Effect of Sodium Humate on the Swelling Characteristics and Agricultural Application of Superabsorbent Hydrogels of Poly (acrylic acid/sodium alginate/sodium humate)

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ABSTRACT

A series of superabsorbent hydrogel (SAHs) based on poly Acrylic Acid (AAc), Sodium Alginate (NaAlg) and Sodium Humate (SH) (AAc/NaAlg/SH) was prepared by free radical solution copolymerization. Hydrogel having sodium humate 9.09 wt% showed maximum water absorbency of 906 g of water per gram of superabsorbent hydrogel. The application of the synthesized superabsorbent hydrogel was investigated in agriculture as soil conditioner for water retention in sandy soil. The study revealed that the synthesized superabsorbent hydrogels could act as an effective water saving material for agricultural applications. Swelling behavior (such as swelling ratio, initial swelling rate constant, swelling exponent, diffusion coefficient and penetration velocity etc.) for all the synthesized superabsorbent hydrogels having various (6.9 to 11 wt %) concentration of SH was studied. Swelling exponent was found in range of (0.712 to 0.802); thus suggesting non fickian diffusion mechanism. The effect of synthesized SAHS on growth of seeds of corn and white gourd are reported.

KEY WORDS: *Superabsorbent hydrogels (SAHs), Sodium Humate (SH), Sodium Alginate (NaAlg), Acrylic Acid (AAc), Swelling Kinetics.*

1. INTRODUCTION

Hydrogels are three dimensional networks which can swell in water and imbibe large amount of water while maintaining its physical dimension and structure. Because of their excellent properties such as hydrophilicity, high swelling capacity and biocompatibility, superabsorbent hydrogels have found potential

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applications in many fields such as disposable diapers, feminine napkins, cosmetic and hygiene products [1-4], drug delivery [5] and soil modifier[6-7]. Now a day's superabsorbents have been used successfully for soil amendments in the agriculture industry for holding of water, and enhancing nutrition in sandy soil due to choosing of monomers like sodium humate [8] and sodium alginate [9]. It was reported by Abd El-Rehim et al [8] that SAHs potentially influence soil permeability, structure, texture, density, evaporation and infiltration rates of water through the soils. The SAHs reduce irrigation frequency; stop erosion and water runoff, as well as increase the air aeration and supply of nutrition. It was also reported by Zhang and Liu et al [10], that in the synthesis and characterization of (acrylic acid and acrylamide) superabsorbent by introducing sodium humate it can be advantageous to the absorption of water, and water retention capacity in sandy soil. Now-a-days carbohydrate and cellulose are primarily used in synthesizing superabsorbent hydrogels and these are very common and easily available in nature [11]. Recently SAHs prepared with natural polymers such as, starch [12], sodium humate and sodium alginate [13], and their derivatives have been investigated. A number of agricultural wastes like hazelnut, orange peels, maize cobs, peanut shells, soybean hulls, jackfruits peels, have been explored and utilized for use in making superabsorbent hydrogel [14], but they have low swelling ratio. To avoid these major problems they have been modified by acrylates for increasing swelling ratio. Similarly sodium alginate (NaAlg) is a biodegradable natural monomer which is used in a variety of commercial applications because of tendency to gelatization [15]. Alginates are linear anionic polysaccharides of (1-4) linked alpha –L- gluronate and β –D-mannuronic acid are obtained mainly from brown alga belonging to the phaeophycea. Alginate and their derivatives are widely used in drug delivery [16] and agriculture applications [17]. Sodium humate was the second monomer chosen for hydrogel synthesizing which is composed of multifunctional aliphatic component and aromatic constituents and contains large number of functional hydrophilic groups such as carboxylates and phenolic hydroxyls groups [18]. In the earlier work of Singh and Singhal [19], they reported that hydrogels based on poly acrylic acid /acrylamide/sodium humate superabsorbent hydrogels were prepared by using ammonium persulfate as an initiator and N, N methylene bisacrylamide as crosslinker. The swelling studies showed that the introduction of sodium humate in to the SAHs (AAc/AAM/SH) obtained $724gg^{-1}$ water absorbency. Zhang et al [20]. have prepared a novel multifunctional superabsorbent hydrogel from the monomers acrylic acid (AAc), acrylamide (AM), sodium humate (SH) and attapulgite (APT), by aqueous solution polymerization, applying N,N^2 - methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator. In this work, they studied the effects of the ratio of AAc to AM, SH and APT concentration on the equilibrium water absorbency. The results revealed that comprehensive performances of the superabsorbent hydrogels were improved by incorporating functional components in a poly (acrylic acid-acrylamide) (PAAc-AM) network. It was also reported by Wang and Wang [21], that in the case of semi IPN superabsorbent hydrogels based on sodium alginate -g- poly (sodium acrylate) and poly vinyl pyrrolidone (PVP) system, the excess of PVP may tangle with the graft polymers chains and the physical crosslinking occurred when the PVP content exceed 15wt%. Uptill now only one research paper has been published on graft co-polymerization of (AAc/NaAlg/SH) by Hua et al [22].They have reported introduction of sodium humate graft in the sodium alginate –g- poly acrylic acid copolymer in aqueous solution, using ammonium persulfate and N,N'-methylenebisacrylamide. They studied the effects of crosslinker, sodium alginate and sodium humate concentration on the water absorbency of the SAHs. The swelling behavior of synthesized hydrogel in solutions having different pH and, the swelling kinetics in different saline solutions was also investigated. The results showed that the introduction of sodium humate into the SAHs system having sodium alginate-g-poly (acrylic acid) enhanced the water absorbency and the SAHs having 10 wt% sodium humate achieved the highest water absorbency.

