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Synthesis and Characterization of Super Absorbent Polymers for Agricultural Purposes

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Abstract: Superabsorbent hydrogels (SAH) are very unique water- absorbing and water holding materials. Superabsorbent polymers are environmentally useful as water retention agents, for purposes such as agricultural applications and combating desertification. In this paper we investigate the preparation of SAH to reach highest yield with maximum swelling. Also effect of different operating parameters was studied. Bench scale results were used for design a pilot scale batch to produce 20 kg o SAH. The future objective of this study is the application of the prepared SAH in agriculture field. The product has already been launching in the cultivation of squash (Cucurbita pepo L.) and the initial results were promising.

Keywords: crosslinking; hydrophilic polymers, swelling, liquid crystals.

Introduction

Water is an essential and a key component of this planet and supports all life that exists on it. Of all the global water, fresh water is the most important to support life on this planet. Availing SAH would significantly contribute to the production of soil conditioner. Arid land reclamation program in Egypt is a central component in the Egyptian social and economic development strategies in the last decades. The success of this program is mandatory to secure food supplies and avail intensive job opportunities. Other targets of reclamation program are to establish new agro-industrial complexes to decrease population and development pressures in the old Nile valley. With the current degradation of significant agricultural areas in the valley, to satisfy demand for housing and urban services, it is necessary to develop new reclaimed lands. The main challenges for most land reclamation projects are the availability and accessibility of funding, water **[1]**.

Superabsorbent hydrogels have been identified as three dimensional crosslinked polymer networks capable of absorbing large quantities of water, but remain insoluble due to chemical or physical crosslinks between individual polymeric chains [2]. Superabsorbent hydrogel (SAH) products constitute a group of polymeric materials, the hydrophilic structure of which renders them capable of holding large amounts of water in their three dimensional networks. Extensive employment of these products in a number of industrial and environmental areas of application is considered to be of prime importance. Superabsorbent hydrogel materials are hydrophilic networks that can absorb and retain huge amounts of water or aqueous solutions.

A superabsorbent hydrogel was prepared through polymerization of acrylic acid/acrylate under potassium persulphate initiation and N-N'-methylene bisacrylamide as a crosslinking agent. The polymers were synthesized by, free radical polymerization techniques. Superabsorbent polymers were first developed by USDA in 1970s for applications in agriculture to improve the water holding capacities of soils to promote seed germination and plant growth and now find extensive applications in disposable pads and sheets, towels used in surgery, adult incontinence and female hygiene products [3]. Superabsorbent polymers can be classified into two types: based on charge non-ionic and ionic **[4]** and based on its affinity towards water – hydrophobic and hydrophilic **[5, 6]**. Ionic SAPs are further classified into cationic and anionic [**7**]. In case of ionic hydrogels many structural factors like crosslinking density, properties of swelling medium like pH, ionic strength of counter ion and its valency influences the swelling properties [**8**]. Hydrogel which swell and contract in response to external conditions like salt, pH and temperature have been studied **[9 -11]**.

In our recent research the preparation and characteristics of superabsorbent from Acrylic acid/ acrylate, N,N′-methylene-bis-acrylamide as a crosslinker and potassium persulphate as an initiator via free radical polymerization technique were studied. Swelling studies of the candidate polymer in tap water and different pH were also done. In addition, overall process steps for 20 kg of SAH (pilot scale) were calculated and described**.** The purpose of this work is applying the product in the agriculture field. The product has already been launching in the cultivation of squash and the initial results were promising.

Materials and Methods

Materials

Acrylic acid (AAc) in the monomeric form was produced by PANREAC QUIMICA, Spain; N-N'-methylene bisacrylamide (MBAAm) as a crosslinking agent was purchased from Sigma–Aldrich, CHEMIE, GmbH, Germany; potassium persulphate (KPS) as initiator was supplied by Sisco Research Lab. Pvt. Ltd., India; potassium hydroxide (KOH) was supplied by SDFCL, India. These reagents were used as laboratory grade chemicals.

