

# Novel High Capacity Swelling Superabsorbent Composite and Its Potential for Controlled Release of Fertilizers

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**ABSTRACT:** A hydrophilic macromolecular network is prepared by performing graft copolymerization of poly (sodium acrylate) chains onto salep and silica gel. The reaction parameters affecting the water absorbency of the superabsorbent composite were optimized using Taguchi method. FT-IR spectroscopy and Thermo Gravimetric Analysis (TGA) were used for confirming the structure of the final product and morphology of the synthesized superabsorbent composite was examined by SEM. The swelling behavior of optimum superabsorbent composite was measured in various swelling media. In addition, swelling kinetics and on-off switching behavior were investigated. In order to evaluate the controlled release potential of the matrix, it was loaded with  $KNO_3$  and  $NH_4NO_3$  as a model agrochemical and the release kinetics was studied.

**KEY WORDS:** Fertilizer release, Salep, Superabsorbent composite, Taguchi method.

## INTRODUCTION

Superabsorbent Composites (SCs) are reinforced polymer networks that can absorb a large amount of water and have more mechanical strength in compared with superabsorbent hydrogels. Because of their good mechanical properties, inorganic materials such as attapulgite, kaolin, alumina, silica gel, mica and clays are one of the best options for enhancing mechanical properties of SCs. Reinforced structure of SCs makes them more pleasure in agriculture.

Agrochemicals are bioactive agents that improve production of crops both in quality and quantity.

Depending on the method of application and climatic conditions, as much as 90% of applied agrochemicals never reach their target to produce desirable biological responses [1]. Also, contamination of ground water by agrochemicals becomes a great problem. One of the most alarming problems is nitrate leaching and subsequent pollution of ground water [2]. The importance of the problem can be assessed by the fact that nitrates and nitrites are implicated in many fatal physiological disorders such as methemoglobinemia in babies, oral cancer, cancer of the colon and rectum or other gastrointestinal

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cancers [3-5]. A number of approaches for remedy of ground water contamination by nitrate include physical methods such as reverse osmosis and nanofiltration [6], chemical methods such as catalytic removal of nitrate from water [7], abiotic degradation of nitrates using zerovalent iron and electrokinetic process [8]. These methods are, however, considered costly even in advanced and developed countries [9]. Thus, the application of nitrate loaded carrier with a technology based on the controlled release of nitrates by the swelling of a polymeric carrier could prove to be a suitable technology against pollution of ground water [1].

Recently, various polymeric supports or microencapsulated biocides have been introduced in agriculture to limit the undesirable side effects associated with conventional formulations of agrochemicals and related biocides [10]. Biodegradable matrices are especially preferred in order to prevent further environmental pollution created by non-degradable carriers. During these, polysaccharide-based SCs have attracted increasing interest, because of their cheapness, abundance, availability and renewability.

Salep [11-12] is a multicomponent polysaccharide which is firstly used in the synthesis of superabsorbent hydrogels in our lab [11-14]. After observation of excellent properties of these superabsorbent hydrogels, we decided to prepare SCs based on salep. Two forms of salep varieties grown in Iran. The first one has branched or palmate (PTS) while the other one has rounded or unbranched tubers (RTS) [15]. PTS type of salep has more content of glucomannans and was chosen for the present study [13-14].

For application of polymers in controlled release technology, in the present work, we have optimized the synthesis of a hydrophilic macromolecular network based on salep/silica gel-g- poly (sodium acrylate) by Taguchi method. To evaluate their potential as controlled release devices, the  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  were used as models of agrochemicals.

The Taguchi method is a powerful tool for designing of experiments [16]. It provides a simple, efficient and systematic approach to optimize the designs for performance, quality and cost. The parameter design is the key step in the Taguchi method to achieve high quality without increasing cost [17-19]. Statistical method of Taguchi is proposed after identification of important as well as effective factors usually through preliminary studies and experiments.

The number of factors and their levels determine orthogonal array and the number of experiments. After performing the experiments, results are to be analyzing through ANOVA (analysis of variance) to determine the partial contribution of each factor and the optimum conditions. Proposed optimum experiment may be one of the experiments done or a new experiment. Also, one can compare the theoretical predicted set of optimum conditions with the experimental results. The Taguchi method has been successfully applied to several industrial plants. Capability in reducing time and cost of experiments is well documented in comparison with other methods [20-21].

## EXPERIMENTAL SECTION

### Chemicals

The palmate-tuber salep (PTS,  $M_n = 1.17 \times 10^6$  g/mol,  $M_w = 1.64 \times 10^6$  g/mol (high  $M_w$ ), PDI= 1.39, eluent= water, flow rate = 1 mL/min, acquisition interval= 0.43 s from GPC results) was purchased from a supplier in Kordestan, Iran. N,N'-methylene bisacrylamide (MBA, from Merck), ammonium persulfate (APS, from Merck), silica gel (230–400 mesh, from Merck) was used as received. Acrylic acid (AA, from Merck) as a monomer distilled before use. All other chemicals were also analytical grade. Double distilled water was used for hydrogel preparation and swelling measurements. As well, it should be noted that all of the analysis on the optimized hydrogel sample were done on the isolated gel fraction after removing the sol fraction.