The present work reports the synthesis of a series of (AAc/NaAlg/SH) Superabsorbent hydrogels by crosslinking terpolymerization in solution form. The effects of SH concentration 6.97%, 8.04%, 9.09%,10.11% and 11 wt% on distilled water absorbency of synthesized SAHs were investigated. The initial swelling rate, diffusion coefficient, penetration velocity and water retention capability were evaluated. The synthesized hydrogels were also characterized by Fourier transforms infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM).

2. EXPERIMENTAL

2.1 Materials

Acrylic acid (AAc), potassium persulphate (KPS), N,N'-methyl bisacrylamide (NMBA), sodium hydroxide (NaOH) were purchased from CDH and all were of Analytical grade, New Delhi. Sodium alginate (NaAlg) was supplied by Thomas Baker and sodium humate (SH) was procured from Aldrich chemical company. Double distilled water was used throughout the experiments.

2.2 Synthesis of poly (AAc-co-NaAlg-co-SH) Superabsorbent hydrogels

A series of superabsorbent poly (AAc-co-NaAlg-co-SH) hydrogels were prepared using acrylic acid, sodium alginate and sodium humate as monomers. Five hydrogel compositions having weight of sodium humate (based on total solid content) 6.97%, 8.04%, 9.09%, 10.11% and 11 wt% were prepared and designated as S_1,S_2,S_3,S_4,S_5, respectively. N, N-methyl bisacrylamide (NMBA) was used as crosslinker, while potassium per sulphate was used as an initiator. The actual feed composition for all hydrogels are shown in **Table 1**. For hydrogels having sodium humate concentration lower than 6.97 wt% the polymerization did not take place and no hydrogel was formed.

2.3 Polymerization procedure of poly (AAc-co-NaAlg-co-SH) superabsorbent hydrogels

The terpolymeric hydrogels were synthesized using solution co-polymerization with water as solvent. A three neck glass flask (500 ml) fitted with stirrer, condenser, and thermometer pocket was taken. The reaction was carried out in oil bath at room temperature 70^{o} C for 6 hours. Firstly Sodium Alginate in specified amount was added in the flask and then 10 ml water was added to it. Then the mixture was vigorously stirred for 30 minutes at 60^{o} C. Then KPS was dissolved in 5ml distilled water and then added in the reaction flask. In this synthesis, 75% neutralized acrylic acid was used. The neutralization of 75% acrylic acid was carried out by using 34.5% solution of sodium hydroxide until pH of acrylic acid is reached up to 4.5 and then the specified amount was added in the three neck flask. The NMBA in the specified amount according to **Table 1**, was dissolved in 5 ml distilled water and introduced into

TABLE 1. Feed ratio for synthesizing a series of poly (AAc/NaAlg/SH) superabsorbent hydrogel

Sample Designation	Monomer ratio wt. (%)(AAc/ NaAlg/SH)	Weight of AAc (gm)	Weight of NaAlg (gm)	Weight of SH (gm)
S_0	90/10	7.2	0.80	0.00
S_1	83.72/9.30/6.97	7.2	0.80	0.60
S_2	82.75/9.19/8.04	7.2	0.80	0.70
S_3	81.83/9.09/9.09	7.2	0.80	0.80
S_4	80.89/8.98/10.11	7.2	0.80	0.90
S_5	80/9/11	7.2	0.80	1.00

Other conditions: NMBA 0.0071(gm), KPS 0.0089(gm) distilled water 30ml for polymerization, temperature 70^{0}C.

three neck flask. Now the reaction mixture in the flask was stirred and heated continuously and sodium humate was dissolved in 10 ml distilled water, and then added to the reaction mixture for six hours. The reaction was continued until the hydrogel was formed. Afterwards hydrogel was removed from flask and washed with 100 ml distilled water for 1 hour, under unstirred condition. This process was repeated 4 times till the water became clear from the residue of sodium humate which is brown in colour. Afterward the washed hydrogel was dried in oven at 70^{o}C up to a constant weight.

2.4 Dynamic Swelling behavior

The completely dried superabsorbent hydrogel having approximately 0.50 ~ 0.51 gm was placed in 1500 ml containing distilled water (sink condition) at room temperature. The swollen hydrogel was taken in bath container at 1 hour intervals; it was kept in the same bath container again. The mass measurements of swollen hydrogel were continued until no increment in weight of hydrogel was observed. The equilibrium swelling ratio (S_{eq}) was calculated by using conventional gravimetric technique with following equation:

$$S_{eq}(g/g) = \frac{Equilibrium\ Swollen\ weight - Dry\ weight}{Dry\ weight} \quad (1)$$

To analyze the controlling mechanism of the swelling process several kinetics models are used to fit experimental data. The overall kinetics of a superabsorbent hydrogel involving long swelling periods may be expressed by well known schotts second order kinetics [23].

$$ds / dt = kr\,(S_{eq}\text{-}S)^2 \quad (2)$$

Where Kr is rate constant of swelling and S_{eq} denotes the swelling percent at equilibrium. Taking integration by applying the initial condition $S_{eq}= S_o$ at time t=to and S_{eq}=S at time t=t then equation (2) becomes

$$t / S = A+ Bt \quad (3)$$

Where A and B are two coefficients whose physical significance is put as follows at a long range time Bt>>A and according to equation (3) B=1/Seq i.e., it is the equilibrium water uptake, at a very short range time A>>Bt and in the limit equation becomes.

$$\frac{\lim}{t \to 0}\left[\frac{dM_t}{dt}\right] = \frac{1}{A} \quad (4)$$

Therefore the intercept A is the reciprocal of the initial swelling rate r_i or $1/ksS^2eq$, t/S vs. t graphs were plotted in Figure 4 (plotted by origin software) and calculated values are shown in Table 3.

