**Superabsorbent hydrogel made of NaAlg-g-poly(AA-co-AAm) and rice husk ash:
synthesis, characterization, and swelling kinetic studies**

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Abstract

The sodium alginate-g-poly(acrylic acid-co-acrylamide)/rice husk ash (NaAlg-g-P(AA-co-AAm)/RHA) superabsorbent nanocomposite was synthesized by the free-radical graft copolymerization of alginate (NaAlg), acrylic acid (AA), acrylamide (AAm), and RHA in aqueous solution. FTIR spectra revealed that the monomers were grafted onto NaAlg chains, and the nanocomposite was formed successfully. Incorporation of RHA into hydrogel matrix formed porous interlinked channels within hydrogel network. Superabsorbent nanocomposite showed greater equilibrium swelling capacity (1070 g/g) compared with neat hydrogel (830 g/g). Moreover, water transport mechanism of all hydrogels was non-Fickian diffusion type. Rheological measurements confirmed effective role of RHA in improving gel strength of superabsorbent nanocomposite. The influence of various factors, such as different loads (0.3, 0.6, 0.9 psi), solution pH, saline solution, and temperature on the swelling behavior of hydrogels was also assessed. Superabsorbent nanocomposite exhibited good pH-dependent swelling reversibility and high water retention capability, making it more efficient water-saving material for agricultural and horticultural applications.

Keywords: Superabsorbent nanocomposite; Sodium alginate; Swelling kinetic; Rice husk ash; Water retention.

1. Introduction

Superabsorbent hydrogels (SHs) are water insoluble three-dimensional crosslinked polymer network that can absorb and retain great amount of aqueous solutions or biological fluids within own structure even under certain pressure (Bao, Ma & Li, 2011; Tally & Atassi, 2015). The good swelling and water retention capacity as well as desirable biodegradability of SHs make them able to be applied in various fields such as agriculture (Curcio & Picci, 2008), hygiene products (Kosemund, Schlatter, Ochsenhirt, Krause, Marsman & Erasala, 2009), wastewater treatment (Kaşgöz, Durmuş & Kaşgöz, 2008), tissue engineering (Wang, Strand, Du & Vårum, 2010), and drug delivery systems (Merino, Martín, Kostarelos, Prato & Vázquez, 2015). Mainly, SHs are synthesized by crosslinking reactions of synthetic or natural-based polymers. The high production cost as well as serious environmental effects of synthetic-based hydrogels have caused their broad utilization to be severely restricted (Rodrigues, Fajardo, Pereira, Ricardo, Feitosa & Muniz, 2012; Wang & Wang, 2010). In contrast, natural polymers have received great attention as the candidate to fabricate superabsorbent due to their advantages such as abundance, biodegradability, and non-toxicity (Roy, Saha, Kitano & Saha, 2012). Sodium alginate (NaAlg), a non-toxic natural polysaccharide derived from brown algae, is composed of (1-4)-linked β -D-mannuronic acid units and α -L-guluronic acid units with various proportions which can be arranged into different sequences in polymeric backbone (Pereira, Carvalho, Vaz, Gil, Mendes & Bártolo, 2013). The unique properties of NaAlg such as nontoxicity, biocompatibility, biodegradability, and relatively low cost have made it the most interesting material in pharmaceutical, biomedical, and agricultural applications (Işıklan, Kurşun & İnal, 2010). Despite these advantages, alginate-based hydrogels suffer from poor mechanical strength. Graft copolymerization of hydrophilic vinyl monomers such as acrylic acid (AA) and acrylamide (AAm) onto alginate chains is one of the most promising methods to improve the

76 mechanical properties of the alginate-based hydrogel networks (Pourjavadi, Amini-Fazl &
77 Hosseinzadeh, 2005; Yadav, Mishra, Sand & Behari, 2011). In addition, incorporation of low
78 cost inorganic nanofillers into hydrogel matrix is another strategy, that can not only reduce
79 final production cost but also can improve mechanical, thermal, and barrier properties, as
80 well as swelling and adsorption characteristics of the pure hydrogels. These novel or
81 improved features of superabsorbent nanocomposites mainly result from the strong interfacial
82 interactions between the nanofillers and polymeric matrix (Hubbe, Rojas, Lucia & Sain,
83 2008; Zhou, Fu, Zhang & Zhan, 2013).