### Instrumental analysis

FT-IR spectra of samples in the form of KBr pellets were recorded using an ABB Bomem MB-100 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was performed using polymer laboratories systems at a heating rate of 20 °C/min under nitrogen atmosphere. Conductivity meter (Systronics, Model No. 303, India) was used for study of agrochemical release. The morphology of the dry samples was examined using a scanning electron microscope, SEM, (Philips, XL30) operated at 20 kV after coating the samples with gold film.

### Experimental design

#### Selection of factors and their levels

The reaction variables including salep/silica gel weight ratio, neutralization percentage of AA, MBA,

APS and AA concentration were selected. These are generally important factors in synthesis of our SCs and four levels for each factor was chosen as shown in Table 1.

#### *Selection of orthogonal array and assignment of factors*

Standard Tables known as Orthogonal Arrays (OA) are used for the design of the experiments in the Taguchi method. An OA with 5 factors and 4 levels are shown in Table 2. This OA is particularly designed with the symbol of L16. Each row in the array represents a trial condition with the factor levels, which are indicated by the numbers. The columns correspond to the factors specified in this study and each column contains four levels. Software package Qualitek-4 version 6.3 was used for selection of OA, optimum conditions and contribution of each factor.

#### *Superabsorbent composite preparation*

In general, certain amount of salep (0.50– 1.25 g) and silica gel (1.0- 0.25 g) was added to 30 mL H<sub>2</sub>O at a three-neck reactor equipped with a mechanical stirrer. The reactor was immersed in a thermostated water bath preset at 80°C. After homogenizing the mixture (200 rpm), AA (2.0-5.0 mL) was added to the reaction mixture and stirring for further 20 minutes. Then, MBA (0.03-0.12 g in 5.0 mL H<sub>2</sub>O) and APS (0.03-0.12 g in 5.0 mL H<sub>2</sub>O) were added. After 30 min, gel like material was prepared. Then certain amounts of NaOH (Nut% = 30 - 90) in 40 mL H<sub>2</sub>O used to partially neutralize the carboxylic acid groups. The reaction product kept in ethanol (200 mL) for 24 h to dewater. The completely hardened gel particles were filtered, washed with fresh ethanol (2 × 50 mL) and dried in an oven at 50 °C for 10 h. The final powdered superabsorbent hydrogel was stored away from moisture, heat and light for further experiments.

#### *Water absorbency measurement*

The degree of swelling was determined by gravimetric method. A tea bag (i.e. a 100 mesh nylon screen) containing powder sample (0.1± 0.01 g) with average particle sizes between 40–60 mesh (250-350 μm) was immersed entirely in distilled water (400 mL) and allowed to soak for 60 min at room temperature. The Equilibrium Swelling (ES) capacity was measured twice at room temperature using Eq. (1):

**Table 1: Experimental control factors and their levels.**

Control factor	Level 1	Level 2	Level 3	Level 4
Salep/silica gel (g)	0.5	1.0	2.0	5.0
AA (mL)	2.0	3.0	4.0	5.0
MBA (g)	0.03	0.06	0.09	0.12
APS (g)	0.03	0.06	0.09	0.12
% Nut	30	50	70	90

**Table 2: Experimental layouts of an L16 orthogonal array according to Taguchi's suggestion (the numbers in each column indicate the levels for the specific factors).**

Trial	A	B	C	D	E
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	1	4	4	4	4
5	2	1	2	3	4
6	2	2	1	4	3
7	2	3	4	1	2
8	2	4	3	2	1
9	3	1	3	4	2
10	3	2	4	3	1
11	3	3	1	2	4
12	3	4	2	1	3
13	4	1	4	2	3
14	4	2	3	1	4
15	4	3	1	4	1
16	4	4	2	3	2

$$ES \text{ (g/g)} = \frac{W_2 - W_1}{W_1} \quad (1)$$

where  $W_1$  and  $W_2$  are the weights of dried and swollen gels, respectively.

### Swelling kinetics

For studying the rate of water absorbency, certain amount of hydrogel ( $0.1 \pm 0.01$  g) with average particle sizes between 40-60 meshes ( $250\text{-}350 \mu\text{m}$ ) was poured into a weighed tea bag and immersed in 400 mL distilled water. At consecutive time intervals, the water absorbency of the hydrogel was measured according to the earlier mentioned method.

### The environmental sensitivity

#### pH sensitivity

pH dependency of hydrogel swelling was performed by interaction of certain amounts of the hydrogel samples ( $0.1 \pm 0.01$  g) with solutions (400 mL) in different pHs. The various solutions were adjusted to the desired pH value by addition of diluted HCl or NaOH.

#### Salinity and on-off switching behavior

Swelling capacity of the hydrogel was measured in different concentration of NaCl salt solutions in accordance with section 2.5. The on-off switching was carried out in distilled water and NaCl (0.1 M) solution.