Preparation of Polyacrylate Superabsorbent Polymer

Preparation of polyacrylate superabsorbent polymer was carried out according to a modified procedure **[12]**. A mixed solution of acrylic acid monomer and potassium acrylate was prepared by mixing the monomer with N, N-methylene bisacrylamide as a crosslinker in

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presence of potassium hydroxide in distilled water under ambient conditions. The mixture solution was stirred at 350 rpm and heated to 70 ºC in a water bath for 15 min., followed by addition of the initiator. The reaction mixture was kept under stirring for few minutes to complete polymerization reaction. The prepared hydrogel was then immersed in excess distilled water to remove any impurities then dried at 80 ºC for about 3 hours. Furthermore effects of variation of MBAAm, KPS and KOH doses were also examined. All of the experiments were duplicated to obtain average results. A bench scale experiment was carried out according to the optimum conditions by which the swelling ratio of the SAH was in a maximum rate and economic.

Measurements and Characterization

Swelling Studies

The swelling characteristics of the prepared hydrogel were measured via gravimetric analysis **[12].** The swelling ratio is the criterion of describing water absorption capacity. Measurement of the swelling ratio of the prepared hydrogel was conducted by the so-called tea-bag method **[13]**, and using distilled water as liquid to be absorbed. The bags used were made of nonwoven polypropylene. The dried weighed samples confined in nonwoven polypropylene bags were placed in different swelling media with different pH values under ambient conditions and taken from swelling media at regular intervals time. The surface water on the swollen hydrogel was removed by soft pressing the bag sample between the folds of a filter paper; the increase in weight was determined.

The equilibrium swelling of the gels was determined as follows: gels were dried for 3 days at room temperature and were then dried under vacuum at 80 ◦C. After weighing the dried samples was determined, the samples were equilibrated in swelling media for a day at room temperature and then weighed again. The swelling ratio (S) and equilibrium swelling ratio (S_{eq}) were calculated from the following equations **[14]:**

$$S(g/g) = \frac{(W_t - W_0)}{W_0} \qquad (1)$$

$$S_{eq}(g/g) = \frac{(W_{eq} - W_0)}{W_0} \qquad (2)$$

Where, W_0, W_t, and W_{eq} are the weights of the samples in the dry state, the swollen state at a certain time, and the completely (equilibrium) swollen state, respectively.

Scanning Electron Microscopy

The morphology of the prepared dry hydrogel and swelled hydrogel were characterized by scanning electronic microscopy technique (Electron prop micro analyzer (JEOL, JXA – 840 A) at National Research Central laboratory- Egypt.

Results and Discussion

A superabsorbent hydrogel was prepared through polymerization of acrylic acid/acrylate using potassium persulphate as initiator and methylene bisacrylamide as a crosslinker. Superabsorbent Hydrogels have been identified as polymeric cross-linked network structure.

Availing SAH would significantly contribute to the production of soil conditioner and conductive gels. The major process operations were: mixing; polymerization; washing; drying and packing. The hydrogel structure is created by the hydrophilic groups present in a polymeric network upon the hydration in an aqueous environment.

Water absorbing capacity or swelling of the polymer can be controlled by two methods - type and degree of cross linking between polymeric chains and morphology of the SAP. Xie et al. **[15]** discusses that the water absorbing property of the SAPs can be greatly affected by type of cross-linking agent used. Also the cross linking agent varies the polymeric chain length – longer polymer chains have more network space and thus increases water absorbing capacity **[4]**. Besides, the length of polymeric chain also affects its water absorption capacity – smaller polymer chains have more polymer ends which do not contribute to water absorption **[16]**.

Superabsorbent hydrogel were prepared and the yield percent was found to be around 92.2 %. The effect of variation of initiator (KPS), crosslinker (MBAAm) doses and AAc/KOH ratio were investigated related to the swelling behaviour of the prepared SAH under investigation. Figure 1 represents the effect of variation of KPS on swellability of SAH. It is shown that swelling ratio increased by increasing KPS dose from 0.2 g to 0.5 g to 48.8 g/g and 54.55 g/g, respectively. Further increase in KPS causes decrease in swelling ratio up to 42 g/g. Thus, the optimum dose of KPS is 0.5 g.