2.5 Media penetration velocity

The penetration rate for synthesized superabsorbent hydrogel was expressed by the weight gain as described by peppas [24, 25]. The penetration rate was calculated using equation

$$U=1/2\rho A^{*}\partial wg/\partial t \tag{5}$$

Where U indicate the penetration velocity, ∂wg / ∂t represent angle of weight gain versus time curve ρ shows the density of water and A*express the area of one face of the sample peace. In the study length of sample peace was 1.6~1.5 cm and width of peace was 1 cm.

2.6 Water uptake mechanism and diffusion coefficient

The polymeric chains contain ions then the charged groups along the polymeric chains repulsion occurred and increase the chain relaxation procedure [26]. The distribution of the water absorption curve with a fractional water uptake F (Mt/M∞) lower than 0.60 as used in Figure 5 was inspect using the following equation 6

$$F= kt^{n} \tag{6}$$

Where M_t the mass of water is absorbed at time t and M ∞ is the mass of water absorbed at equilibrium, k is characteristics constant of the hydrogel and the exponential n is determined the diffusion. Table (3) shows calculated experimental data of constant n and k values. When n indicate 0.45-0.50, the swelling process is diffusion controlled and was ‘fickian type’ transport and 0.50 <n> 1.0 it indicates ‘non fickian / anomalous transport’ and n indicate 1 to express ‘relaxation controlled’ transport. The short time approximation manner determined the diffusion coefficient of AAc/NaAlg/SH SAHs manner[27]. The diffusion coefficient D; used to study water monomer into the SAHs were determined from the slopes of the plots between F Vs $t^{1/2}$. The diffusion coefficient of AAc/NaAlg/SH was calculated from the following relation [28].

$$F=4\left[\frac{Dt}{\pi r^{2}}\right]^{\frac{1}{2}}-\pi\left[\frac{Dt}{\pi r^{2}}\right]-\frac{\pi}{3}\left[\left[\frac{Dt}{\pi r^{2}}\right]\right]^{\frac{3}{2}} \tag{7}$$

Where D is in cm^2/min, t in min and r is the radius of cylindrical SAHs. Comparison on equation 6 and 7 shows the empirical equation 8 that is

$$K=4\left(\frac{D}{\pi r^{2}}\right)^{\frac{1}{2}} \tag{8}$$

For hydrogels F Vs $t^{1/2}$ were calculated from the slopes of the lines shown in Table 3.

2.7 Estimation in water retention properties in sandy soil

AAc/NaAlg/SH Superabsorbent hydrogels sample containing (0.2, 0.4, 0.8 wt %) was mixed with 300 gram of dry sandy soil in to the beaker. After this amount of 60 gram of water was slowly added to these beakers and weighed every day. A controlled experiment without the superabsorbent hydrogels was also carried out.

2.8 Fourier transforms infrared spectroscopy (FTIR) studies

The FTIR of poly (AAc/NaAlg /SH) superabsorbent system were recorded on a Perkin Elmer spectrophotometer using pellet of pottassium bromide.

2.9 Scanning electron microscopy

The surface morphology of various poly (AAc/NaAlg/SH) hydrogels was examined under scanning electron microscope (SEM). Dried hydrogels were covered with a thin layer of pure gold in S150 Sputer coater, and imaged in a SEM (LEO Electron Microscopy Ltd. England).

3. Results and Discussion

3.1 Fourier transforms infrared spectroscopy (FTIR)

FTIR of NaAlg/AAc, SH, (SAHs) NaAlg are shown in Figure (1). In Fig (1d) the absorption bands at 1613 and 1419 cm^{-1} for the COO^{-} group shift to 1567 and 1458 cm^{-1} respectively and the absorption band 940 cm^{-1} and 894 cm^{-1} disappeared in IR spectrum of NaAlg/AAc Fig(1b) suggested the reaction of AAc on NaAlg. Comparing with IR Spectrum of Figure (1a) the absorption bands at 1711 cm^{-1}(C=O stretching of COOH of SH) 1611 cm^{-1}(-COO asymmetric stretching of SH) and 1268 cm^{-1} (phenolic C-O stretching of SH) almost vanished in the spectrum of AAc/NaAlg/SH superabsorbent hydrogels. The results attained

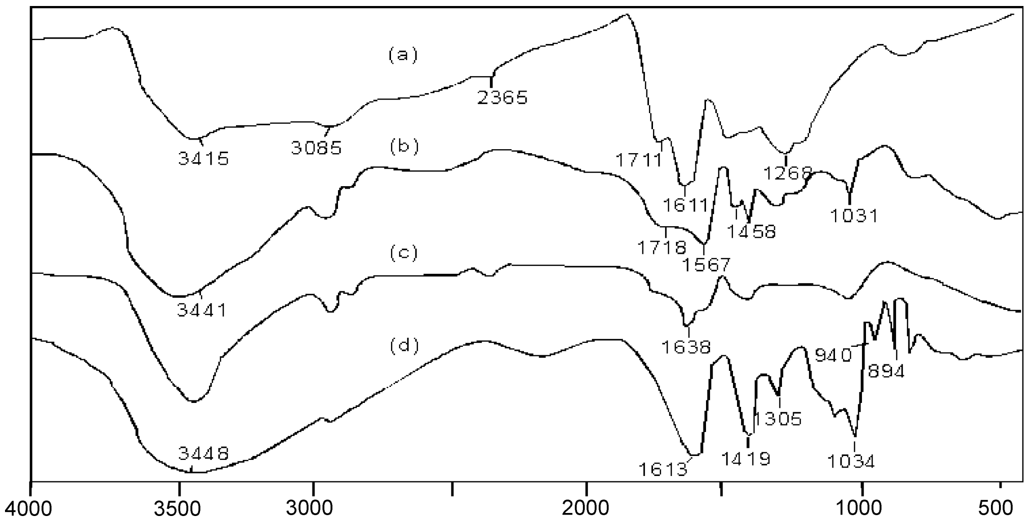

Fig. 1. FTIR spectra of (a) SH,(b)NaAlg/AAc,(c)AAc/SH/NaAlg,(d)NaAlg Superabsorbent hydrogels.

from IR analysis showed that the reaction of both sodium alginate and sodium humate with Acrylic acid monomer polymerize through the synthesis of SAHs. The freestanding radicals on NaAlg promote the polymerization of AAc and SH formed superabsorbent web [22].