#### Solvent-induced phase transition

The procedures for these experiments are the same as previous section. Here, instead of distilled water, mixture of solvents was used.

### Release study

#### Fertilizer loading

The loading was performed by equilibrating preweighted pieces of the dried gel with the saturated aqueous solution of  $\text{KNO}_3$  or  $\text{NH}_4\text{NO}_3$ . After drying the gel, the loading percent was calculated similar to Eq. (1).

#### Measuring of fertilizer release

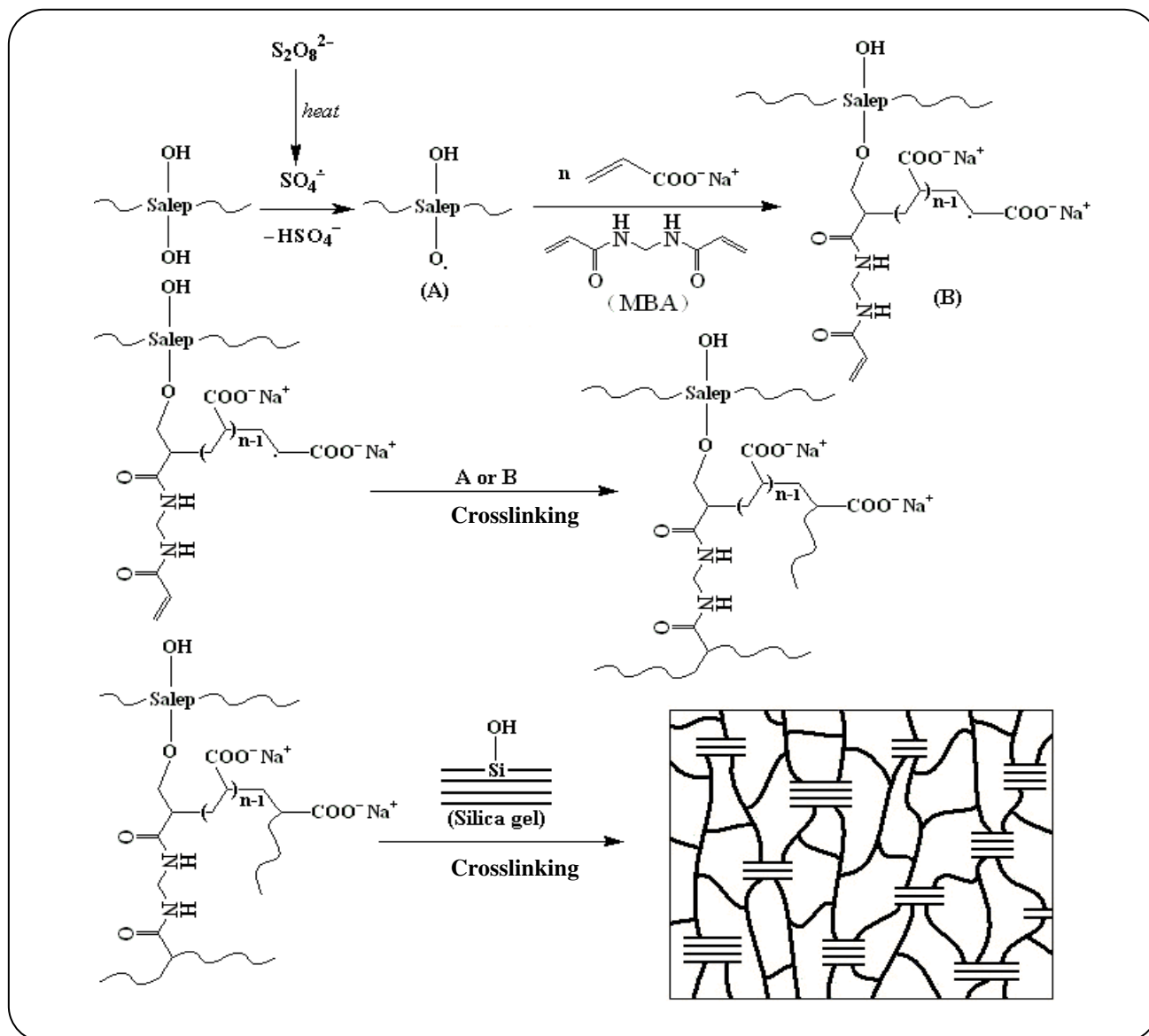
To study the release of  $\text{KNO}_3$  or  $\text{NH}_4\text{NO}_3$ , the loaded gels of known weights were placed in a measured volume (200 mL) of distilled water (release medium) under unstirred condition. The released amount of agrochemicals at different time intervals was determined by measuring the conductivity of the release medium using conductivity meter at desired time intervals.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The superabsorbent composite was prepared by the graft copolymerization of AA onto salep in the presence of a crosslinking agent (MBA), powdery silica gel and APS as an initiator. In the first step, the initiator (APS) decomposes on heating and produces sulfate anion radicals. The anion radical can abstract hydrogen atoms from the hydroxyl groups or anomeric carbons of the salep backbones. This system results in active centers capable of radically initiating the polymerization of AA, leading to a graft copolymer. Due to the presence of crosslinking agents (MBA and silica gel), the copolymer contains a crosslinked structure (Scheme 1). Infrared spectroscopy was carried out to help confirming the chemical structure of the superabsorbent composite. The FT-IR spectra of the initial substrates are shown in Fig. 1. Fig. 1(a) shows the characteristic absorption bands of salep around  $1680 \text{ cm}^{-1}$ , which are attributed to the carbonyl stretching modes of glucomannan. The broad band at  $3200\text{-}3500 \text{ cm}^{-1}$  is due to the stretching absorption of the hydroxyl groups of the polysaccharide. In Fig. 1(b), similar to salep, the peaks of hydroxyl and carboxylate groups of poly (acrylic acid) are presented. Fig. 1(c) presents the spectrum of silica gel. Hydroxyl groups in the layered silicate structure produced absorption bands at  $3200\text{-}3500 \text{ cm}^{-1}$ . Fig. 2(a) represents the FT-IR of physical mixture of salep/ silica gel/ poly (acrylic acid). In Fig. 2(b), a new absorption peak appears at  $1731 \text{ cm}^{-1}$ , can be correlated to the ester groups that formed during the graft copolymerization. The carboxylate groups of the grafted poly (acrylic acid) can react with the hydroxyl groups on the silica gel surface, and this result in ester formation [29].

