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ORIGINAL PAPER

Controlled release characteristics of methylenebisacrylamide crosslinked superabsorbent polymer for water and fertilizer conservation in agriculture sector

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Abstract

A series of superabsorbent polymers (SAPs) were synthesized free-radically using hydroxyethyl methacrylate (HEMA), acrylic acid (AA) and its potassium salt, methacrylic acid (MAA) and its potassium salt as monomers, and N,N'-Methylenebisacrylamide (N,N^1-MBA) as crosslinker. The synthesized SAPs were evaluated for their chemical structure (FT-IR), thermal stability (TGA/DTG), surface morphology (SEM), and water, fertilizers uptake and release characteristics (swelling and deswelling). A SAP with the optimized composition of monomer and crosslinker had absorbed 898 g/g of water, and 68% of urea and 51% of potash from the 1% corresponding fertilizer solutions. The equilibrium swollen SAP had released the absorbed water completely over 21 days, but only 28% of potash and 43% of urea were released from the fertilizer-loaded SAPs under identical conditions with the same duration of release time. The water uptake followed Fickian diffusion mechanism for the optimized SAP. Thus obtained experimental results revealed that the synthesized SAP may be used as the matrix for the controlled release of water and fertilizers in the agricultural sector.

Keywords Crosslinking · Swellability · Water retention · Fertilizer management · Controlled release

Introduction

The superabsorbent polymers (SAPs) are chemically crosslinked hydrophilic polymers with 3D network. These can imbibe and retain several grams of aqueous fluids namely blood, urine and electrolyte solution without dissolving [1–4] unlike the traditional absorbent materials. SAPs are being used for diverse applications since 1938. The wide spectrum applications of SAP are due to its modifiable physicochemical properties either by physical blending or by crosslinking. Increased entropy of network during absorption, movable counter-ions, an attraction between water and polymer, and high hydrophilicity facilitates water absorption during swelling [4]. Due to the aforesaid features, SAPs are increasingly used in disposable diapers [5], hygienic napkins [6], drug delivery [7–9], tissue engineering, mammalian cell immobilization as matrices, body water elimination [9], agriculture and horticulture sector for the controlled release [10–13]. In addition, they are also used in civil structures [14] as water retention agent, metal ions and dyes adsorption from industrial effluents [15, 16], collection of radioactive ions [17], oil drying [18], coal dewatering [19], sensors [20], firefighting [21], municipal landfills [22]. Besides, SAPs are also employed [15–22] in sludge conditioning, preservation of vegetables and fruits, thickening sewage, communication cables for humidity control, and artificial snowmaking system [15–22].

The population explosion also needs more food production to meet the present needs. To enhance food production surplus inorganic nutrients in the form of superphosphate, di-ammonium phosphate, potash, complex fertilizers, urea, etc. are amended in the agricultural field. But, an excessive addition of synthetic fertilizer cause noticeable

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environmental pollution namely eutrophication and nitrate pollution [23–25] by unutilized fertilizers. Besides, the climate change induced inadequate rainfall and minimized water conservation practice had reduced the surface and groundwater availability significantly, which result in the formation of semi-arid and arid regions. Hence to use water economically in these regions, N,N^1-Methylene-bisacrylamide (N,N^1-MBA) crosslinked SAPs with remarkable water, fertilizer uptake ability along with good release characteristics were prepared using potassium acrylate (KA), acrylic acid (AA), potassium methacrylate (KMA), methacrylic acid (MAA) and 2-hydroxyethyl methacrylate (HEMA) monomers. The hitherto unreported combinations of monomers and crosslinkers displayed high uptakes and good water retention as expected. The synthesized SAP (optimum composition) displayed 898 g/g of water, which is significantly higher than those reported for certain SAPs based on acrylic acid and N,N^1-MBA crosslinker. For instance, the SAP [26] prepared using acrylic acid and acrylamide grafted on wheat straw had absorbed 322 g/g of water and released the absorbed nitrogen fertilizer to the extent of 80% in a single absorption–desorption cycle. Similarly, N,N^1-MBA crosslinked acrylic acid based SAP [27] had absorbed 880 g/g of water and 56% of urea, and the SAP prepared by Teodorescu et al. [28] using acrylic acid and N,N^1-MBA had displayed 130 g/g of water uptake and 48% release of fertilizer under experimental conditions. Besides, potassium salts of acrylic acid and methacrylic acid are used as comonomers in the present investigation which facilitates more amount of potassium availability for the plant after its service under the soil. The synthesized SAPs are named as AMHM-1 to AMHM -25 with reference to their chemical composition (Table 1).

Experimental

Materials

MAA, AA (Himedia, Mumbai) monomers were purified by vacuum distillation and KPS (potassium persulphate, NICE, Cochin) was purified through recrystallization with ultrapure water. The crosslinker (N, N^1-MBA, Aldrich), potassium hydroxide, Water Lock and Water Keep G 500 (USA) were purchased and used as received, and HEMA (Aldrich) was

Table 1 Monomer feed composition and water uptake of synthesized AMHM polymers

SAP Code	Molar concentration of monomers (M)				pH	Swellability (g/g)
	AA	MAA	HEMA	N,N^1-MBA		
AMHM-1	0.05	0.05	0.05	0.01	3	220
AMHM-2	0.05	0.05	0.05	0.01	3.5	246
AMHM-3	0.05	0.05	0.05	0.01	4	258
AMHM-4	0.05	0.05	0.05	0.01	4.5	496
AMHM-5	0.05	0.05	0.05	0.01	5.0	232
AMHM-6	0.05	0.05	0.05	0.01	4.5	467
AMHM-7	0.06	0.05	0.05	0.01	4.5	543
AMHM-8	0.07	0.05	0.05	0.01	4.5	598
AMHM-9	0.08	0.05	0.05	0.01	4.5	630
AMHM-10	0.09	0.05	0.05	0.01	4.5	652
AMHM-11	0.10	0.05	0.05	0.01	4.5	670
AMHM-12	0.08	0.06	0.05	0.01	4.5	691
AMHM-13	0.08	0.07	0.05	0.01	4.5	701
AMHM-14	0.08	0.08	0.05	0.01	4.5	683
AMHM-15	0.08	0.09	0.05	0.01	4.5	692
AMHM-16	0.08	0.10	0.05	0.01	4.5	701
AMHM-17	0.08	0.07	0.06	0.01	4.5	711
AMHM-18	0.08	0.07	0.07	0.01	4.5	738
AMHM-19	0.08	0.07	0.08	0.01	4.5	765
AMHM-20	0.08	0.07	0.09	0.01	4.5	745
AMHM-21	0.08	0.07	0.06	0.0005	4.5	843
AMHM-22	0.08	0.07	0.06	0.005	4.5	898
AMHM-23	0.08	0.07	0.06	0.1	4.5	573
AMHM-24	0.08	0.07	0.06	0.15	4.5	340
AMHM-25	0.08	0.07	0.06	0.2	4.5	301

purified through column and subsequent distillation under reduced pressure.

