are shown in Fig. 4. The results are similar to those for potassium nitrate. All the CMSP hydrogels achieved about 50%  $\text{NH}_4\text{NO}_3$  release in 2 days and 60–85%  $\text{NH}_4\text{NO}_3$  release in under 10 days. Higher levels of 86–92%  $\text{NH}_4\text{NO}_3$  release were achieved within 50 days. As a result of the rapid release, the  $\text{NH}_4\text{NO}_3$  could accumulate in the soils, and this could lead to  $\text{NH}_4\text{NO}_3$  release exceeding the crop demand (Snyder et al. 2009). Consistently and in alignment with the  $\text{KNO}_3$  study, Fig. 4 shows that within a narrow range (ca. 20–30th day) of the release study there is sudden high release of  $\text{NH}_4\text{NO}_3$  from the CMSP HG DS 0.4 %GF 35, CMSP HG DS 0.6 %GF 35 and GF46 and CMSP HG DS 0.8 %GF 35 and 48. This may be attributed to the “burst effect” phenomena which arise when loaded CMSP hydrogels are put in the release medium, and the biodegradation of the CMSP hydrogel

takes place and releases the significant amount of the entrapped  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  (Bajpai and Giri 2002).

Both the profiles show that the release of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  increases with the increase in DS but decreases with the increase in the %GF. The average molecular weight of CMSP increases with increasing DS as a result of an increase in the number of  $-\text{CH}_2\text{COONa}$  groups per glucose unit and, as a result, higher cross-linking could occur and more surface area available for  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  loading (Nomura et al. 1990; Pushpamalar 2010). The increase of %GF could have caused the macromolecular chain to become dense with the increase in cross-linking and form a tight network that restricts the flexibility of the macromolecular chain and leads to difficulty for the water molecule to penetrate out from the CMSP hydrogel, causing the slow release kinetics of  $\text{KNO}_3$ .

All our prepared CMSP hydrogels have degraded after a maximum release of  $\text{KNO}_3$ . Within experimental error, the results show that the CMSP hydrogels did not attain full (100%) release over the period. This can be explained by denitrification from the following pathway:

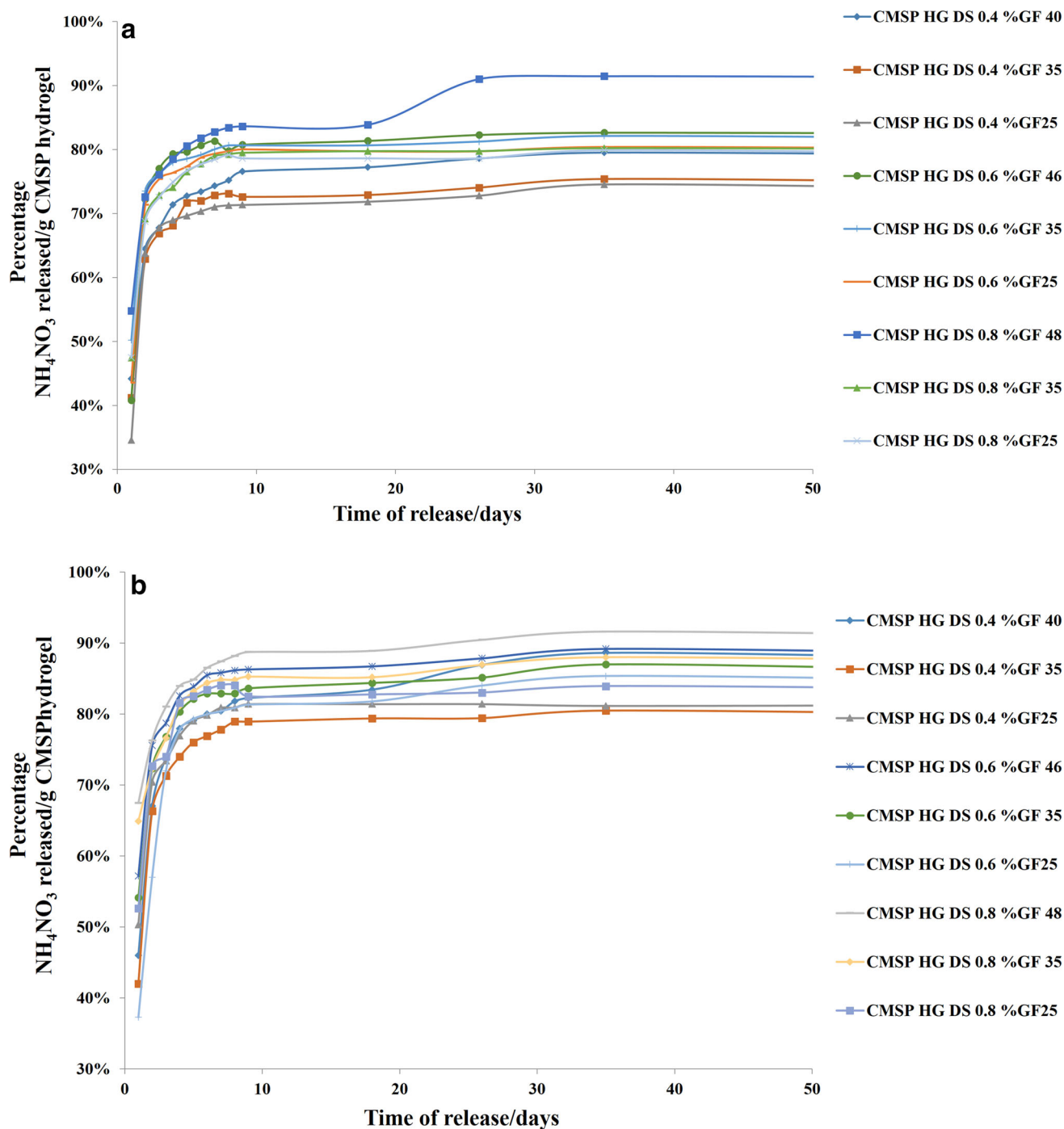


The conversion of  $\text{NO}_3^-$  to  $\text{N}_2$  can be complete but small and variable portion of the nitrogen is often emitted as an  $\text{N}_2\text{O}$  gas. Emissions of  $\text{N}_2$  and  $\text{N}_2\text{O}$  gases are sporadic, occurring before, during and after the plant growing season. Flushes of these gases can happen in aerated soils which have become moistened or saturated from precipitation or irrigation (Kim et al. 2013; van der Weerden et al. 2016).

It has been established that a highly swelling hydrogel should release a greater amount of  $\text{KNO}_3$  entrapped within the hydrogel (Bajpai and Giri 2002). In this process, the release of solute from the loaded hydrogel involves the absorption of exogenous water into the matrix and simultaneous release of  $\text{KNO}_3$  through diffusion. We recently established that the diffusion of water out of the CMSP hydrogel is fastest for DS 0.4, and slowest for similar hydrogels with a DS of 0.8 (Pushpamalar 2010). Consistently, the diffusion of water is much slower in the CMSP hydrogel of %GF  $\geq 40$ . This may be due to the higher cross-linking density in the CMSP hydrogel with higher %GF which reduces the size of the pores in the structure of CMSP hydrogel from which the water diffuses. This retardation leads to a decrease in swelling ratio and the diffusion coefficient (Amsden 1998; Pushpamalar et al. 2013b).