Thermal analysis is a good method for characterization of crosslinked networks and films TGA traces of silica gel-free salep-g-poly (Na-AA) hydrogel, and salep-g-poly (Na-AA)/silica gel composite are presented in Fig. 3. The improvement of thermal stability in superabsorbent composite may be concluded from this figure. The data are summarized in Table 3. According to this table, values related to the composite such as  $T_{10}$  ( $306.9 \text{ }^\circ\text{C}$ ) and char yield at  $600^\circ\text{C}$  (56.7%) are higher compared to that of the salep-g-poly (Na-AA) hydrogel ( $T_{10} = 207.1 \text{ }^\circ\text{C}$  and char yield at  $600^\circ\text{C}$ : 31.1%). As one can see, the synthesized composite was found to be the more thermally stable samples studied. The silica gel particles in the network may act as heat barriers and



*Scheme 1: Proposed mechanism pathway for synthesis of (salep/ silica gel)-g-P(AA-Na) superabsorbent composite.*

as a consequence enhance the overall thermal stability of the synthesized composite.

Furthermore, the reaction of salep/ silica (in the absence of sodium acrylate) was run under the optimum condition and finally no gel was formed. In another control test, we just polymerized sodium acrylate under the optimum condition in the absence of salep. In this case, a gel is formed but the absorbency is completely different from our hydrogel.

Fig. 4 shows two SEM pictures of SC and compare it with the SEM photograph of salep (Fig. 4 (c)). In spite of

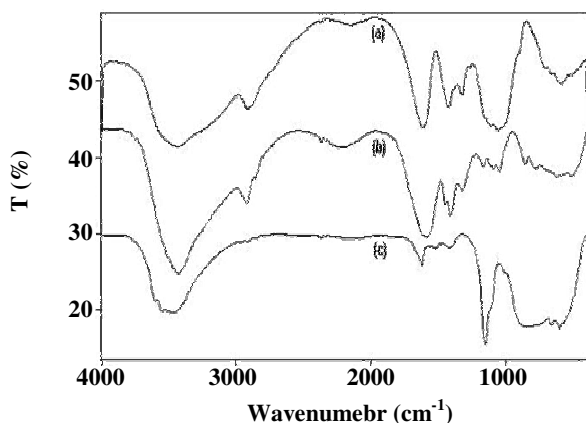
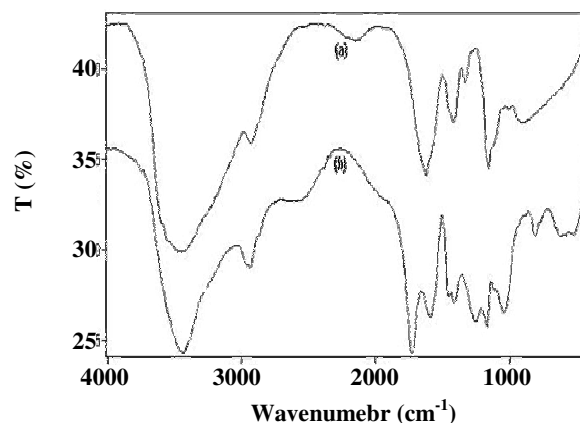
salep, the SC has a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. All of the above analysis confirmed the incorporation of salep, AA and silica gel in the composite structure.