3.2 Morphological studies

3.3 Scanning electron microscopy (SEM)

Scanning electron microscopy technique was applied to identify the differences in surface morphology of SAHs resulting from the varying SH content. The SEM micrographs of poly (AAc/NaAlg/SH) S_0, S_1, S_3, S_5 (control, 6.97, 9.09, 11 wt %) are shown in **Figure 2 (a,b,c,d)** respectively**.** The surface morphology of (AAc/NaAlg/SH) superabsorbent hydrogel is different from that of control (AAc/NaAlg). In (AAc/NaAlg) superabsorbent hydrogel (S_0) has largely plain surface with some granular flake like structures; however the samples introduced with sodium humate exhibited an undulant comparatively loose, porous (Figure 2 b).The surface of hydrogel S_3 is shown in **Figure 2** c it exhibits a very rough, intermeshing surface containing deep frequent deep depressions. This indicates that for this particular hydrogel, water can enter directly inside hydrogel in addition to diffusion. This particular surface configuration is responsible for water absorbency. Buchhloz et al [29] explained that open pores in superabsorbent hydrogels are little reservoirs for water storage when there is means to convey the water in to the unlock pores. The pores are the regions of water penetration, in which the interaction of hydrophilic groups with water molecules occurs, leading to high water absorbency. This surface area is beneficial for the penetration of water into the polymer network, and increases the water absorbency of SAHs. Fig 2 d (S_5) shows some irregular shaped formations on surface, which may be formed due to excess sodium humate present as filler.

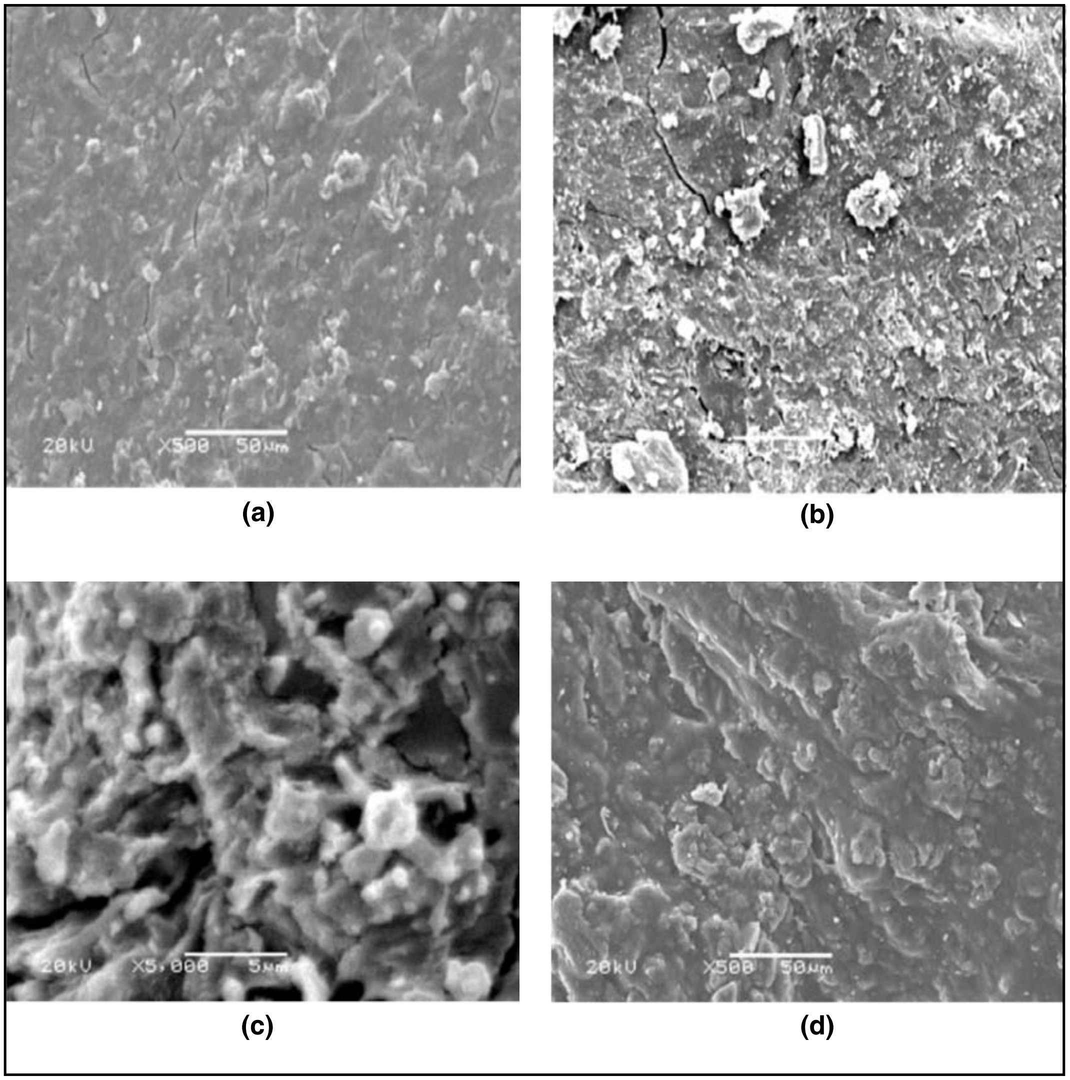

Fig. 2 (a) SEM of micrographs of Poly (AAc/NaAlg) superabsorbent hydrogel $S_{0,}$ (b) (AAc/NaAlg/SH) superabsorbent hydrogel $S_{1,}$ (c) (AAc/NaAlg/SH) superabsorbent hydrogel $S_{3,}$ (d) (AAc/NaAlg/SH) superabsorbent hydrogel $S_{5.}$