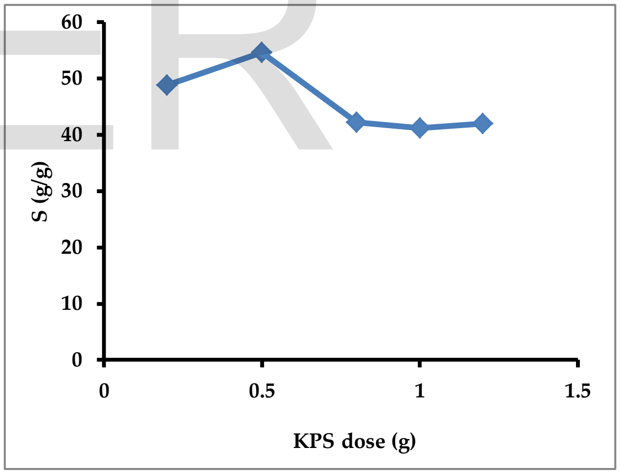

Figure 1: Effect of variation of KPS dose on SAH swelling ratio

Figure 2 illustrates the effect of MBBAm dose as a crosslinker on SAH swelling ratio. It is shown that swelling ratio increases by increasing the crosslinker dose from 0.04g to 0.1g to 47.3 g/g to 54.55 g/g, respectively. Further increase in MBAAm dose inhibits the swellability of the SAH under investigation. This is may be due to complication of the net of crosslinkes.

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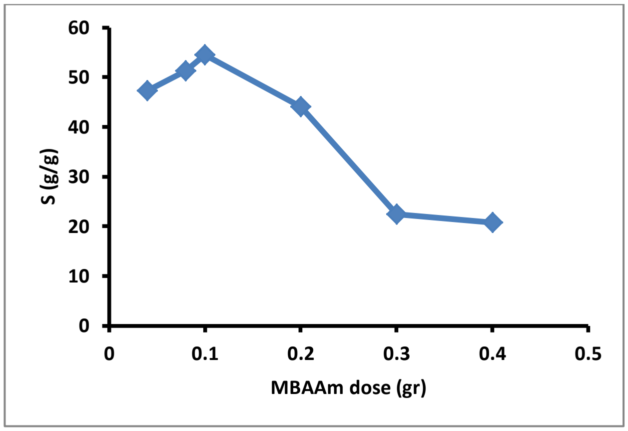

Figure 2: Effect of variation of MBAAm dose on SAH swelling ratio

Figure 3 represents the effect of variation of AAc/KOH ratio on SAH swelling ratio. It is shown that swelling ratio increases from 54.2 g/g to 56.4 g/g by increasing the AAc/KOH ratio from 0.7 mole/mole to 0.9 mole/mole, then further increase leads to a lack in swellability.

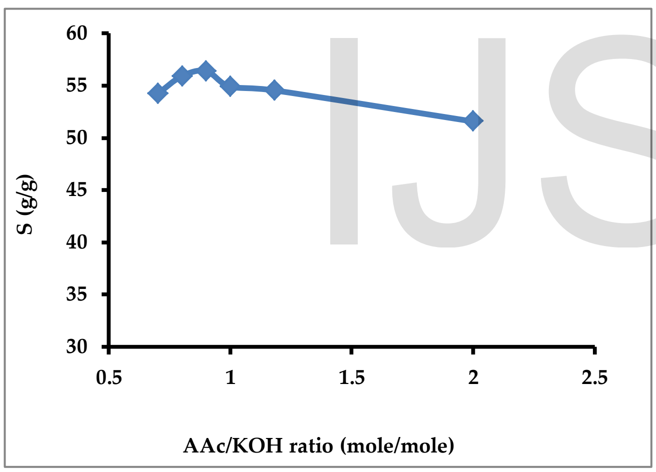

Figure 3: Effect of variation of AAc/KOH ratio on SAH swelling ratio

The swelling capacity of the prepared SAH under investigation in distilled water, tap water and different pH values (3, 5, 8 and 10) were carried out at room temperature (25 ± 1°C). The results shown in figure 4 revealed that, increasing alkalinity of the swelling media enhanced the swellability of the prepared SAH till pH, 8. Further increase in alkalinity of the swelling media decreases the swellability of SAP.