#### **Optimization of water absorbency**

According to previous works [22-23, 29], the variables affecting the ultimate swelling capacity are salep/silica gel weight ratio, AA, MBA, APS concentrations and neutralization percentage of AA. After

**Table 3: Thermal properties of the optimized superabsorbent composite.**

Polymer	Temperature (°C) at weight loss			
	5%	10%	30%	Y <sup>a</sup> (wt%)
Salep-g-p(Na-AA)	143.4	207.1	363.3	31.1
Salep-g-p(Na-AA)/ silica gel composite	239.2	306.9	443.6	56.7

**Fig. 1: FT-IR spectra of (a) salep, (b) P(AA-Na) and (c) silica gel.****Fig. 2: FT-IR spectra of (a) physical mixture of (salep/ silica gel)/ P(AA-Na) and (b) (salep/ silica gel)-g-(PAA-Na) superabsorbent composite.**

identification of effective parameters (factors) and based on past experiences, levels of factors were determined (Table 1). Software Qualitek-4 proposed the L16 OA (5 factors and 4 levels) (Table 2). Methods of performing experiments were given in Table 4. The water absorbency of samples are given in Table 5. Finding the optimum conditions and contribution of each factor was performed by ANOVA, neglecting the interaction between factors. The optimum conditions are shown in Table 6 (salep/silica gel weight ratio= 0.5, AA= 2 mL, MBA= 0.03 g, APS= 0.06 g and neutralization percentage of AA= 50%).

### Swelling kinetics

Fig. 5 represent the swelling capacity of the hydrogel in distilled water at consecutive time intervals. Initially, the rate of water uptake sharply increases and then begins to level off. The equilibrium swelling was achieved after 30 minutes approximately. A power law behavior is obvious from Fig. 5. The data may be well fitted with a Voigt-based equation (Eq. 2) [24]:

$$S_t = S_e (1 - e^{-t/\tau}) \quad (2)$$

where  $S_t$  (g/g) is swelling at time  $t$ ,  $S_e$  is equilibrium swelling (power parameter, g/g);  $t$  is time (min) for swelling, and  $\tau$  (min) stand for the "rate parameter". For calculate the rate parameter, by using the above formula and a little rearrangement, one can be plot  $\ln(1 - (S_t/S_e))$  versus time ( $t$ ). The slope of the straight line fitted (slope =  $-1/\tau$ ) gives the rate parameter. According to Fig. 5 and using Eq. (2), the rate parameters for swelling of the hydrogel in water are found to be 3.5 min. Since the  $\tau$  value is a measure of swelling rate (i.e., the lower the  $\tau$  value, the higher the rate of swelling), it can be used for comparative evaluating the rate of water absorbency of SCs on the condition that the particle size of the comparing samples are the same or, at least, in the same range.

### The environmental sensitivity

#### pH sensitivity

The swelling behavior of the SC was studied at room temperature at various pH values between 1 and 13 (Fig. 6). To prepare the pH media, standard HCl (pH= 1) and NaOH (pH= 13) solutions were diluted with distilled water to reach the desired acidic and basic pHs,

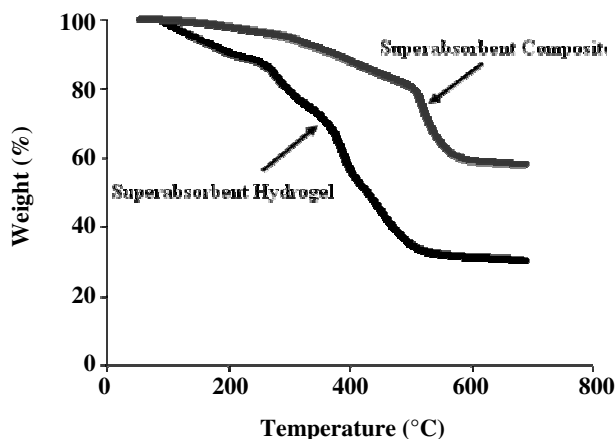


Fig. 3: TGA of superabsorbent composite and superabsorbent hydrogel.