All the CMSP hydrogels in this paper studied for slow fertilizer release possess useful characteristics such as





**Fig. 4**  $\text{NH}_4\text{NO}_3$  release plot of **a** 20% and **b** 40% w/v  $\text{NH}_4\text{NO}_3$ -loaded CMSP hydrogels in distilled water at 25 °C

biodegradability in soil, loading and release of the model fertilizers ( $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$ ) was achieved, and significant swelling in water under a range of different conditions has been observed (e.g., temperature, pH, inorganic solutions). (Pushpamalar et al. 2013a, b) The order of best performance of our CMSP hydrogels in all slow release characteristics is: CMSP HG DS 0.8 %GF 48 > CMSP HG

DS 0.8 %GF 35 > CMSP HG DS 0.8 %GF 25 > CMSP HG DS 0.6 %GF 46 > CMSP HG DS 0.6 %GF 35 > CMSP HG DS 0.6 %GF 25 > CMSP HG DS 0.4 %GF 40 > CMSP HG DS 0.4 %GF 35 > CMSP HG DS 0.4 %GF 25.

To determine the diffusional release rate coefficient ( $n$ ), the percentage of release of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  by a gram

**Table 1** Diffusional release rate coefficient of the aqueous KNO<sub>3</sub>-loaded CMSP hydrogels for the initial release

Types of CMSP hydrogel	Diffusional release rate coefficient (cm <sup>2</sup> min <sup>-1</sup> )	
	10% w/v loaded KNO <sub>3</sub>	20% w/v loaded KNO <sub>3</sub>
DS 0.4 with %GF 25	0.0167	0.0162
DS 0.4 with %GF 35	0.0126	0.0155
DS 0.4 with %GF 40	0.0096	0.0133
DS 0.6 with %GF 25	0.0169	0.0183
DS 0.6 with %GF 35	0.0167	0.0153
DS 0.6 with %GF 46	0.0156	0.0147
DS 0.8 with %GF 25	0.019	0.0197
DS 0.8 with %GF 35	0.011	0.0147
DS 0.8 with %GF 48	0.0094	0.012

**Table 2** Diffusional release rate coefficient of the NH<sub>4</sub>NO<sub>3</sub>-loaded CMSP hydrogels for the initial release

CMSP Hydrogel	Diffusional release rate coefficient (cm <sup>2</sup> min <sup>-1</sup> )	
	20% w/v loaded NH <sub>4</sub> NO <sub>3</sub>	40% w/v loaded NH <sub>4</sub> NO <sub>3</sub>
DS 0.4 with %GF 25	0.0186	0.0155
DS 0.4 with %GF 35	0.0138	0.0134
DS 0.4 with %GF 40	0.0129	0.0128
DS 0.6 with %GF 25	0.0200	0.0125
DS 0.6 with %GF 35	0.0177	0.0117
DS 0.6 with %GF 46	0.0148	0.0116
DS 0.8 with %GF 25	0.0139	0.0127
DS 0.8 with %GF 35	0.0135	0.0056
DS 0.8 with %GF 48	0.0113	0.0047

**Table 3** Values of calculated diffusional release kinetic mechanism exponent and release mechanism of the KNO<sub>3</sub>-loaded CMSP hydrogels

CMSP hydrogel	10% w/v loaded KNO <sub>3</sub>		20% w/v loaded KNO <sub>3</sub>	
	Diffusional release kinetic mechanism exponent ( <i>n</i> )	Transport mechanism	Diffusional release kinetic mechanism exponent ( <i>n</i> )	Transport mechanism
DS 0.4 with %GF 25	0.920	Non-Fickian	0.344	Fickian
DS 0.4 with %GF 35	0.884	Non-Fickian	0.307	Fickian
DS 0.4 with %GF 40	0.534	Non-Fickian	0.217	Fickian
DS 0.6 with %GF 25	0.864	Non-Fickian	0.241	Fickian
DS 0.6 with %GF 35	0.818	Non-Fickian	0.224	Fickian
DS 0.6 with %GF 46	0.700	Non-Fickian	0.189	Fickian
DS 0.8 with %GF 25	0.896	Non-Fickian	0.604	Non-Fickian
DS 0.8 with %GF 35	0.429	Fickian	0.486	Fickian
DS 0.8 with %GF 48	0.364	Fickian	0.312	Fickian

of the cross-linked CMSP hydrogel was plotted against the square root of immersion time (Pushpamalar 2010). The diffusional release rate coefficients are calculated from the linear slope for respective KNO<sub>3</sub>, and NH<sub>4</sub>NO<sub>3</sub>-loaded CMSP hydrogel and are listed in Tables 1 and 2, respectively.