SAP synthesis

SAPs with various monomer feed concentrations were prepared [29] free-radically by copolymerizing HEMA, and AA, MAA and their potassium salts using N,N^1-MBA (crosslinker) and KPS (initiator). The monomers, initiator and crosslinker were dissolved in a 50 ml tube and the solution was deoxygenated using pure nitrogen. The required amounts of KMA and KA were prepared by partially neutralizing MAA and AA respectively using a known amount of KOH. This was preferred to enhance high swelling ability. Besides, after the service of SAP in soil the released potassium will be utilized by plants as primary nutrients. The polymerization reaction was carried by keeping the mixture in the thermostated water bath at 70 °C and the percent conversion (> 95%) was monitored gravimetrically. An ice-cooled methanol was used to remove the residual monomer contents in the polymer by repeated washing, further the polymer was purified using Soxhlet extraction (methanol-acetone as mixture of solvent) and dried at 50 °C.

Characterization of SAP

Fourier transform-infrared (FT–IR) spectroscopy

The representative FT-IR spectra of SAPs have been recorded on potassium bromide pellet using Shimadzu FT–IR– 8400S (400–4000 cm^{-1}).

Thermogravimetry (TG/ DTG)

The thermal degradation studies of synthesized SAPs were performed on TGA Q 500 V20.10 Build 36 with a heating rate of 10 °C /min for the temperature range between 30 °C and 800 °C.

Scanning electron microscopy (SEM)

The morphological features of the freeze-dried foam shaped, dried (after swelling) and powdered AMHM samples were analyzed using ZEISS EVO Series SEM model EVO 50 after gold coating at different magnifications.

Swelling measurements

The extent of SAP swellability was determined both in deionized water and synthetic fertilizer solutions (potash and urea) using the tea-bag method [29]. This was performed by keeping a known amount of polymer in a 100 mesh size tea-bag. The swellability at different time intervals was measured by keeping a known amount of polymer in deionized water. Similarly, the percentage uptakes of fertilizers were measured in aqueous fertilizer solutions (1 to 5 wt. %) taken in a thermostated vessel (27 °C). The swelling profiles were constructed at different time intervals for the synthesized polymers (AMHM-1 to AMHM -25). The rate of absorption (R- mole/min) was calculated from the initial slope of the constructed profile (up-to 60% swelling). The DS (degree of swelling) was calculated as per Eq. (1)

$$\mathrm{DS} = \frac{\mathrm{W_2} - \mathrm{W_1}}{\mathrm{W_2}} \tag{1}$$

The weights of swollen (W_2) and dry (W_1) polymers were measured during every swelling measurement. Water uptake and the release by the swollen polymers were performed at 30 °C. The typical composition of SAP (AMHM-22) showed maximum absorption in deionized water. Hence, this composition was used for water uptake analysis under irrigated clay, red and sandy soils. This was performed by keeping 1 kg of each soil in separate plastic trays (30 × 15 × 8 cm), subsequently, one gram of AMHM-22 was uniformly scattered on these soil surfaces. Followed by a known quantity of these soils were uniformly spread on the polymer added soil concerned and a calculated amount of deionized water (V_a) was added and kept aside for 4 h. The unabsorbed water (V_u) stagnated on each soil surface was collected and the total amount of water absorbed (V_a-V_u) by the respective soil along with polymer was quantified. Similarly, a blank test was also performed and the volume (V_b) of water absorption during the blank test for each soil was measured. Using these data the volume of water absorption by AMHM-22 under soil was calculated [(V_a –V_u)-V_b].

Swelling kinetics

The diffusion mechanism of water into the SAP was identified using Hixson–Crowell, Korsmeyer–Peppas and first-order kinetic models [30] using the Eqs. (2), (3) and (4) respectively.

$$\left(1 - \frac{W_t}{W_\infty}\right)^{1/3} = 1 - kt \tag{2}$$

$$F = \frac{W_t}{W_\infty} = kt^n \tag{3}$$

$$F = \frac{W_t}{W_\infty} = 1 - exp^{-kt} \tag{4}$$

The weights of swollen SAP (W_t) at time 't' and at the infinite time (W∞) were measured every time. The term 'F' (constant) represents the ratio of W_t /W∞. The diffusion mechanism was regulated by equilibrium constant (k) and swelling power (n) and these values can be obtained from the slope and intercept of the plot ln (F) vs. ln (t) respectively at desired temperatures. The K_{HC} and K_{KP} denote Hixson–Crowell and Korsmeyer–Peppas kinetic parameters respectively, and R^2 indicates the correlation coefficient.

Porosity measurement

The porosity of the synthesized polymer was measured [31] based on the solvent replacement method. To gauge this, a known quantity of polymer was taken in a tea-bag and it was dipped in ethanol for 12 h. After removing the excess ethanol in the polymer, the porosity was measured as per Eq. (5).

$$\mathrm{Porosity} = \frac{M_2 - M_1}{\rho V} \times 100 \tag{5}$$

where, M_2 and M_1 – weights of SAP after and before ethanol uptake respectively. The parameters ρ and V denotes the density of absolute ethanol and polymer-volume respectively.

Total dissolved solids (TDS)

The solids (water-soluble) that are present in water (used for irrigation in the local field) and in soils (saturated water extract) were determined using DiST 1 Hanna TDS meter at 27 °C.

Absorbency under load (AUL)

The polymer that is amended in soil may experience significant stress due to load, which results in decreased water uptake. Hence, water-uptake has to be evaluated under load to check the feasibility of polymer for field application. To measure [29–32] AUL value, a known weight (e.g. 0.90 ± 0.01 g) of dried SAP sample was uniformly sprayed on the surface of polyester gauze that was placed on the sintered glass. A load (Teflon, $d = 60$ mm, variable height) was positioned on the dry SAP particles while it could be freely slipped in a glass cylinder ($d = 60$ mm, $h = 50$ mm). 0.9% NaCl solution was added till the liquid level reaches the height of the sintered glass filter. The entire setup was closed to minimize evaporation of the solvent and the resultant concentration change of saline solution. The weight of SAP after 60 min was calculated using the Eq. (1).