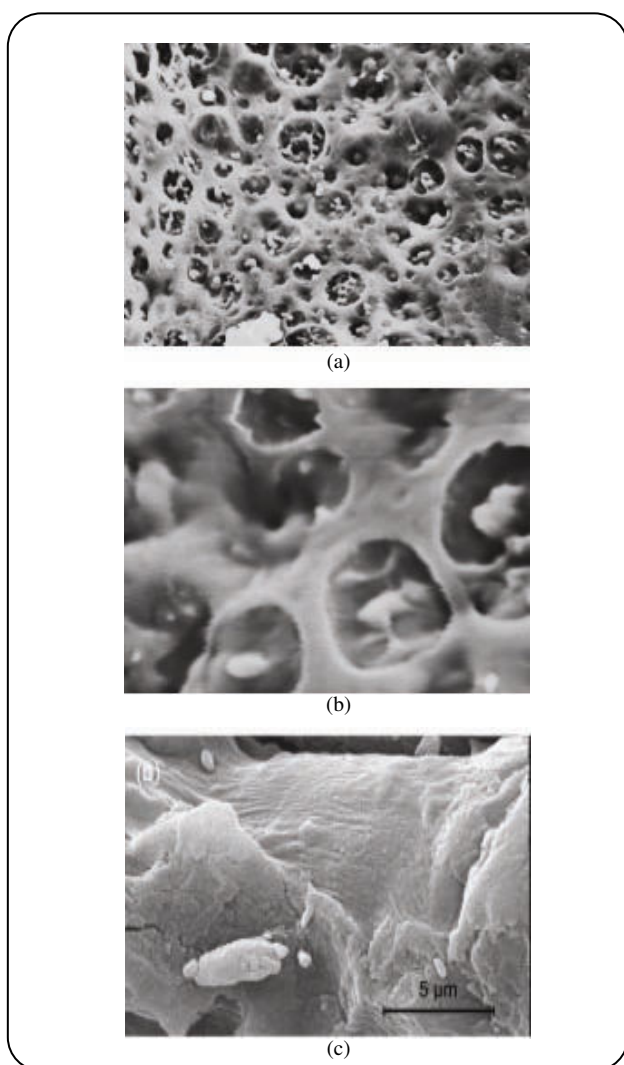


Fig. 4: SEM photographs of (a,b) Salep/ silica gel-g-P(AA-Na) superabsorbent composite synthesized under optimized conditions and (c) Salep.

respectively. The swelling of the hydrogel increased with increasing pH from 1 to 7, but it is decreased in the pH range between 7 and 14. The maximum water absorbency of the hydrogel was achieved at pH 7. At this point, the  $-\text{COO}^-$  groups are at optimum value (regarding to the 50% neutralization percent), resulting in high anion-anion repulsion and high swelling capacity. In acidic solution, ionic strength of the medium is increased and the charge of the  $-\text{COO}^-$  anions shielded by the counter ions so that prevented efficient repulsion. Furthermore, at the pHs far from 7, the ionic strength of the medium is increased and consequently the swelling is decreased.

#### Salinity and on-off switching behavior

The ionic strength of the environment affects the swelling capacity of SCs. The swelling of the superabsorbent composites in saline solutions appreciably decreases comparing to the values measured in deionized water. This phenomenon, commonly observed in the swelling of all ionic hydrogels, is often attributed to a screening effect of the additional cations causing a nonefficient anion-anion electrostatic repulsion. This led to a decreased osmotic pressure (ionic pressure) difference between the hydrogel network and the external solution [25]. Fig. 7 shows the effect of various concentration of NaCl on the water absorbency of the SC. The well-known relationship between swelling and salt solution concentration is stated in Eq. (3) [26]:

$$\text{Swelling} = k [\text{salt}]^{-n} \quad (3)$$

where  $k$  and  $n$  are constants for an individual superabsorbent composite. The  $k$  value is swelling at a high concentration of salt and the value of  $n$  is a measure of the dependency of swelling on salt concentration. Optimum sample was tested to be swelled and deswelled alternatively in distilled water and 0.10 M sodium chloride solution. As shown in Fig. 8, the sorption-desorption behavior is quite repeatable. This repeatable behavior of our hydrogel in the presence of an external stimulus put it in the smart polymers category.

#### Solvent-induced phase transition

In the present study, the swelling changes of the optimized composite sample were examined in various water-solvent systems. The swelling-loss in these mixtures can be easily explained. Anionic groups are

**Table 4: A four-level orthogonal array (L16).**

Trial	Salep/silica gel	AA (mL)	MBA (g)	APS (g)	% Nut
1	0.5	2.0	0.03	0.03	30
2	0.5	3.0	0.06	0.06	50
3	0.5	4.0	0.09	0.09	70
4	0.5	5.0	0.12	0.12	90
5	1.0	2.0	0.06	0.09	90
6	1.0	3.0	0.03	0.12	70
7	1.0	4.0	0.12	0.03	50
8	1.0	5.0	0.09	0.06	30
9	2.0	2.0	0.09	0.12	50
10	2.0	3.0	0.12	0.09	30
11	2.0	4.0	0.03	0.06	90
12	2.0	5.0	0.06	0.03	70
13	5.0	2.0	0.12	0.06	70
14	5.0	3.0	0.09	0.03	90
15	5.0	4.0	0.06	0.12	30
16	5.0	5.0	0.03	0.09	50

**Table 5: Experimental results for swelling of superabsorbents for 16 trials.**

Trial	1	2	3	4	5	6	7	8
ES (g/g)	2180	1364	580	332	537	311	376	359
Trial	9	10	11	12	13	14	15	16
ES (g/g)	430	367	2030	512	433	622	432	1376