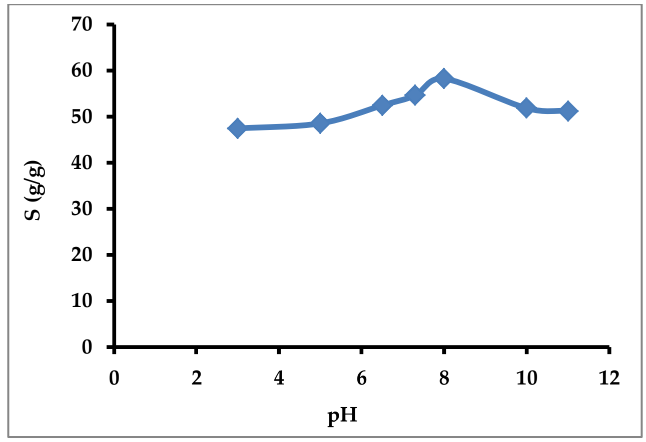

Figure 4: Swelling behaviour of SAH at different pH values.

Swelling behaviour

Swelling experiments were carried out at room temperature (25 ± 1°C) to evaluate the swelling capacity in tap water of the prepared SAH under investigation. The increase in the weight of the swollen SAH was directly related to the time of swelling. That is, the increase in the weight of the swollen hydrogel increased with increasing time of swelling (Figure 5). The swelling behavior observed was associated with the absorption mechanism, which, in turn, was determined by the diffusion process.

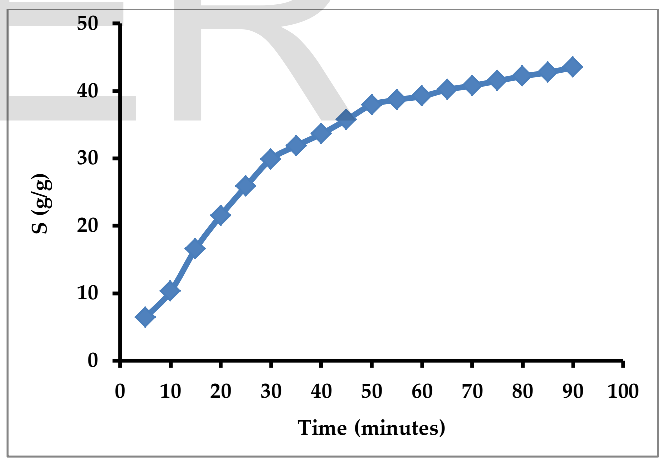

Figure 5: Swelling behaviour of SAH prepared at optimum conditions

Swelling kinetics

The controlling mechanism of the swelling processes was visualized through kinetic models. The latter were used to examine the data derived from the experimental work. A simple kinetic analysis is represented by a second-order equation, as given **[17]:**

$$\frac{dS}{dt} = k_S\left(S_{eq} - S\right)^2 \qquad (3)$$

where ks is the swelling rate constant and Seq is the degree of swelling at the state of equilibrium. After integration, when the initial

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conditions S = 0 at t = 0 and S = S at t = t, were applicable, eq. (3) became as follows:

$$\frac{t}{S} = A + Bt \qquad (4)$$

where B = 1/Seq is the inverse of the maximum or equilibrium swelling and A =1/$k_S S_{eq}^2$ is the reciprocal of the rate of swelling at the initial state [$(dS/dt)_o$] of the hydrogel. We examined the kinetic models by plotting t/S versus t for the prepared SAH with optimum conditions. The swelling parameters, including initial swelling rate (r), kS, and maximum equilibrium swelling [$(S_{eq})_{max}$], were calculated from the equations of the straight line given in Figure **6**. The calculated values are listed in Table I.

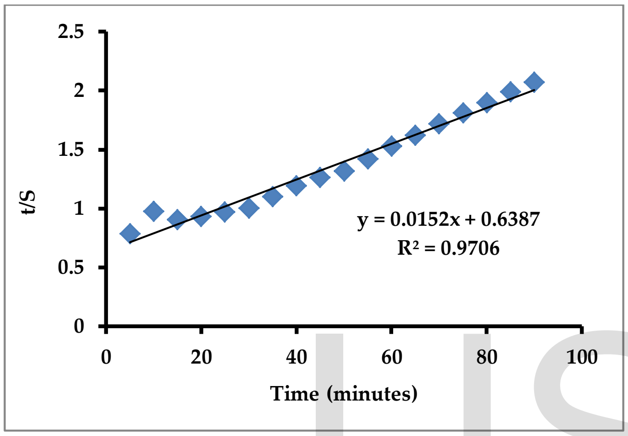

Figure 6: Swelling rate relations of SAH

The mechanism of water diffusion in swellable polymeric hydrogels has attracted much attention because of its many biomedicine, environmental, pharmaceutical, and agriculture applications. The diffusion of water implied that the hydrogel could be evaluated with the following equation **[17]**:

$$S(g/g) = \frac{(W_t - W_0)}{W_0} = Kt^n \qquad (5)$$

where K is the swelling constant and n is the swelling exponent calculated from the slopes of the lines of Ln S versus Ln t plots. For cylindrical shapes, n = 0.45-0.50 and corresponds to Fickian diffusion, whereas 0.50 < n < 1.0 indicates that diffusion is non-Fickian **[18]**. This equation is applied to the initial stages of swelling and plots of Ln(S) versus Ln (t) yield straight lines. For the hydrogels, Ln(S) versus Ln (t) plots was drawn using the kinetics of swelling and some representative results are shown in Figure 7. The swelling exponents $\boldsymbol{n}$ were calculated from the slopes of the lines and are listed in Table 1. The value of the diffusional exponent is 0.652. Hence, the diffusion of water into SAH had a non-Fickian character. The value of $\boldsymbol{n}$ higher than 0.5 indicating diffusion of water to the interior of all the SAH, follows an anomalous mechanism. The anomalous behaviour of the hydrogel is due to the regularity of the chain and strong interaction via the formation of hydrogen bonding, leading to a compact structure which would prove the anomalous aspects of diffusion even for a molecule as small as water **[12].**

Table 1: Some Swelling Parameters of SAH

Swelling parameters	SAH (optimum conditions)
Experimentalequilibrium swelling	54.55
$(S_{eq})_{max}$ (g/g)	66.7
$K_s \times 10^4$	3.53
r	1.57
n	0.652

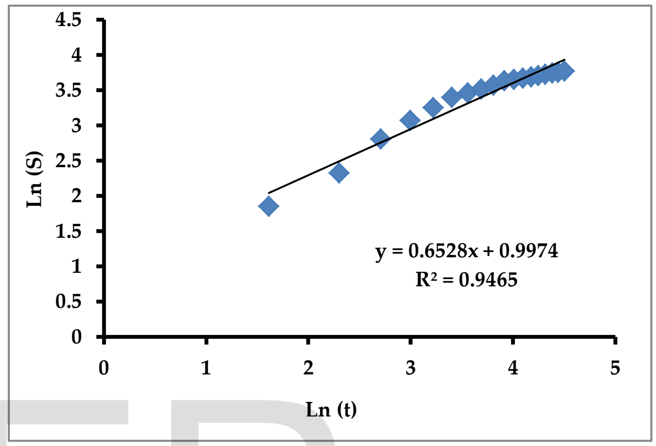

Figure 7: Swelling kinetic relations of SAH

Scanning Electron Microscopy

The surface characteristics of dry and swelled SAH were investigated by scanning electronic microscopy (SEM). Figure 8 shows the images of SEM for dry SAH prepared by different ratios of AAc/KOH.

Figures 8 (a,b, c and d), represent the surface morphology of dry SAH prepared with different ratios of AAc/KOH**.** The figures show a uniform nature with limited cracks on its surface and presence of KOH particles which increase by decreasing AAc/KOH ratio.

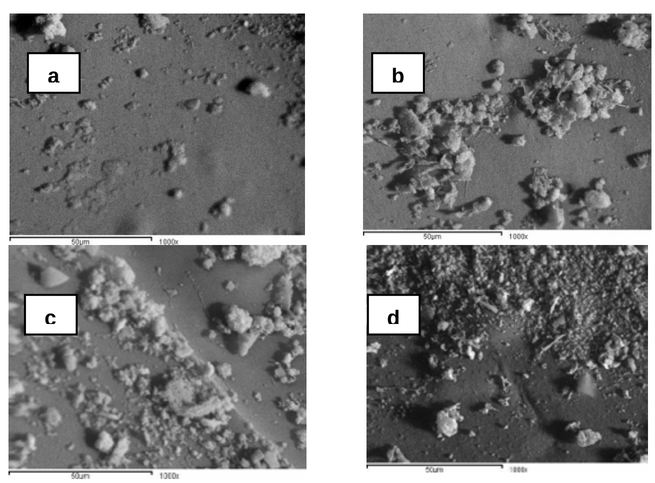

Figure 8: SEM images of dry SAH prepared with different ratios of AAc/KOH.