3.4 Effect of Sodium Humate concentration on water absorbency

In this work a superabsorbent hydrogel (S_0) containing only AAc/NaAlg was synthesized as control, to compare the performance of superabsorbent hydrogels containing sodium humate, Figure 3 shows the relationship between SH concentration variation and equilibrium swelling ratio. It was observed that foremost there was a moderate increase in the equilibrium swelling ratio that is from 365 to 752 gg^{-1} for the S_1-S_2 superabsorbent hydrogels having (6.9 to 8.04 wt%) SH concentration. Furthermore the sodium humate concentration (8.04-9.09 wt %) it was observed that the equilibrium swelling ratio vigorously increased to 906 gg^{-1}. Additional of SH concentration the water absorbency gradually decreases. The equilibrium swelling increases due to presence of a large number of hydrophilic functional groups such as –OH groups and amino groups [30], hence these phenomena shows that during the polymerization procedure SH reacts with AAc/NaAlg and forms a polymer web which enhances the water absorbency. Furthermore, increasing the SH concentration above 10.11 wt %, the water absorbency decreases because of surplus SH the same as filler and the space for holding more water reduces. It has been reported by Wu, Wei, Lin and Lin deliberate that surplus of kaolin particles are physically crammed in the network starch –g –AAm /mineral powder of the system decrease the water absorbency for the AAc/NaAlg/SH polymeric web may act as a similar mechanism [31]. When the water absorbency of AAc/NaAlg/SH superabsorbent hydrogel of S_3 hydrogel was compared with other researches Table 2, we found that the synthesized S_3 SAHs is best absorption ability of the superabsorbent is 906 g of water per gram of SAHs in distilled water.

SH have many functional groups which have the ability to react with AAc and NaAlg during polymerization or crosslinking process. Superabsorbent Figure 2(c) sample designation S_3 exhibits slightly highly porous surface having increased surface area and roughness, due to

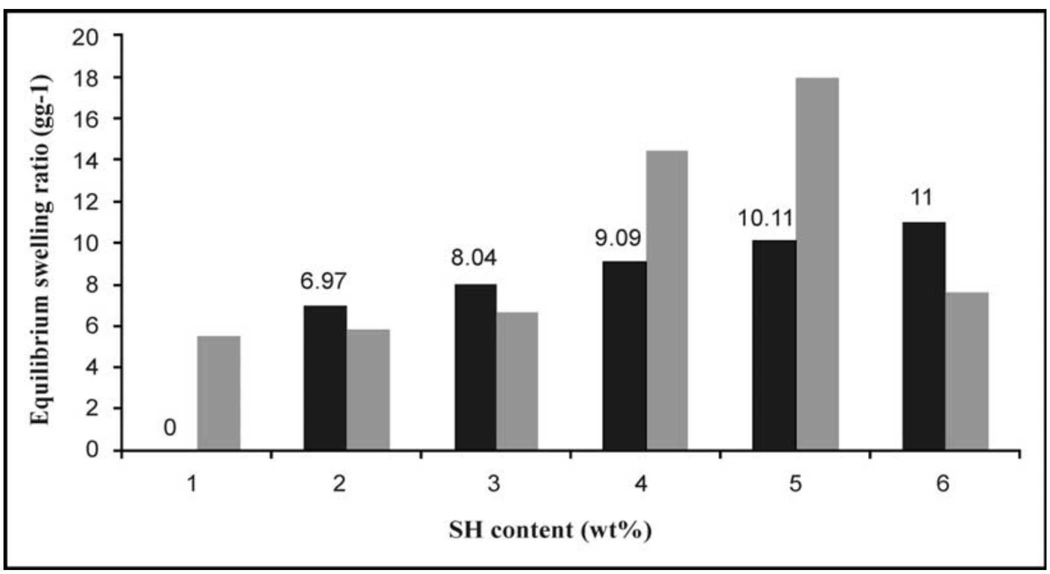

Fig. 3. Effect of Sodium humate concentration at 6.97%, 8.04%, 9.09%, 10.11%, 11wt% wt percent with control on the equilibrium swelling ratio of the synthesized (AAc/NaAlg/SH) Superabsorbent hydrogel.

TABLE 2. For Absorption Capacities of distilled water by various absorbent.

Monomers used in superabsorbent hydrogels	**Technique of polymerization**	**Water Absorbency (g/g) water of SAHs**	**Applications Studied**	**Reference**
Poly(Acrylic acid-co Butyl methyl cellulose)	Graft co-polymerization	51g/g	Study of swelling kinetics and salt-sensitivity behaviour of a superabsorbing hydrogel	Sadeghi 2011, [32]
Chitosan, Poly (acrylic acid), Attapulgite	Graft polymerization	159.6 g/g	Factor influencing water absorbing of SAHs were investigated	Zhang 2007, [33]
Chitosan, Poly acrylic acid, Sodium Humate.	Graft polymerization	183 g/g	Swelling rate and swelling behaviour were investigated	Liu 2007, [34]
Superabsorbent formulation based on Wheat Straw and Attapulgite	Graft Co-polymerization	186g/g	The water retention capacity and slow release behaviour of Nitrogen & Boron from the product were investigated	Xie, Liu, Ni, Zhang, Wang 2011, [35]
Carboxymethyl Cellulose, Acrylamide	Radiation induced graft copolymerization of acrylamide on to Carboxymethyl cellulose	190 g/g	Controlled release potential, SAP was loaded with (KNO_3) were studied	Hemvichian 2014, (36)
Cellulose nano fibrils and Chitosan, Poly (Acrylic acid)	Graft copolymerization	381 to 486	Study of salt solution is in order of monovalent, divalent, trivalent cation	Spagnol 2012, [37]
Wheat straw and acrylic acid	Chemical method	417 g/g	Amount of initiator and crosslinker, temperature and neutralization degree of acrylic acid that influence water absorbencies of superabsorbent were investigated	Liu 2009, [38]