Uptake and release studies of fertilizers

The extent of fertilizer uptake and release characteristics of SAP was measured by keeping 1 g AMHM-22 in 1–5% potash and urea solutions taken in a separate container. To measure the amount (%) of fertilizers released, the fertilizer loaded SAP (AMHM-22) was placed in 100 ml deionized water and the released fertilizer from the polymer was quantified gravimetrically (for every 2 ml solution). This measurement was repeated for every two days and the released fertilizer was calculated [28] according to Eq. (6).

$$\text{The percentage of fertilizer release} = \frac{(\Delta W)n \times [100 - (n-1) \times 2]/2 + \sum_{i=1}^{n-1} (\Delta W)i}{Wo} \tag{6}$$

The parameters W_0 and $(\Delta W)_i$ are represents the weight of fertilizer loaded on polymer and the amount of fertilizer released in the i^{th} 2 mL respectively. In a single experiment, the number of release measurements was termed as "n".

Result and discussion

SAP polymerization mechanism

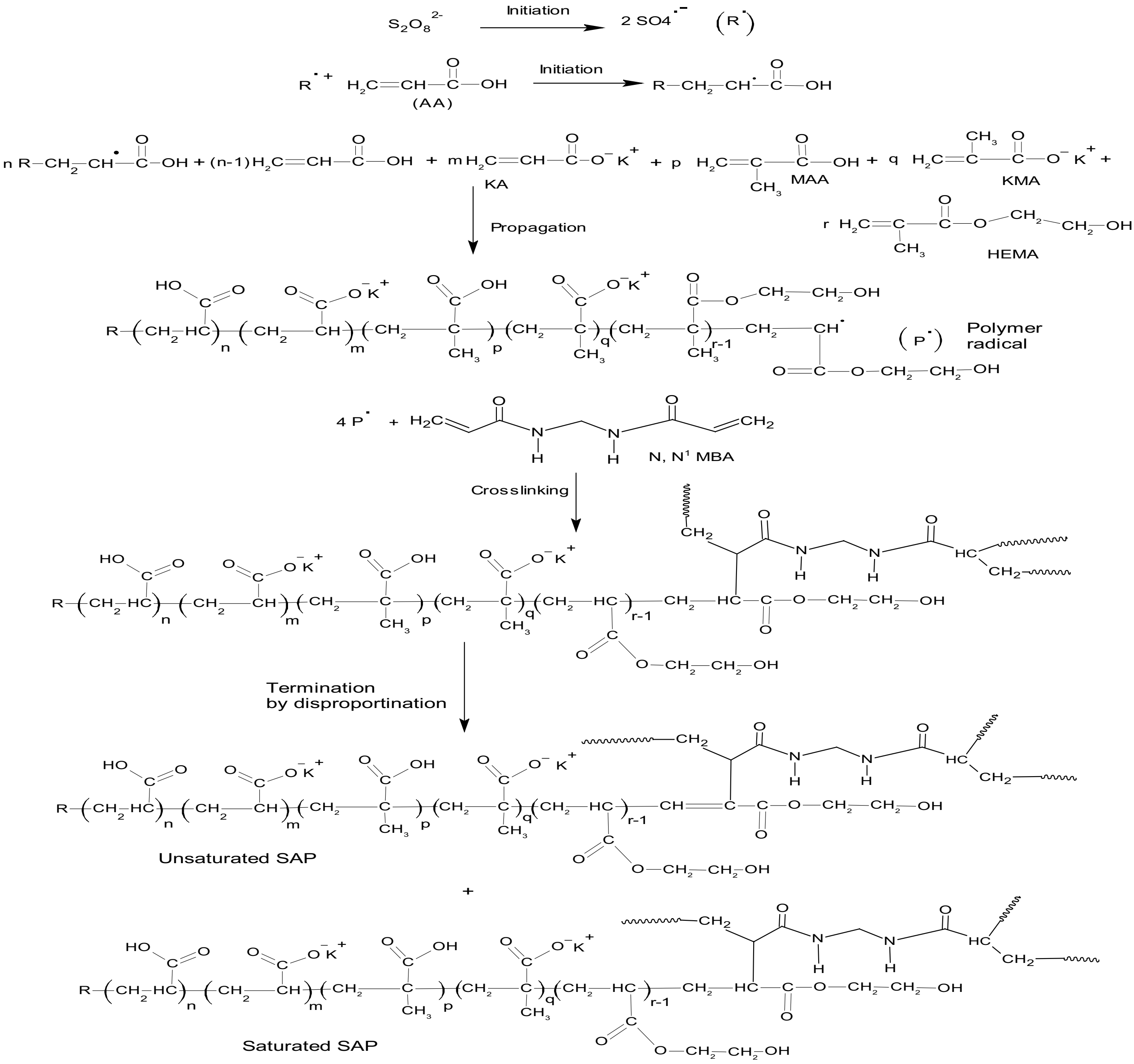
The crosslinked SAPs were synthesized through free-radical polymerization mechanism as shown in Scheme 1. The mechanism demonstrated that the crosslinking among macro-radicals were facilitated through crosslinker (scheme 1) and the termination of propagated polymer chain radicals may be occurred either by the disproportionation or coupling or chain transfer [29, 33] methods. The termination of polymer radicals via disproportionation resulted in saturated and unsaturated polymers (contains terminal double bond).

FT-IR analysis

The chemical structures of SAPs were evaluated using FT-IR and the representative FT-IR spectra of SAPs that are having the same monomer concentration but different concentrations of crosslinker (AMHM-21, AMHM-22 and AMHM-23) are presented in Fig. 1. The results revealed [34, 35] that the crosslinker and monomer units are present in SAPs. For example, the observed peaks ranged from 1720 to 1730 cm^{-1} were assigned to carbonyl groups. The characteristics stretching frequencies at 1400 cm^{-1} were due to the existence of asymmetric and symmetric stretching of carboxylate anion (C-O) in SAP. The notable peaks at 1670 and 1180 cm^{-1} confirmed the availability of amide and ester linkages in SAPs. The absence of a characteristic vinyl peak at 1640 cm^{-1} implied that no monomer residues were present in the purified polymer.

Thermogravimetric (TG) analysis

The representative thermograms of AMHM-22 and AMHM-23 displayed multi-step degradations as given in Fig. 2. The initial weight loss noticed around 250 °C



Scheme 1 The proposed mechanism for the free radical thermal copolymerization

could be assigned to the degradation [36] of SAP originated via saturated-terminal ends, scission of crosslinks, olefinic bonds, and main chain scissions (neighboring carboxylic acid moiety). The copolymer prepared using higher crosslinker concentration (AMHM-23) exhibited an enhanced degradation temperature compared to AMHM-22, which may be attributed to the development of more crosslinks. The degradation initiated via decarboxylation of carboxylic moiety [36] of both the polymers was observed around 350 °C. The TG traces of both AMHM-22 and AMHM-23 displayed multistep degradations at various temperatures. The percentage weight loss of both the polymers seemed to be different due to the enhanced crosslinking in AMHM-23. But, both the polymers were thermally stable enough beyond 550 °C in the air atmosphere.