As we know from previous discussions, increasing the concentration of KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> resulted in an enhancement of the percentage of KNO<sub>3</sub>- and NH<sub>4</sub>NO<sub>3</sub>-loaded (*w/w* %) within the CMSP hydrogel matrix. The increase in loading of KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> also increases the diffusional release rate coefficient as expected because

**Table 4** Values of calculated diffusional release kinetic mechanism exponent and release mechanism of the  $\text{NH}_4\text{NO}_3$ -loaded CMSP hydrogels

CMSP hydrogel	20% w/v loaded $\text{NH}_4\text{NO}_3$		40% w/v loaded $\text{NH}_4\text{NO}_3$	
	Diffusional release kinetic mechanism exponent ( $n$ )	Transport mechanism	Diffusional release kinetic mechanism exponent ( $n$ )	Transport mechanism
DS 0.4 with %GF 25	0.8841	Non-Fickian	0.2605	Fickian
DS 0.4 with %GF 35	0.6026	Non-Fickian	0.1795	Fickian
DS 0.4 with %GF 40	0.5468	Non-Fickian	0.1073	Fickian
DS 0.6 with %GF 25	0.8169	Non-Fickian	0.5835	Non-Fickian
DS 0.6 with %GF 35	0.6991	Non-Fickian	0.1498	Fickian
DS 0.6 with %GF 46	0.5461	Non-Fickian	0.1028	Fickian
DS 0.8 with %GF 25	0.5390	Non-Fickian	0.1490	Fickian
DS 0.8 with %GF 35	0.5326	Non-Fickian	0.1450	Fickian
DS 0.8 with GF 48	0.4077	Fickian	0.1410	Fickian

of the larger the initial load; the faster is the movement of the  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  penetrating the surface of the loaded CMSP hydrogel. The rate of diffusional release coefficient in Tables 1 and 2 shows a decrease with increase in %GF. We have rationalized this as at higher %GF; the CMSP hydrogel has a greater cross-linking network and the CMSP macromolecular chains become dense which hinder the mobility of the  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  molecules to penetrate into the network, resulting in the decrease of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  release (Bajpai and Giri 2002; El-Mohdy 2007).

The graph of  $\ln F$  versus  $\ln t$  for aqueous 10 and 20% w/v loaded  $\text{KNO}_3$  and aqueous 20 and 40% w/v loaded  $\text{NH}_4\text{NO}_3$  CMSP hydrogels, respectively (not shown). Here the diffusional release kinetic mechanism exponent ( $n$ ) of the  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  is determined from the slope of the straight lines and collected in Tables 3 and 4, respectively. This equation is applied to the initial stages of release and plots of  $\ln F$  versus  $\ln t$  yield straight lines for up to 2 days of immersion. For Fickian diffusion,  $n < 0.5$ , where the model fertilizer release process is controlled by diffusional transport, and non-Fickian diffusion  $n$  usually lies between  $0.5 < n < 1.0$  where the polymeric matrix relaxation dominates the model fertilizer release process (Bajpai and Giri 2002; Francis et al. 2004; Saraydin et al. 1995, 1996)