Cellulose, Acrylic acid, Acrylamide	Free radical graft copolymerization	490 g/g	Reaction temperature, initiator amount, monomer amount were investigated	Wu Fan 2012, [39]
Poly(Acrylic acid, Acrylamide, Organomontmorillonite) Sodium Humate	Graft copolymerization	591 g/g	Water retention capacity were investigated	Zheng 2007, [40]
Poly Acrylic acid, Acrylamide, Sodium Humate	Solution polymerization	1100g/g	Swelling in 0.9wt% of NaCl solution was investigated	Zhang 2006, [41]
Poly (AAc-co-acrylamide) Sodium Humate	Solution polymerization	1184g/g	Water retention capability in sand soil	Zhang 2006, [10]
Sodium Alginate, Sodium Humate, Acrylic acid	Graft copolymerization	1380 g/g	The swelling behaviour in solution of various pH and the swelling kinetics in saline solution were investigated	Hua 2009, [22]

which, the swelling increases. In addition to these pores, cracks and gaps can also be observed on the surface. The pores are the regions of solvent penetration, in which the interaction of hydrophilic groups with solvent molecules occurs, resulting in high water absorbency. This observation revealed that the introduction of SH facilitates porosity in the SAHs network structure and increases the surface area, which enhance diffusion of aqueous fluid into the SAHs network resulting in increased equilibrium water absorbency. However, on further increasing the SH content above 10.11wt%, resulted in a decrease of absorption capacity. The microstructure shown in case of SAHs (fig. 2(d) sample designation S_5) shows few coarse and irregular shaped formation with lesser cracks having the dispersed second phase, which clarify that excess SH particle do not involve in the formation of SAHs network and remain as filler.

3.5 Dynamic swelling studies

The swelling kinetics of superabsorbent hydrogels such as size distribution of pores, precise exterior area depends on its microstructure[42]. Scanning electron microscope Figure 2 shows the incorporation of sodium humate 6.97% to 11wt% concentration designated S_1 to S_5 are shown in Table 1. Sodium humate concentration affects the swelling kinetics of synthesized superabsorbent hydrogels. Table (3) showed various experimental data such as initial swelling rate, swelling rate constant, equilibrium swelling ratio because of variation in the SH concentration 6.97%, 8.04%, 9.09%, 10.11% and 11 wt%. Swelling rate increases till the swelling ratio increases (365.95, 752.95, 906.19, 408.11, 312.45), and gradually decreases which is shown in Table (3) and Figure 4. As mentioned by Lee and Wu. [43], the initial swelling progress is primarily because of water penetration into the polymeric web through the diffusion. The incorporation of SH can improve the surface structure and increase the surface area of the resulting superabsorbent Figure 2(c); this makes water to diffuse more easily into the polymeric web and leads to the increase in the swelling rate.

TABLE 3. Swelling parameters of AAc/NaAlg/SH superabsorbent hydrogels

Sample designation	Eq Swelling ratio (Calculated value as per equation discussed in section 2.3)	Swelling rate constant (k_sx10^6)	Swelling exponent, 'n'	Initial swelling rate (r_ig water/g gel min g)	Diffusion coefficient (D X10^{-3}) $cm^2 m^{-1}$	Diffusion constant (K)	Penetration Velocity (u×10^{-3})	Eq Swelling ratio (Experimental values)
S_1	365.95	11.0	0.712	1.19	32.18	-0.682	8.4	366.95
S_2	752.95	8.0	0.741	4.36	48.91	-0.720	14.3	753.95
S_3	906.19	6.0	0.802	6.83	54.69	-0.765	15.4	907.19
S_4	408.11	4.6	0.728	1.36	35.82	-0.706	9.6	409.11
S_5	312.45	3.2	0.723	1.03	28.32	-0.695	5.8	313.45

Standard deviation: ±0.0001 to 0.0004 and regression coefficient (R^2) in all cases: 0.99

However, the ratio of strong affinity for water decreases when the concentration of SH increase beyond 9.09 wt %.These results indicate that the incorporation of moderate amount of SH is favorable to enhance the swelling rate, but the excessive addition of SH

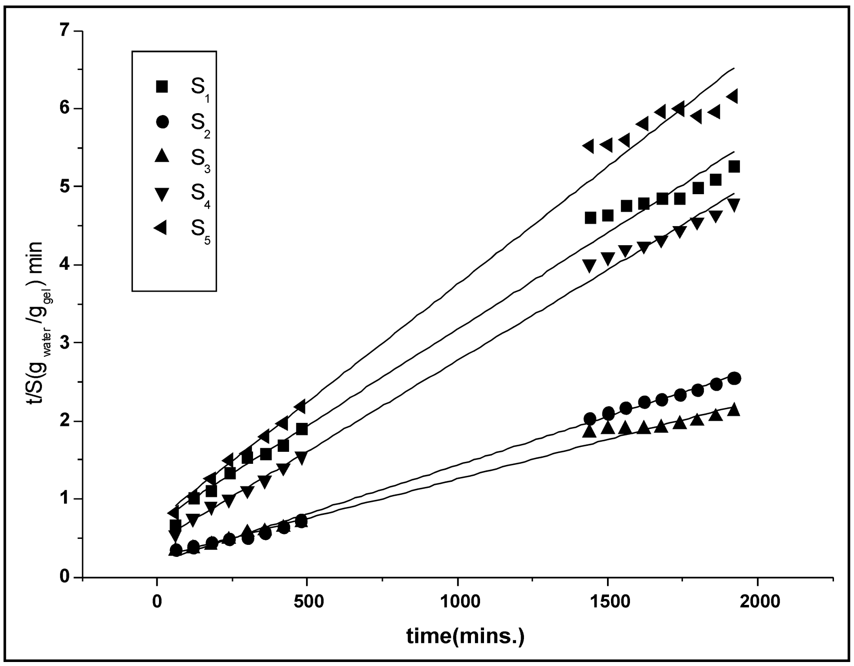

Fig. 4. Swelling kinetics curves of AAc/NaAlg/SH superabsorbent hydrogel at 6.97%, 8.04%, 9.09%, 10.11% and 11 wt% having weight of Sodium Humate.

decreased it. Similar results were found in the study of swelling behavior of (GG-poly-acrylate)/ sodium humate [44].