**Table 6: Optimum conditions suggested by Taguchi method.**

Factor	Level description	Optimum conditions
Salep/silica gel	1	0.5
AA (mL)	1	2.0
MBA (g)	1	0.03
APS (g)	2	0.06
% Nut	2	50

simply solvated by water molecules. However, it is widely restricted in the organic solvent-water systems. In comparison with water, the organic solvent molecules (for example ethanol and acetone) can not solvate the anionic groups. As a consequence, the swelling capacities are considerably decreased. It can also be concluded from Fig. 9 that in a fixed ratio of solvent-water (e.g., a 30:70 w/w solvent-water mixture), the swelling in ethanol is more than acetone. This can be explained using the *Hildebrand* Eq. (4) [27]:

$$\Delta H_m / (V\Phi_1\Phi_2) = (\delta_1 - \delta_2)^2 \quad (4)$$



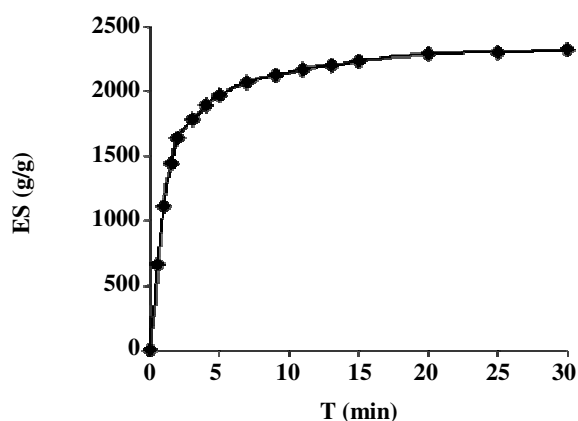


Fig. 5: The swelling kinetics of optimized sample in distilled water.

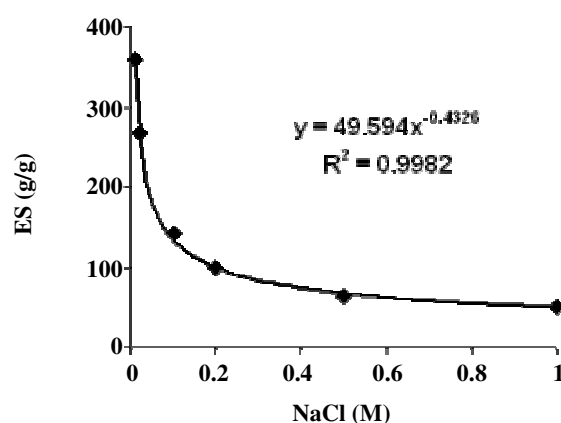


Fig. 7: The swelling capacity variation of (salep/ silica gel)-g-P(AA-Na) in various concentrations of NaCl solution.

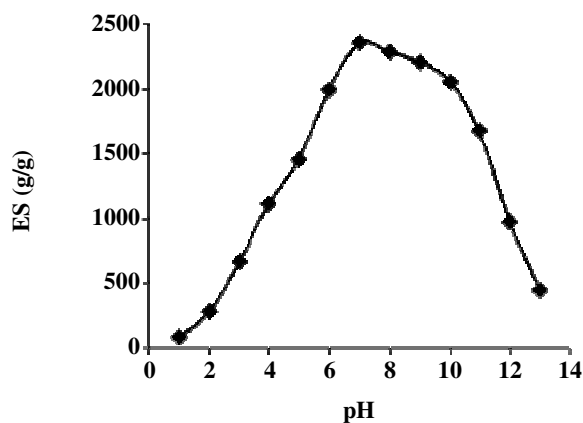


Fig. 6: Swelling dependency of (salep/ silica gel)-g-P(AA-Na) on pH.

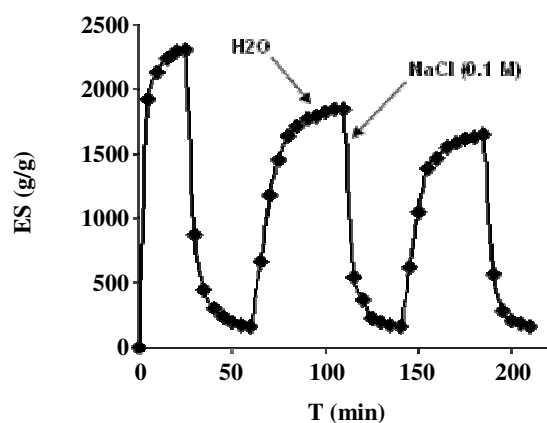


Fig. 8: On-off switching behavior of the optimized superabsorbent composite: swelling in distilled water and deswelling in NaCl (0.1 M).

Where  $\Delta H_m$  is the enthalpy change on mixing of a polymer and a solvent,  $\Phi_1$  and  $\Phi_2$  are the volume fractions for the solvent and the polymer,  $V$  is the whole volume of the solution, and  $\delta_1$  and  $\delta_2$  are the solubility parameters for the solvent and the polymer, respectively. This equation clearly indicates that to dissolve a polymer in a solvent, the  $\delta$  values must be close to each other. As a consequence, to predict the solubility of a polymer, the  $\delta$  values should be calculated. As swelling capacity of the synthesized hydrogel in water is maximum, the  $\delta$  value of water ( $23.4 \text{ (cal/cm}^3)^{1/2}$ ) can be regarded as the solubility parameter of it. The solubility parameter for solvent-water mixtures ( $\delta_{mix}$ ) can be calculated using following Eq. (5) [28]:

$$\delta_{mix} = \delta_1\Phi_1 + \delta_2\Phi_2 \quad (5)$$

Where  $\Phi_1$  and  $\Phi_2$  are the volume fraction, and  $\delta_1$  and  $\delta_2$  are the solubility parameters of the two solvents. According to data summarized in Table 7, with increasing of  $\delta_{mix}$  values toward 23.4, the hydrogel can be highly swollen as in pure water. In other words, the swelling capacity of the hydrogel in the solvent-water mixture will be close to that in pure water if  $\delta_{mix}$  is close to  $\delta_{water}$ .