The values of the diffusional release kinetic mechanism exponent ( $n$ ) of CMSP hydrogels with DS 0.4 of aqueous 10% w/v loaded  $\text{KNO}_3$  and aqueous 20% w/v loaded  $\text{KNO}_3$  lies between 0.53–0.92 and 0.22–0.34, indicating both non-Fickian and Fickian behavior, respectively. It is observed that the transport mechanism for CMSP hydrogels loaded with aqueous 10% w/v  $\text{KNO}_3$  is non-Fickian except for CMSP hydrogel of DS 0.8 of %GF 35 and 48. For the

aqueous 20% w/v loaded  $\text{KNO}_3$ , the transport mechanism is Fickian except for CMSP hydrogel of DS 0.8 of %GF25. This type of transport mechanism observed may be due to the chain length increases with increasing DS of the CMSP. Such a system allows for a faster relaxation of the network, resulting in Fickian nature, where the  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  molecules transport become diffusion controlled. In the non-Fickian states, the diffusion of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  molecules is much slower than the relaxation of the CMSP hydrogel, where the polymers chains are not sufficiently mobile to permit immediate penetration of the fertilizers out of polymer core.

The values of the diffusional release kinetic mechanism exponent of CMSP hydrogel with DS 0.4 of aqueous 20% w/v loaded  $\text{NH}_4\text{NO}_3$  and aqueous 40% w/v loaded  $\text{NH}_4\text{NO}_3$  are between 0.54–0.88 and 0.11–0.26, also indicating both non-Fickian and Fickian behavior, respectively. The similarity in results suggests that provided the nitrate use soluble; the cation has little effect on the rates of nitrate release. It is noticed that with the increase in loading of  $\text{NH}_4\text{NO}_3$  the transport mechanism is shifted to Fickian in nature and this observation is due to the larger initial load, which resulted in a faster movement of the  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  penetrating the surface of the loaded CMSP hydrogels. A larger loading may also facilitate the relaxation of CMSP macromolecular chains and where the  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  transport becomes diffusion controlled (Bajpai and Giri 2002; El-Mohdy 2007).

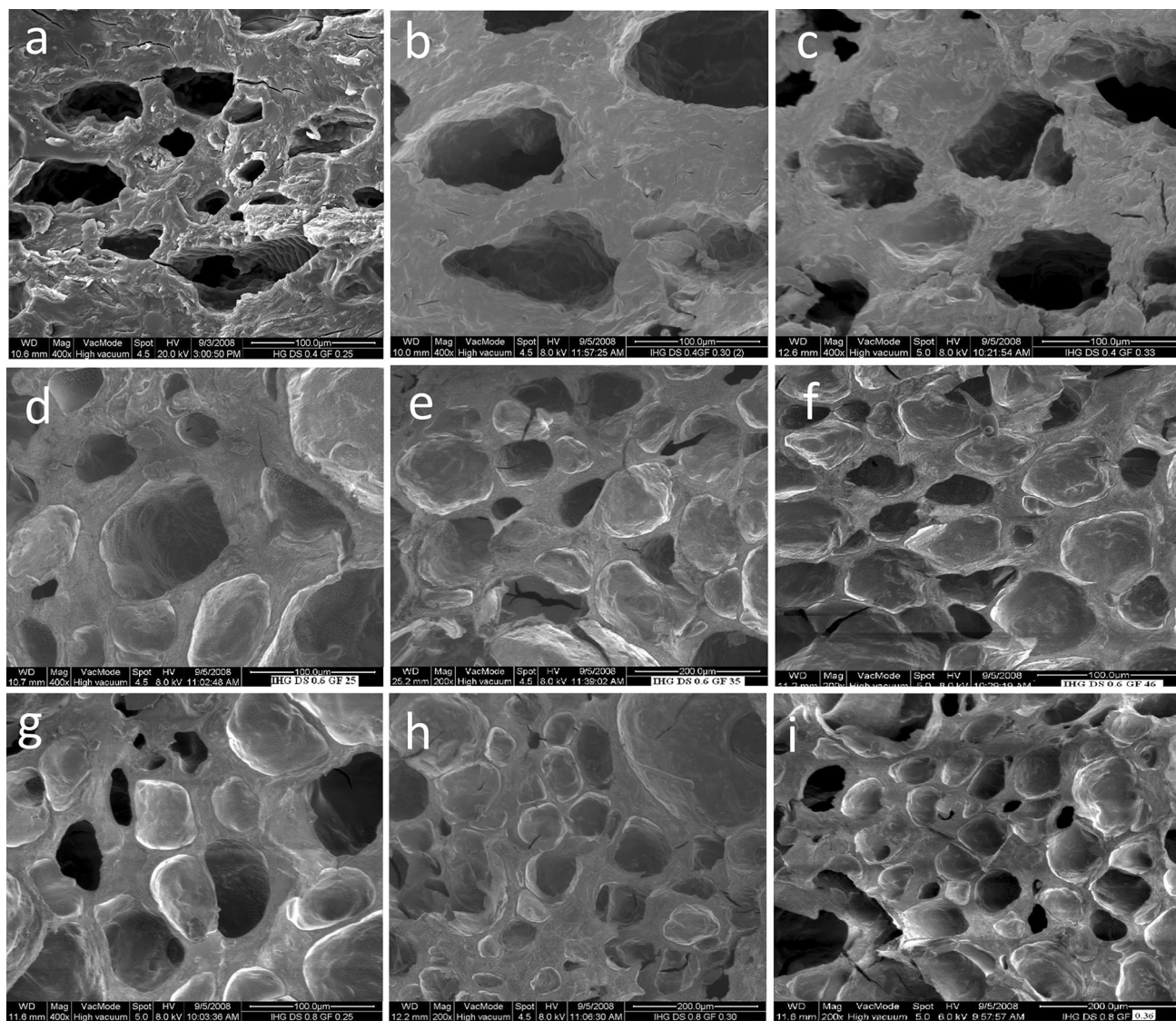
From the results obtained, we can conclude that these CMSP hydrogels could be applied as a slow release mechanism in the agricultural sector including vegetable, fruit, and paddy planting areas. In practicality, since most of the loaded  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  are being released within