3.6 Media penetration velocity

Table 3 shows the value of swelling rate constant (K_s) and media penetration velocity (U). Figure 3 represent with the increase in SH content, the value of 'U' increases and value of K_s decreases which indicates a higher affinity for water. It can be clear from table 3 that increasing of SH concentration gives a platform for polymer chain relaxation thus allowing the media to move more freely. Apart from this when SH concentration increases 10.11 wt% to 11 wt% K_s increases and U slightly decreases. The Swelling mechanism results were different than those of poly (AAm –co-AAc) [45].

3.7 Water uptake mechanism

Table 3 explained that the swelling exponent 'n' for the samples (S_1-S_5) with different Sodium Humate (6.97% to 11 wt %) concentration varies from 0.712 to 0.802; thus suggesting the anomalous or non fickian type diffusion [46]. Table 3 shows diffusion coefficient (D), which was determined by equation (7). It is clear that diffusion coefficient values lie between 28.32×10^{-3} to 54.69×10^{-3} $cm^2 min^{-1}$. It is clarifies from the Table 3 and Figure 5 that a consequence of the slow relaxation rate of the polymer matrix or rates of solvent diffusion and polymer relaxation are resembling [47]. It can be examined from the Table 3 the value of diffusion coefficient (S_1-S_5) 28.32×10^{-3} to 54.69×10^{-3} $cm^2 min^{-1}$ shows the relatively higher diffusion coefficient which indicates the easier and fast penetration of water molecules in to the SAHs network.

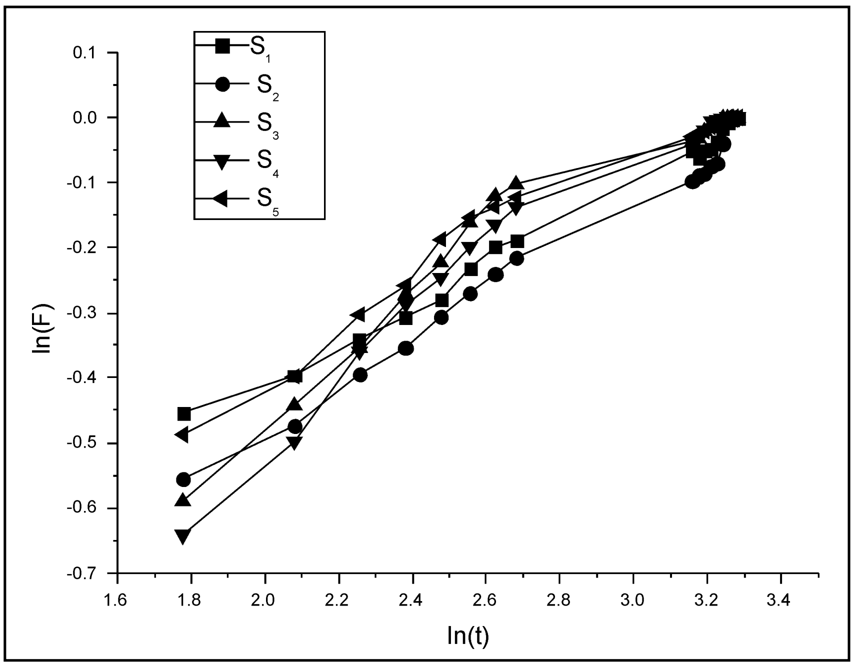

Fig. 5. Plots of ln (F) vs. ln (t) of AAc/NaAlg/SH superabsorbent hydrogel.

3.8 Estimation in water retention properties in sandy soil

Soil modification is vital factor for the water retention in sandy soil by the superabsorbent (SAHs) as well as essential for its applications in agriculture. Figure 6 shows the water retention capability Vs time of different wt % (0.2%, 0.4%, and 0.8%) of the AAc/NaAlg/SH superabsorbent hydrogel with S_3 (9.09 wt %) of sodium humate in sandy soil. Figure 6 shows that content of water remained in sandy soil decreases with the increasing time. In the case of sandy soil containing 0.4 and 0.8 wt% AAc/NaAlg/SH superabsorbent hydrogel 25.12% and 31.26% respectively of the leadoff absorbed water was still reserved for the 30 day. These results indicate AAc/NaAlg/SH can increase the water retention capability of soil, but in case of sandy soil containing 0.2 wt% AAc/NaAlg/SH superabsorbent hydrogel lost all of its absorbed water for 20 day, and sandy soil containing control SAHs was absorbed water in 15 days. In the case of sandy soil containing 0.4 and 0.8 wt% AAc/NaAlg/SH superabsorbent hydrogel 25.12% and 31.26% respectively of the initial absorbed water was still reserved for the 30 days which gives