#### Release study

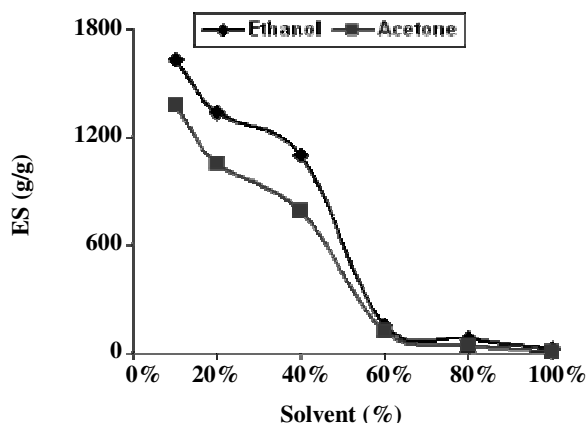
An important aspect of SCs is to study the release of an active agent from swellable polymeric matrix. The release kinetic of a loaded SC is closely related to its structure. It has been already established that a highly swelling SC can trap and release a greater amount of target compound. To examine the ability of our system in agrochemical release, liberation of  $\text{NH}_4\text{NO}_3$  and  $\text{KNO}_3$

**Table 7: The solvent–water concentrations in which the superabsorbent composite exhibits volume- phase transition.**

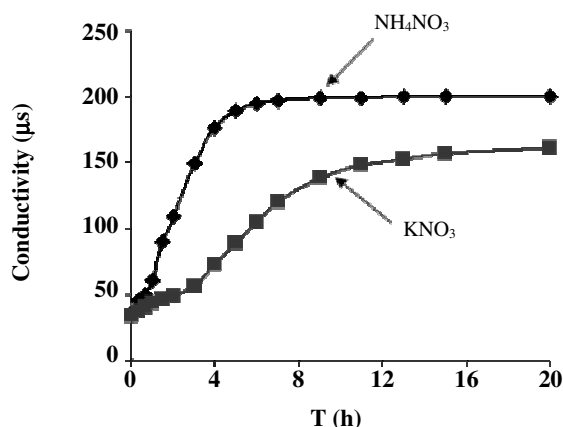
Solvent	$\delta$ (or $\delta_{\text{mix}}$ ) <sup>a</sup>	ES (g/g)
Water	23.4	2355
Ethanol/ water (30:70)	20.2	1245
Ethanol	12.7	22
Acetone/ water (30:70)	19.35	910
Acetone	9.9	11

**Table 8: Data for agrochemical controlled release.**

Agrochemical	Load (g) <sup>a</sup>	Release (%)	Final released amount (g) <sup>a</sup>
KNO <sub>3</sub>	16.5	85.5	14.1
NH <sub>4</sub> NO <sub>3</sub>	19.7	88	17.3



**Fig. 9: Effect of organic solvents (ethanol and acetone) on the water absorbency of superabsorbent composite.**



**Fig. 10: Controlled release of agrochemicals in optimized superabsorbent composite.**

salts was studied. The release of solute from loaded gel involves the discharge of solute from polymer matrix via diffusion, as governed by Fick's law. As one can see (Fig. 10), our SC releases agrochemicals during several hours. The delivery of ammonium nitrate was almost completed (200  $\mu\text{s}$ ) after 8 hours and the delivery of potassium nitrate was completed (161  $\mu\text{s}$ ) after 20 hours. According to Table 8, our SC releases agrochemicals about 85-90%. It was related to incomplete reversible behavior of hydrogels on swelling/deswelling in various media [13, 14]. Also, the final released amount of SC (Table 8) indicates high potential capacity of entitled SC as a fertilizer delivery system.

## CONCLUSIONS

Salep/ silica gel in conjugation with cross-linked PAA forms a novel type of highly swelling SC which imbibe at a range of 300–2400 g/g of dry gel. Factors (salep/silica gel weight ratio, AA, MBA, APS concentration and neutralization percent of AA) affecting the swelling capacity of SC, were optimized with valuable Taguchi method. The composite formation was confirmed by Fourier transform infrared spectroscopy (FT-IR), SEM photographs and TGA analysis. As well, the swelling behavior of the SC was investigated on pH, ionic strength and composition of the immersion medium. The agrochemical release results clearly showed great potentiality of our system to act as a carrier for controlled release of agrochemicals.

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