SEM

The representative SEM micrographs of freeze-dried SAP (AMHM -22) were displayed in Fig. 3. The observed pores and porous morphology in water swollen SAP were due to the evaporation of water during freeze-drying (Fig. 3(c & d)). During swelling the uniform water absorption has created numerous pores on the polymer and the analysis of SEM pictures indicated that the structure of pores are irregular and interconnected. Besides, the porous structures

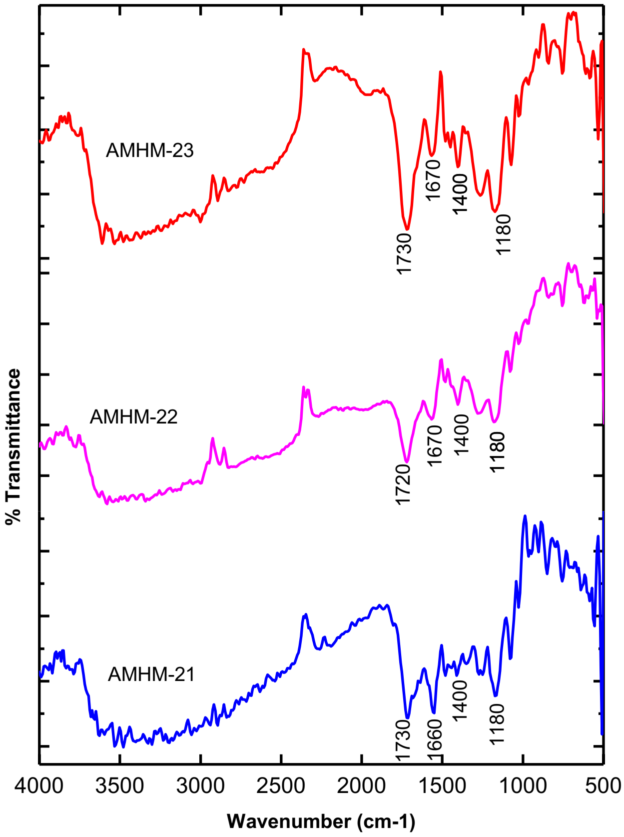


Fig. 1 FT-IR spectra of AMHM-21 AMHM-22 and AMHM-23

were also formed during the polymerization process due to intermolecular crosslinking that facilitates the water uptake and swelling processes. However, investigation of Fig. 3a and 3b revealed that no pores [37–39] was observed in the powdered sample of AMHM-22.

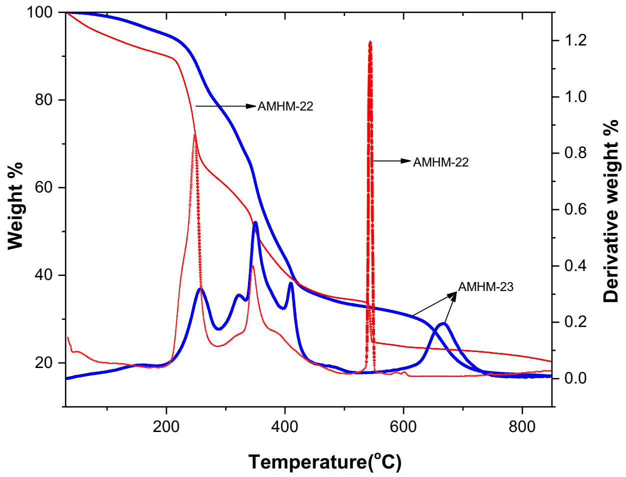


Fig. 2 TG/DTG traces of AMHM-22 and AMHM-23

Uptake and release studies

The water uptake profile of AMHM at ambient temperature is demonstrated in Fig. 4. The analysis of Fig. 4 indicated that AMHM-22 displayed a maximum water uptake. The percentage uptakes and release profiles of synthetic fertilizers (urea and potash) by AMHM-22 at ambient temperature were displayed in Figs. 5 and 6 respectively. Analysis of these figures concluded that the uptake rates of water and fertilizers were greater than release rates due to hydrogen bond formation through enhanced crosslinking with fertilizers and water molecules [37]. Besides, variation in osmotic pressure and the resulted change in solution concentration during up-take and release will also support the high uptake rates. The amount of water, urea and potash uptakes were noted as 898 g/g, 68% and 51% (from their 1% solution) respectively by AMHM-22. The equilibrium swelled AMHM-22 had released the water completely over 21 days, and the percentage of urea and potash release were found to be 43 and 28% respectively. The swelling measurements for these polymers were performed for a wide range of temperatures (15–60 °C) and it was predicted that AMHM-22 displayed maximum swellability at ambient temperature compared to other SAPs studied in this work. The increased water uptakes by SAP samples (AMHM-2 to AMHM-22) were due [40] to the change in the concentration of polar hydrophilic groups, swelling character, and crosslinked bonding strength. Besides, the change in the concentration [41] of monomers will also lead to increased water uptake due to the changes in the hydrophilicity of SAP. Hence, the typical composition (AMHM 22) of monomers had displayed maximum uptake, this may be attributed to the presence of enhanced hydrophilicity, swelling character, entropy, water-polymer interaction, and osmotic force induced by mobile ions. Therefore, AMHM-22 was used as a representative sample for various physicochemical characterizations.