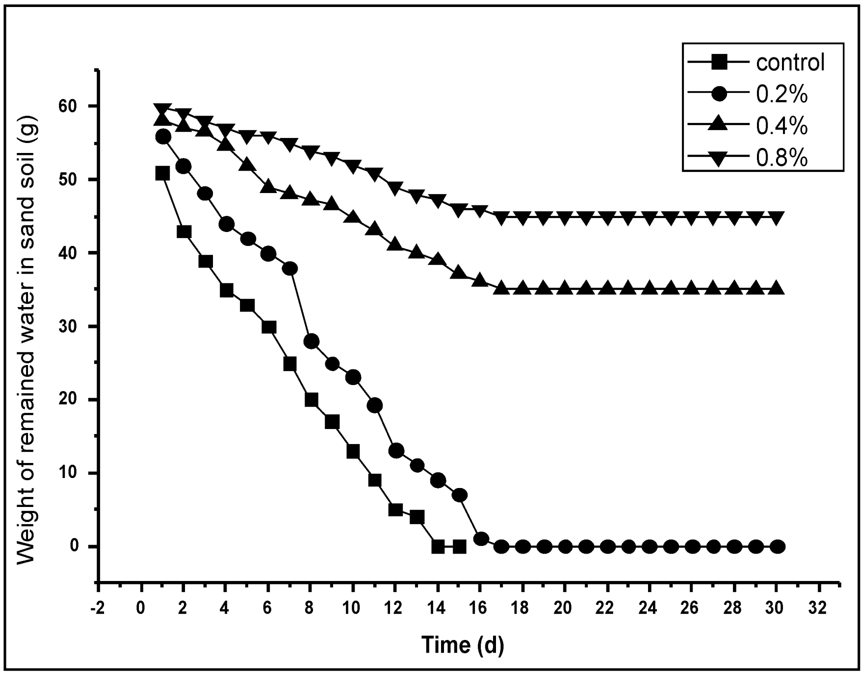

Fig. 6. Estimation in water retention properties of AAc/NaAlg/SH SAHs contain 9.09 wt% sodium humate in soil.

evidence that the unique properties of poly (AAc/NaAlg/SH) superabsorbent hydrogel such as absorption, swelling behavior, biocompability are the main reasons for their wide usage of SAHs [48, 49].

3.9 Effect on plant growth

About 4.5 billion part of earth, which amounts to almost 30% of the total solid land of the world, has been tarnished by human activities. The ecological reinstatement of these domains is a major challenge for mankind since they are the only choice left for growing the quantity of arable earth and producing grub for the ever budding global inhabitants [50]. One of the most important applications of SAHs is for agriculture and horticulture purpose, for effective utilization of water in dry areas [51]. In this way, the testing of poly (AAc/NaAlg/SH) SAHs S_3 9.09wt% sodium humate content for water was also carried out under environmental conditions by growing the plant of corn and white gourd. Figure 7 and 8 shows two sets of pots (set I and set II) growing plant of corn and white gourd. Figure 7 contains two set of pots (set 7, I and set 7, II) of corn and (7, I and 7, II) contain same amount (500 gram) of soil but in set 7, (II) (0.4wt% of S_3 SAHS sample based on weight of total soil) SAHs was also added in research work of Yao and Zhou [52]. In both sets, 7(I&II) 8(I&II) was sustained by adding 400 g water. In Figure 7, (set I) plant did not grow in comparison to Figure 7, (set II). Similarly Figure 8 contain two sets of pots (set I and set II) of white gourd (8, I and 8, II) contain same amount (500 gram) of soil but in set 8 (II) (0.4wt% of S_3 SAHS sample based on weight of total soil) SAHs was also added in research work of Yao

Fig. 7. Growth of corn, SAHs S_3 act as a soil conditioner for set-I ; 0.0%SAH and set-II 0.4 % SAH(based on soil weight)

Fig. 8. Growth of corn, SAHs S_3 act as a soil conditioner for white gourd set-I0.0% SAH and set-II 0.4 % SAH(based on soil weight)

and Zhou [52]. In Figure 8 (set I) plant did not grow in comparison to Figure 8 (set II). Figure 7 and 8 shows growth of corn and white gourd for 45 days. The excess amount of water was utilized by SAHs in Figure 7(set II) and 8 (set II) shows the effect of AAc/NaAlg/SH superabsorbent in seeds of corn and white gourd. Therefore, there is significant affects on the plants growth and their production.

In the effect of plant growth, the water content (400 gm) used in both the case with and without SAHs, The plant of both corn and white gourd set -7 and 8 set II which contain (AAc/NaAlg/SH) SAHs shows the good growth because the excess of water was utilized by the super-absorbent and this water was sufficient for more 45 days, it can be clear from the figure 7 and 8 set (II) that SAHs affects the plant growth of white gourd and corn.

Conclusion

In the present study a series of novel superabsorbent hydrogels based on acrylic acid (AAc), sodium alginate (NaAlg), sodium humate (SH) were prepared, having higher water absorbency (906 gg^{-1}). When percentage of sodium humate content (in wt percentage sample designation (S_1 and S_2) increased from 6.97 to 8.04 wt%, the swelling ratio was nearly doubled i.e. increased 365.95^{-1} to $752.95gg^{-1}$. Further increase in SH concentration to 9.09 wt% it exhibited maximum swelling ratio 906 gg^{-1}. In addition of sodium humate concentration 10.11 to 11 wt% the swelling ratio decreased. Therefore synthesized SAHs with the varying SH content from (6.97 to 9.09 wt %) the swelling exponent found in the range of 0.712 to 0.802, thus suggesting non fickian type diffusion. The swelling mechanism through these synthesized (AAc/NaAlg/SH) SAHs with varying SH content (6.97 to 9.09 wt %) with diffusion coefficients were determined. Water retention capability in sandy soil containing 0.4 and 0.8 wt% of AAc/NaAlg/SH synthesized superabsorbent hydrogel, having 25.12% and 31.26% respectively, of the initial absorbed water was still retained for 30 days. These results indicate AAc/NaAlg/SH can boost the water retention capability of soil. Superabsorbent hydrogels (SAHs) based on natural resources sodium alginate and sodium humate exhibit improved water absorption and water retention capacities and swelling rates; and can be used effectively for growing plants in sandy soil.

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