50 days, it could be used as short time slow release agent. The CMSP hydrogels of DS 0.4 could be applied to the vegetable plantation as it would degrade within 3 months. CMSP hydrogel of DS 0.6 and 0.8 could be used in fruits and paddy plantations as they would need to release fertilizers over longer periods and it could also be used in vegetable plantations as these hydrogels degrade after 5 months.

### Scanning electron microscopy (SEM) observations

Figure 5 shows the SEM photographs of cross-sectional interior structures of CMC hydrogels of DS 0.4, 0.6 and 0.8 with %GF 25, 35 and  $\geq 40$ . These photographs show that CMC hydrogels form highly porous honeycomb-like structures at all levels of DS. The existence of the porosity confirms the three-dimensional structure of the hydrogel (Pourjavadi et al. 2011). The CMC hydrogels of DS 0.4 (Fig. 5a–c) show pores of irregular round shapes and sizes within a smooth overall superstructure. The CMC hydrogel



**Fig. 5** SEM photographs of CMC hydrogels of DS 0.4 (a–c with magnification of 400x), 0.6 (d with magnification of 400x and, e and f at 200x) and 0.8 (g with magnification of 400x and, h and i at 200x) with %GF 25, 35 and  $\geq 40$ , respectively, after irradiated with EB

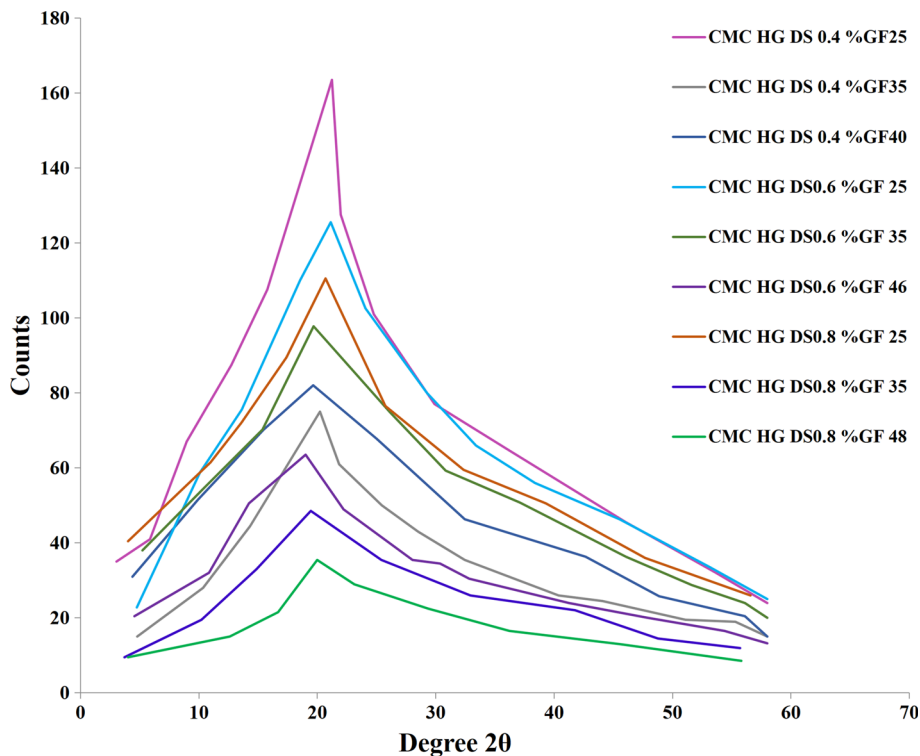


with DS 0.6 %GF 25 (Fig. 5d and e) has a structure with large and small pores in the network. CMC hydrogel with DS 0.6 %GF 46 (Fig. 5f) shows more regular round pores with medium size and a few large pores and a more ordered arrangement formed with slightly more dense and compact superstructure. The CMC hydrogel of DS 0.8 (Fig. 5g–i) shows most regular pores, and the arrangement of the pores appears to be more ordered, much more dense and compact superstructure. From the SEM photograph taken, it is observed that the number of pores that appears in the network of CMC hydrogel is in the increasing order of DS 0.4, 0.6 and 0.8 and %GF 25, 35 and  $\geq 40$ , respectively. From the SEM photographs of all the CMC hydrogels, it is observed that there is an increase in the order of