Swelling kinetics and diffusion

The Fickian and non-Fickian diffusion models [30] were used to describe the mechanism of transport kinetics of solvent/solution into the polymer system. Fick's diffusion indicated to what extent the diffusion is controlled by thermodynamic forces namely the gradient of chemical potential or concentration differences induced by constant diffusion coefficients relatively through kinetic profiles of penetrant redistribution in the polymer matrix. But, the non-Fickian (anomalous) diffusion model helps us to understand the transport which is facilitated by the physical and physicochemical processes namely molecular relaxation, segmental mobility retardation, functional interaction between penetrant and macromolecules, crystallization, etc., especially when a polymer is in

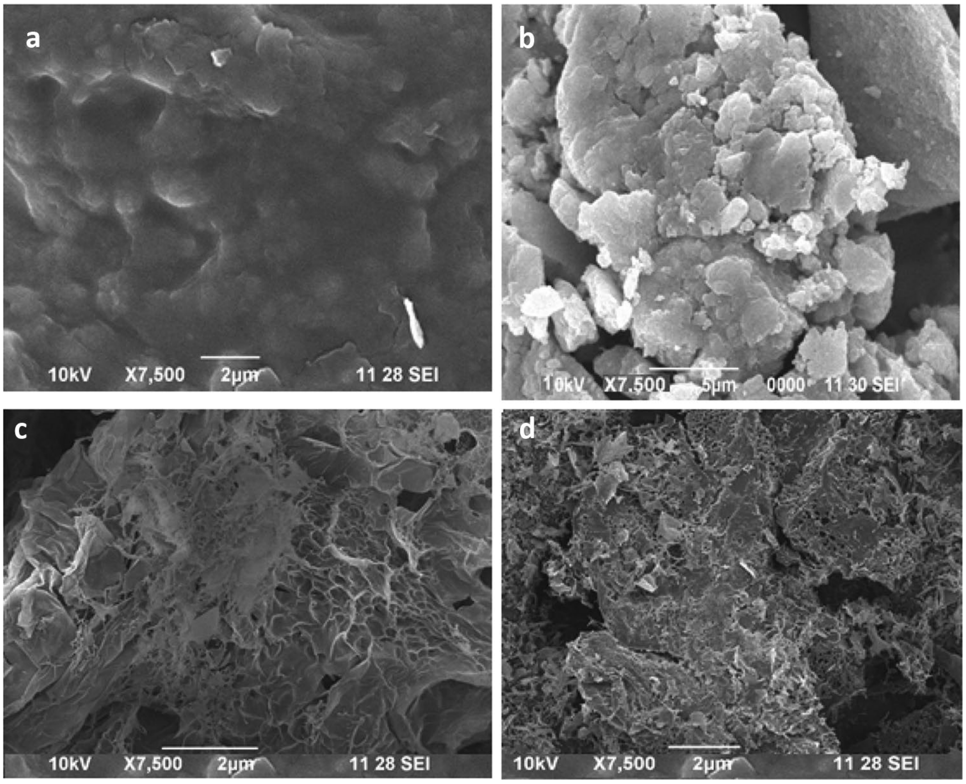


Fig. 3 SEM micrographic images of AMHM-22 (**a**, **b** and **c**), and AMHM-23 (**d**)

glassy-state. The swelling kinetics of AMHM-21, AMHM-22 and AMHM-23 (prepared using the same monomers concentrations and different concentrations of crosslinker) were tested using the Eqs. (2), (3) and (4). The solvent diffusion into the polymer during uptake is always influenced by the network chain and the interaction between polymer and solvent. The solvent diffusion was categorized [30] as Fickian and non-Fickian based on solvent movement and polymer relaxation rate. A Fickian diffusion ($n < 0.5$) took place both in AMHM-21, and AMHM-22 which could be attributed to the free mobility of polymer network at low crosslinker concentrations. But, at the high crosslinker concentration (AMHM-23) the mobility of chains are restricted by more number of crosslinks. Hence, non-Fickian diffusion was observed in AMHM-23. The analyses of Hixson–Crowell and first-order kinetics models have also corroborated the observed results for the chosen polymer–solvent systems. The non-Fickian model diffusion occurs whenever the water molecules encountered considerable resistance ($n > 0.5$) during

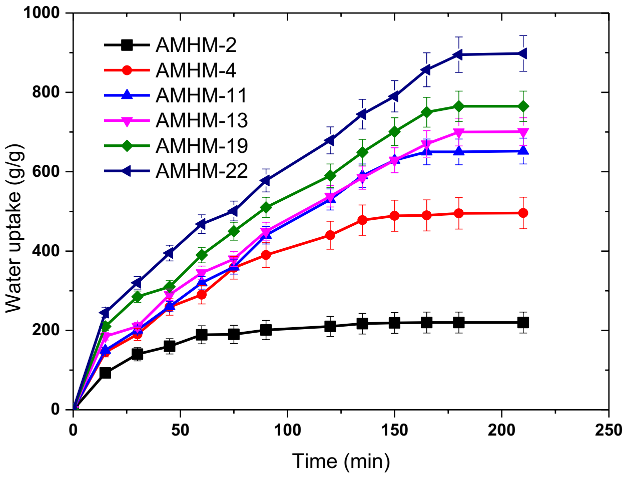


Fig. 4 Water uptake profiles of AMHM-2, AMHM-4, AMHM-11, AMHM-13, AMHM-19 and AMHM-22