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Figure 9 (a,b, c and d), represent surface morphology of swelled SAH prepared with different ratios of AAc/KOH. The figures show a smooth surface and a cracks appeared due to swelling. The presence of KOH particles on surface of both dry and swelled SAH sample increases by decreasing AAc/KOH ratio.

Figure 10a shows a photograph image of dry SAH, it seems like a hard crystal particles while Figure 10b represents the swelled SAH and seems to be like a water crystals.

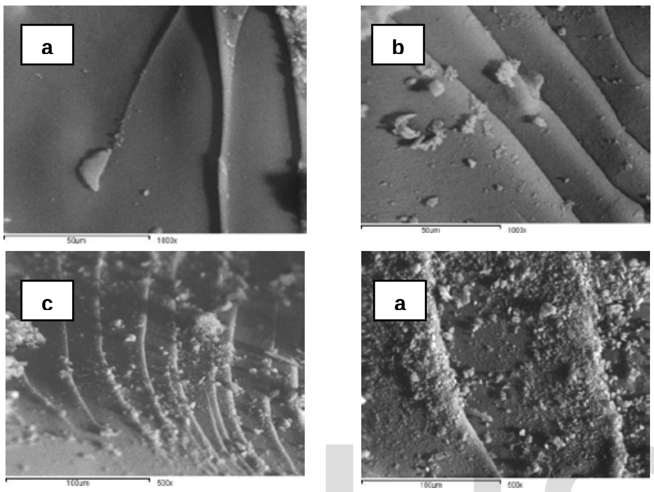

Figure 9: SEM images of swelled SAH prepared with different ratios of AAc/KOH

Figure10: Photograph images of dry and swelled SAH

Block diagram of the preparation of SAH

A bench scale experiment was carried out according to the optimum conditions by which the swelling ratio of the SAH was in a maximum rate and economic. The adopted methodological milestones for preparation of SAH comprises: A mixed solution of AAc monomer and potassium acrylate was prepared by agitating the monomer with MBAAm as a crosslinker in presence of KOH in distilled water under ambient conditions. The mixture solution was stirred and heated to 70 oC, followed by addition of the initiator (KPS). The reaction mixture was kept under stirring for few minutes to complete polymerization reaction. The prepared SAH was then washed in excess water to remove any impurities then dried at 80oC for about 3 hours. The overall processing steps for SAH are representing by the flow sheet illustrated in Figure 11.

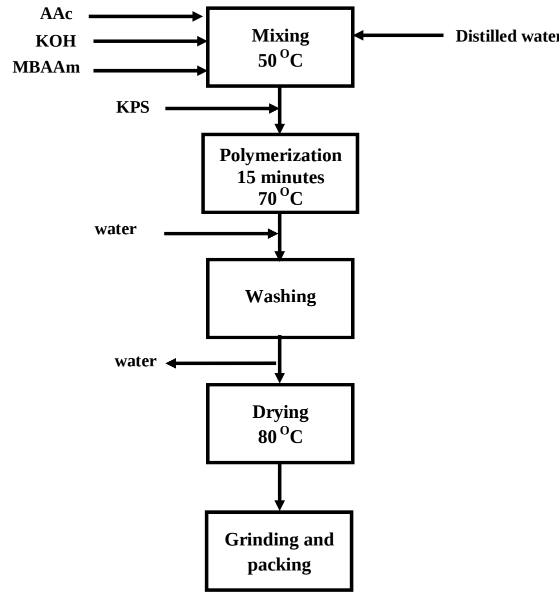

Figure 11: The processing steps of SAH production.

Conclusion

A superabsorbent hydrogel was prepared through polymerization of acrylic acid/acrylate under potassium persulphate initiation and methylene bisacrylamide as a crosslinker. The effect of variation of initiator (KPS), crosslinker (MBAAm) doses and AAc/KOH ratio were investigated related to the swelling behaviour of the prepared SAH under investigation. The optimum conditions to prepare an efficient and economic SAH are AAc, 60.2 %; KOH, 37.4 %; KPS, 2 %; MBAAm, 0.4 % and AAc/KOH ratio, 0.9 mole/mole. Superabsorbent hydrogel were prepared using the optimum condition and in a bench scale and the yield was about 92.2 %.

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