arrangement of the pores, density and compactness of the structure in the increasing order of DS 0.4, 0.6 and 0.8 and %GF 25, 35 and  $\geq 40$ , respectively. These could be attributed to a higher level of cross-linking in CMC hydrogels of higher DS and %GF (Sun and Chu 2006). These results also show that with increasing the degree of cross-linking density (%GF), the pore size decreased due to the decreasing distance between polymer chains. This porous structure is an advantage to micro-molecules to diffuse into the interior of the hydrogel, and the size of the pores in the porous structure depends on the DS and %GF (Zhao and Mitomo 2009).

### X-ray diffractometry studies on CMC hydrogels

X-ray diffraction analysis was carried out on the CMC samples to ascertain the changes in the crystalline structure upon cross-linking by electron beam irradiation. Figure 6 shows a representation of the x-ray diffractograms of CMC hydrogels of DS 0.4, 0.6 and 0.8, respectively. From this figure, it is observed that there is a diffraction peak observed in the range of  $2\theta = 19^\circ\text{--}21^\circ$  for all the CMC hydrogels. The CMC hydrogels with DS 0.4 have the highest intensity (counts) for all CMC hydrogels of %GF 25, 35 and  $\geq 40$  followed by the CMC hydrogels with DS 0.6 of %GF 25, 35 and 46 and then CMC hydrogels with DS 0.8 of %GF 25, 35 and 48, respectively. In the CMC hydrogels of DS 0.4, there are many hydroxyl groups available for H-bonding and therefore capable of forming a three-dimensional ordered structure, which results in higher crystalline phases relative to CMC hydrogels of DS 0.6 and 0.8. The electrostatic interactions between CMC polymers also will increase with the increase of DS which inhibits the formation of ordered structure. We can conclude that the higher the peak intensity, the higher is the chain orientation degree and hence the higher the crystallinity. This is consistent with the previously reported results in which it is summarized that the crystallinity of CMC decreases with the increase in the DS (Zia et al. 2009).