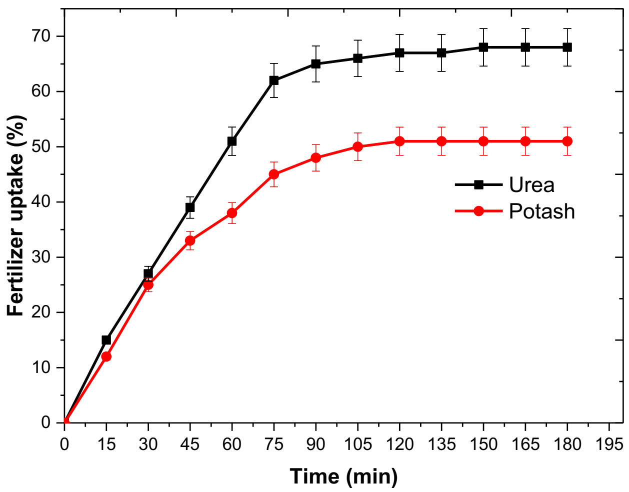


Fig. 5 Urea and potash uptake profiles of AMHM-22 at 27 °C

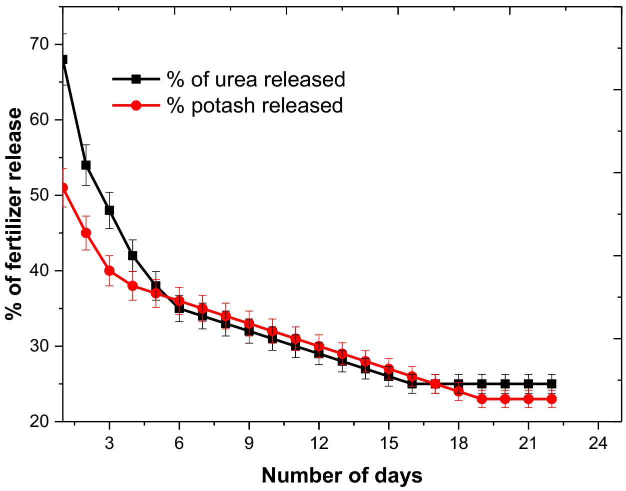


Fig. 6 Urea and potash release profiles of AMHM-22 at 27 °C

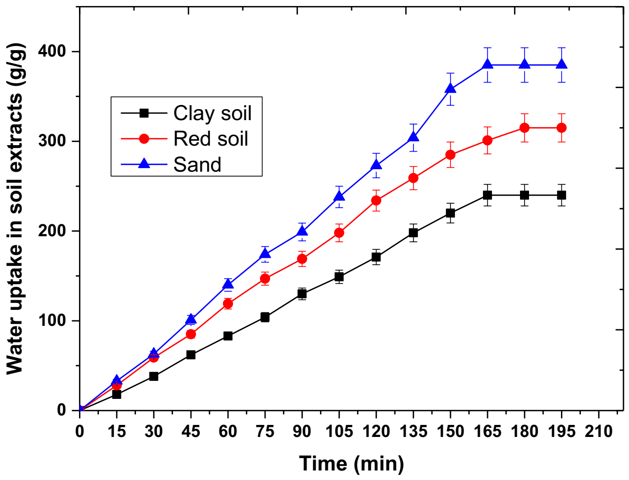


Fig. 7 Water (clay, red and sandy soil extracts) uptake profile of AMHM-22 at 27 °C

swelling and the reduced mobility of the chains in the network. Hence, decreased water uptake took place in AMHM-23. The values of ‘k’ and ‘n’ have been calculated from the Eqs. (2), (3) and (4) and presented in Table 2.

Porosity measurement

The concentration of the crosslinker has greatly influenced the porosity of the polymer. To analyze this, the influence of N,N^1-MBA concentration on the porosity of synthesized AMHM is displayed in Fig. 3 (d). The observed results showed that the crosslinker concentration had significantly altered the porosity of SAP, further it implied that a decrease in the porosity was observed with increased concentration of crosslinker. The increased concentration of comonomers likely to increase the viscosity [30] of solution that reduced air bubbles outflow from the solution which leads to the entrapment of air bubbles. On drying, thus trapped air will also create porous structure on polymer. Further, enhanced crosslinker concentration will facilitate high crosslinking density which may result in more molecular entanglement between monomer and polymer, and a decrease in porosity.

Swellability under load and soils

The degree of swellability of AMHM-22 decreased when the applied load was increased. This investigation indicated that water uptake becomes zero if the applied load was enhanced to one ton. However, the synthesized SAP could exhibit considerable swellability until 0.7 ton of applied load. This study revealed that AMHM-22 was capable enough to imbibe water below 0.7 ton. To measure the practical applicability of AMHM-22 in clay, red and sandy soils, the water extracts of these soils were used to construct a swelling profile as shown in Fig. 7. This profile implied that water uptake of AMHM-22 in clay, red and sandy soil extracts were 240, 315 and 385 g/g respectively in laboratory conditions. The enhanced hydraulic conductivity of water and high ionic strength in the fertilizers amended soils may also bring down the swellability to a certain extent [42] compared to freshwater. This was also supported by TDS values (ppm) of water extracts of clay (395), red soil (286) and sand (214). However, water uptake of AMHM-22 in soil extracts was comparatively higher than commercially available SAPs such as Water Lock and Water Keep. Further, the formation of additional crosslinks with water soluble cations such as Ca^{2+}, Mg^{2+}, Al^{3+}, etc., may also bring down water uptake in

Table 2 Correlated kinetic parameters for diffusion mechanism in AMHM-21, AMHM-22 and AMHM-23

SAP Code	Hixson–Crowell			Korsmeyer–Peppas				First-order kinetics		
	k_{HC}	R^2	Des. R^2	n	k_{KP}	R^2	Type of Diffusion mechanism	k_1	R^2	Des F
AMHM-21	0.11	0.98	≤0.95	**0.29**	**0.30**	**0.98**	**Fickian**	0.15	0.51	≥0.6
AMHM-22	0.12	0.97	≤0.95	**0.27**	**0.31**	**0.99**	**Fickian**	0.19	0.51	≥0.6
AMHM-23	0.12	0.99	≤0.95	0.09	0.61	0.71	Non-Fickian	**0.30**	**0.75**	**≥0.6**

soil extracts [43]. This investigation revealed that AMHM-22 amendment soil had increased the saturated water content [44] and good water holding capacity.

Factors affecting water uptake

Feed solution composition

The water uptake characteristics of AMHM-22 was significantly influenced by the feed concentration. The profiles of water uptake for different feed compositions are given in Fig. 8. The plot (Fig. 8 (a)) showed that the increased concentration of salt had initially increased the water uptake, and the maximum uptake was observed at 0.5623 (salt/acid ratio). The further increase in the salt/acid ratio had reduced the water uptake considerably. This behavior was due to the operation of osmotic pressure [45] and the creation of hydrogen bonds at a lower concentration of salt. The influence of HEMA concentration on water absorption of polymer is displayed in Fig. 8 (b). The polymer synthesized using the lower concentration of HEMA displayed a significant reduction in water uptake due to the minimized hydrogen bonds exhibited by the hydrophilic groups [39]. The DS values increased until 0.08 M concentration of HEMA and decreased beyond 0.08 M concentration of HEMA. This could be attributed to the increased concentration of HEMA beyond certain limit will modify sorption rate of solvent, rate of approach to equilibrium swelling and the transport mechanism controlling solvent sorption. Hence, the minimum water uptake

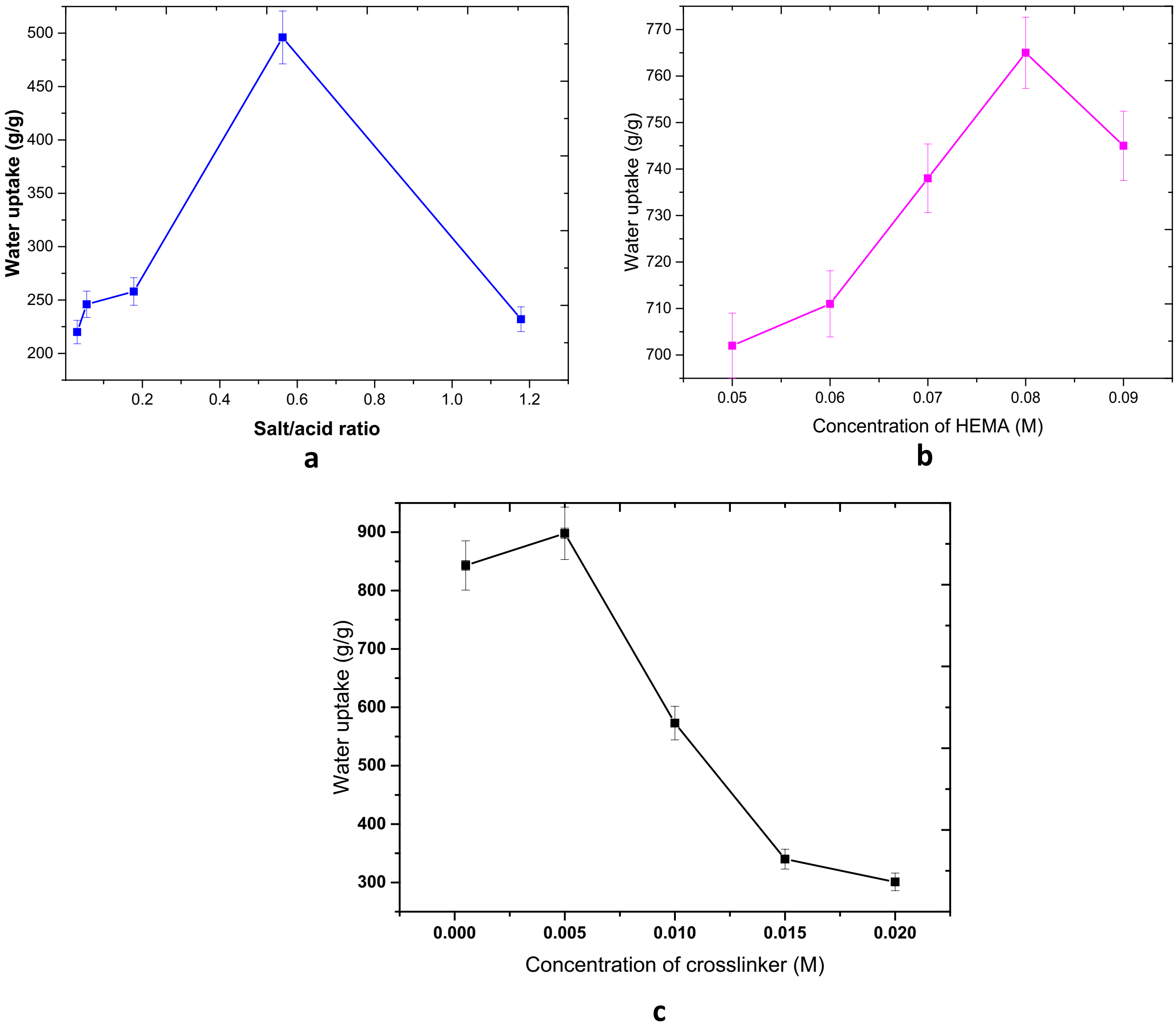


Fig. 8 Influence of salt/acid ratio (**a**), concentrations of HEMA (**b**) and N,N.^{1}-MBA (**c**) on swellability

was noticed if the concentration of HEMA goes beyond 0.08 M. Another noteworthy component that influences water uptake is crosslinker concentration. For instance, enhanced water uptake was observed for the lower values of crosslinker concentration and the decreased water uptake was noticed [29] at a higher crosslinker concentration. Figure 8(c) revealed that a small variation in the crosslinker concentration had significantly altered the uptake. This could be attributed to the increased crosslink density and reduced porosity of the network at a higher crosslinker concentration. Hence, the maximum uptake (898 g/g) was noticed at 0.005 M crosslinker concentration and the reduced uptake was observed at < 0.005 M concentration of crosslinker. This could be ascribed to the formation of weak crosslinks. However, in the absence of crosslinker due to the reduced attraction between polymer networks, the polymer may undergo dissolution or induces weak links between polymer networks during swelling. Hence, a notable water uptake is not observed for the polymer that prepared without crosslinker.

Physical parameters

Temperature

Figure 9a indicated the influence of temperature on the DS of synthesized SAP. The water uptake profile for the temperature range 20–55 °C revealed that the maximum swelling (898 g/g) was noticed at ambient temperature. The swellability at 20 °C was found to be 842 g/g. The phenomenal water uptake in the range of 20–30 °C was due to chain flexibility and a high degree of water diffusion. However, these were reduced at higher temperature [42] which leads to a minimized water uptake. This was due to the disentanglement of polymeric