**Fig. 6** X-ray diffractograms of CMC hydrogels of DSs of 0.4, 0.6 and 0.8 with %GF 25, 35 and  $\geq 40$ , respectively





From these results, it is observed that the peak intensity decreases with the increase in the %GF for all the CMC hydrogels. The decreasing intensity of the crystalline peak with an increase in %GF may be due to increasing cross-linking which inhibits or prevents the close packing of the CMC macromolecular chains by reducing the degree of freedom in the 3D conformation and limiting the formation of the crystalline regions. This reduction of crystallinity would play a crucial role in influencing the CMC hydrogels biodegradability, water absorption and swelling, as it is exhibited by results in the following sections (Costa-Júnior et al. 2009). A study on developing novel polymer blends using chitosan and poly(vinyl alcohol) and chemically cross-linked by glutaraldehyde exhibited similar observations on x-ray diffractogram of the blend, whereby increasing the cross-linking in the blend decreased the intensity peak due to a reduction in crystallinity (Costa-Júnior et al. 2009).

## Conclusion

We have prepared nine superabsorbent hydrogels based on sago pulp containing cellulose, lignin, and hemicellulose and have shown that they absorb large amounts of water and biodegrade completely over time. Nine different CMSP hydrogels were successfully prepared by EB irradiation by varying the irradiation dose (kGy) and % CMSP concentration. The nine CMSP hydrogels are CMSP HG DS 0.8 %GF 48, CMSP HG DS 0.8 %GF 35, CMSP HG DS 0.8 %GF 25, CMSP HG DS 0.6 %GF 46, CMSP HG DS 0.6 %GF 35, CMSP HG DS 0.6 %GF 25, CMSP HG DS 0.4 %GF 40, CMSP HG DS 0.4 %GF 35 and CMSP HG DS 0.4 %GF 25. All the CMSP hydrogels are susceptible to soil biodegradation with the rate of biodegradation, on average,  $2.9 \pm 0.4\%$  per week. CMSP hydrogels of DS 0.4 completely degrade in 3 months and CMSP hydrogels of DS 0.6 and 0.8 in 5 months. The biodegradability of the CMSP hydrogel in the soil is an essential factor to use the CMSP hydrogels as a carrier for slow release fertilizer and it is an effective polymer for environmental conservation.

Slow release systems for agricultural fertilizers were designed by loading  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  physically into the CMSP hydrogels. The results show that the percentage of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  loading (as a *w/w* %) on CMSP hydrogel enhances with increasing  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  concentration, respectively. The results from  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  released study shows that the diffusion rate of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  is decreased with the increase of DS

and %GF, and these CMSP hydrogels could be used as a slow release  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  in the agricultural sector. These CMSP hydrogels might be used in vegetable, fruit, and paddy planting areas. Since most of the loaded  $\text{KNO}_3$  is being released over 50 days, CMSP hydrogels could be used as short time slow release of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  and obtain the benefits from the fertilizers treatment from the labor of a single application. The SEM micrographs reveal the highly porous honeycomb-like structure of the CMC hydrogels where the number of pores increases with the increase of DS and the size of the pores decreases with the increase of %GF. X-ray diffractograms of CMC hydrogels show that the crystallinity decreases with the increase of DS and %GF.

The results of the present work indicate that the cross-linked CMSP hydrogels are endowed with a slow release property, biodegradability and a soil moisture preservation property at the same time. The CMSP hydrogels are an example of a multifunctional water managing material which may find application in agricultural and in the renewal of arid and desert environments. These slow release CMSP hydrogels will be tested in the future for their effect on palm oil crops and other industrial plantations.

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