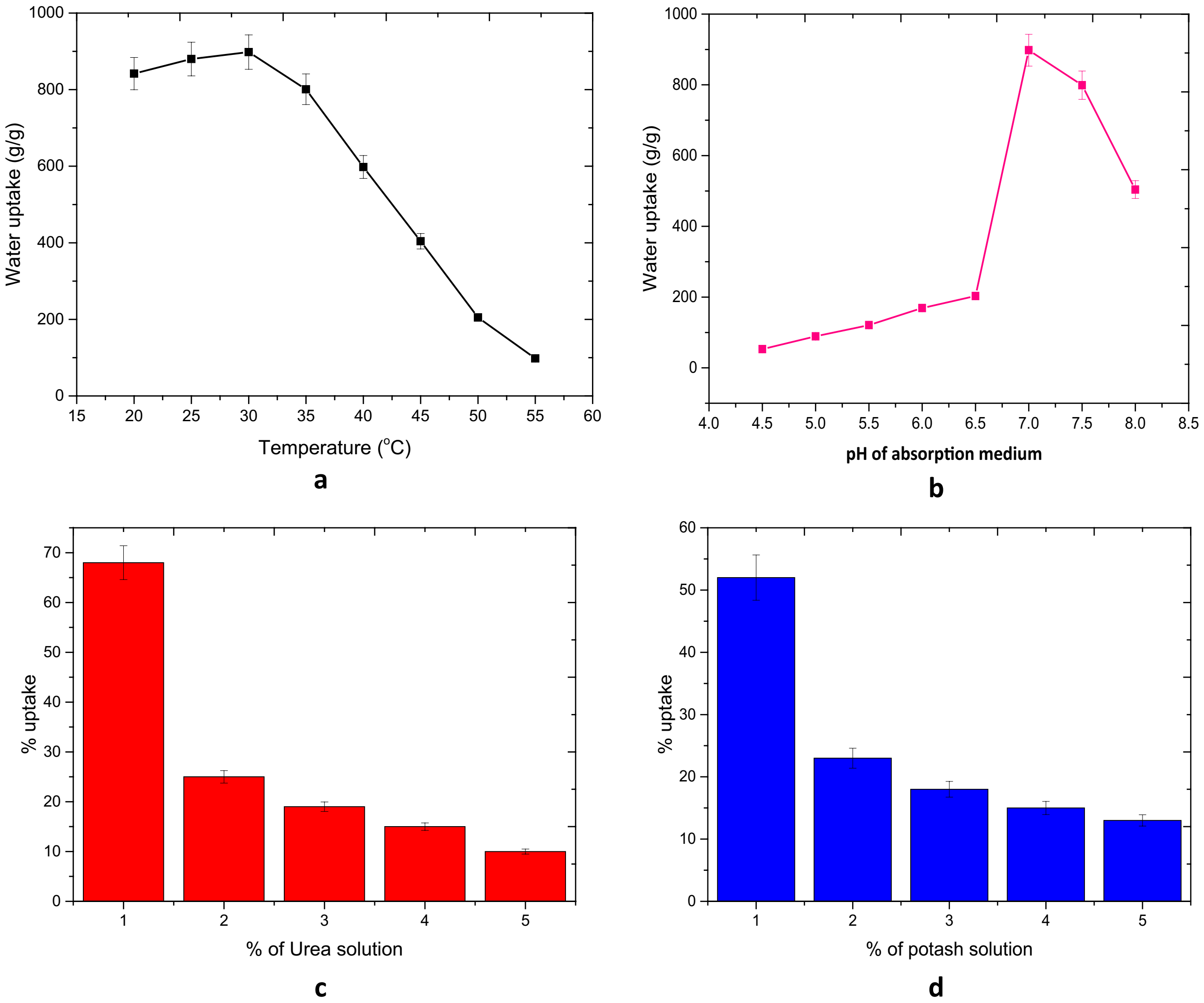


Fig. 9 Effect of pH (**a**), temperature (**b**), concentration of urea (**c**) and concentration of potash (**d**) on swellability

Table 3 Comparison of fertilizer uptakes of AMHM-22 with the reported materials

Chemical constituent of SAP	Type(s) of Fertilizer(s)	% of fertilizer(s) released in a single cycle	Water uptake (g/g)
crosslinked polyacrylamide chains onto carboxymethyl cellulose and poly(vinyl alcohol)[51]	Potash	90	600
N,N^1- MBA crosslinked poly(acrylic acid)[52]	Urea, superphosphate and potash	70	1000
wheat straw-*g*-poly(acrylic acid)[53]	Urea	78.5	862
N,N^1- MBA crosslinked poly(acrylic acid)[54]	Urea	80	600
Poly(acrylic acid-*co*-acrylamide)grafted on starch[55]	Urea	70	80
poly(acrylamide) and methylcellulose[56]	Ammonium sulphate and potassium phosphate	68	480
Poly(acrylic acid-*co*-acrylamide) crosslinked via N,N^1- MBA[57]	Urea	60	700
Sodium alginate-*g*- poly(acrylic acid- acrylamide) composite[58]	Urea, superphosphate and potash	38. 58 and 73 (N, P and K respectively)	397
Partially neutralized acrylic acid crosslinked using N,N^1-methylene bisacrylamide[59]	Urea	98.5	965

chains and the destruction of hydrogen bonds between copolymer and hydrophilic groups [46]. The elevated temperature would bring down the pore size due to the network chain contraction which also resulted in a decreased water uptake [46].

pH

For field application, pH of the soil will also alter SAP swellability substantially. Hence, the degree of AMHM-22 swelling was investigated in buffers having different pH values and the corresponding profile is depicted in Fig. 9(b). The profile indicated that the maximum uptake (898 g/g) was noticed at neutral pH. The pH around slightly basic conditions, majority of the carboxylic groups present in the network is ionized and an electrostatic repulsive force among –COO$^-$ groups may result in an enhanced water uptake [42]. The pH below 7, protonation of all the carboxylate groups causes minimized repulsive forces among anions which result in the collapse of the polymer network. Hence, reduced swellability was observed at lower pH values. For a higher pH value (greater than 9.0), the degree of swelling was reached to 101 g/g, which could be attributed to the operation of more repulsive forces among carboxylate anion in the network [47].

Ionic strength

The fertilizer uptake characteristics of AMHM-22 were analyzed in various concentrations (1- 5%) of potash and urea solutions at 27 °C in a thermostated vessel and the constructed profiles were presented in Fig. 9 (c) and (d). The uptake profiles showed that both water and fertilizer uptake ability of polymer decreased with the increased concentration of fertilizer solutions. The undesired swelling behavior of AMHM-22 in fertilizer solution was due to the operation of reduced osmotic pressure, which resulted in charge screening effect [42, 48] in anionic SAPs.

Demerits of AMHM-22 in soil condition

The swelling ability of AMHM-22 was significantly influenced by salinity and TDS values of water [49, 50] and soil pressure. The decreased swellability of SAP under soil conditions was due to the network shrinkage [51] caused by the applied load. Generally, water-swellable polymers are known to be quite fragile, which makes the network to undergo collapse in the soil during repeated swelling and deswelling processes and this property of SAP may bring down its water holding capacity [52]. Moreover, SAP service in the soil may be vanished over a period of time, hence high degree of SAP amendment may be required to compensate these losses, which may increase the production cost of crops.

Fertilizer and water uptakes comparative study

The water and fertilizers uptakes and release characteristics of the synthesized polymer have been compared with the reported polymers [28, 53–60] which are having similar or partially similar chemical architectures and those values are given in Table 3. The analysis of water and fertilizer uptakes and release characteristics of the reported materials [53–60] revealed that the water uptake and fertilizers release are purely based on the monomers and crosslinker concentration. Hence, the compositions that displayed maximum water and fertilizers uptakes have been considered for comparative study. The study indicated that the synthesized polymer (AMHM-22) exhibited enhanced [53, 57–60] water uptake and the controlled release of fertilizers.

Conclusions

SAPs with appreciable swellability were synthesized using HEMA, AA, MAA, KA, KMA, and N,N^1-MBA crosslinker, and characterized for their structure, thermal stability, surface morphology, uptake and release characteristics. The controlled release characteristic of the synthesized SAP (maximum swellability) can release water gradually over 21 days without sacrificing its structural integrity. Hence, the synthesized SAP can be commercially exploited for field applications. However, considerable focus is also required to optimize the composition of SAPs for the enhanced mechanical strength after numerous absorption–desorption cycles, high swellability for the wide range of pH, ionic strength of swelling medium and high uptake ability under load. Since nanotechnology is contributing a lot to the development of superior materials, this may likely to play a major impact in the production of high performance and ultra-high strength SAP with a quick rate of absorption, high swellability and less impact on the environment by reducing the particle size to nano-scale range.

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Declarations

Conflicts of interests The authors declare that they have no conflicts of interests or personal relationships that could have appeared to influence the work reported in this paper.

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