84 Silica (SiO_2) is a basic raw material that is broadly used in technological applications as
85 thixotropic agent, thermal insulator, and polymer filler (Liou, 2004). Compared to the
86 conventional approaches to silica production, incineration of rice husk (RH), an agro-
87 industrial by-product of rice milling, is a more facile and cost effective pathway yielding
88 silica nanoparticles with high purity and high surface area (Chandrasekhar, Pramada &
89 Praveen, 2005). Incorporation of silica nanoparticles into hydrogel matrix can enhance
90 swelling capacity of SHs, which is an essential factor for their exploitation in agricultural and
91 horticultural applications. Also, hydrophilicity effect of the introduced silica nanoparticles
92 can improve water retention capability of the hydrogel composite. Moreover, hydrogen-
93 bonding interactions among functional groups of the hydrogel and hydroxyl groups of silica
94 nanoparticles can build additional physical crosslinkages within hydrogel network, inducing
95 an improvement in mechanical strength of hydrogel sample (Cândido et al., 2013; Olad,
96 Gharekhani, Mirmohseni & Bybordi). Additionally, silica, an essential micronutrient in
97 plants, can be easily absorbed by root tip of plants after degradation of hydrogels in soil
98 medium. It greatly affects the growth quality of plants because its deficiency causes
99 imbalances in other nutrients. Silica also effectively improves the leaf and stalk erectness in
100 plants, enhances the resistance of plants against pests, diseases, and freezing, and alleviates

transpiration losses in plants (Suriyaprabha, Karunakaran, Yuvakkumar, Prabu, Rajendran & Kannan, 2012; Yuvakkumar, Elango, Rajendran, Kannan & Prabu, 2011). These good characteristics enable silica nanoparticles to be used as filler in various hydrogel matrixes. Jean de and coworkers (Cândido, Leitão, Ricardo, Feitosa, Muniz & Rodrigues, 2012), synthesized hydrogel composites based on the poly(acrylamide-co-acrylate)/rice husk ash. They showed that the hydrogel composite has salt and pH sensitive behavior. Moreover, the hydrogel composite had lower swelling capacity loss during swelling/drying cycles compared to the neat hydrogel. The effect of various rice husk ash (RHA) samples, obtained at different temperature conditions, on the swelling behavior of the hydrogel composites was also studied in another work (Cândido et al., 2013).

The aim of this work was to develop NaAlg-graft-poly(AA-co-AAm)/RHA (SH/RHA) superabsorbent nanocomposite and evaluate its possible use in agricultural and horticultural applications. To reduce the production cost and also to improve or even create novel properties in the synthesized hydrogel, RHA, a cost effective silica source, was adopted as filler. The effects of the incorporation of silica nanoparticles into hydrogel network on the water absorption capacity, swelling kinetic, water absorbency under load (AUL), mechanical strength, and reswelling capability, as well as water retention behavior at constant temperature were evaluated. Besides, the pH-dependent swelling reversibility and deswelling kinetic in different saline solutions were investigated.

2. Experimental

2.1. Materials

Sodium alginate (NaAlg, chemical grade, viscosity of 5.0–40.0 cps for a 1% solution at 25 °C) was purchased from Sigma-Aldrich (USA). Acrylamide (AAm), acrylic acid (AA), N,N'-methylene bisacrylamide (MBA), ammonium persulfate (APS), sodium chloride, calcium

chloride, and ferric chloride hexahydrate were purchased from Merck (Germany), and were used as received. Ethanol was brought from Mojallali reagent chemicals Co. (Iran, Tabriz). The rice husk was procured from a supplier in Rasht, Iran. All reactants possessed analytical grade and distilled water was used throughout the work.

2.2. Nano-silica preparation

Initially, RHs were washed and rinsed off thoroughly with distilled water to remove adhered soil and dust. Thereafter, to remove metal impurities, acid leaching process was performed first by reflux boiling in 3% (v/v) HCl aqueous solution, and then by reflux boiling in 10% (v/v) H₂SO₄ aqueous solution at a ratio of 50 g RH/L under stirring in a glass round-bottomed flask at 100 °C for 2 h. After each step, acid leached RHs were filtered, washed with distilled water several times, and dried in a vacuum oven at 100 °C for 24 h. Finally, the dried RHs were burned in a furnace at 900 °C for 5 h to achieve white ash, containing silica nanoparticles.

2.3. Synthesis of superabsorbent nanocomposite (SH/RHA)

A pre-determined amount of NaAlg powder (1 g) was gradually dissolved in 30 mL distilled water in a 250-mL four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a nitrogen line. Then, a certain amount of RHA (15 wt%, with respect to NaAlg) was poured into a sticky solution of NaAlg under continuous stirring. The prepared solution was heated slowly to 60 °C, and after being purged with nitrogen to remove dissolved oxygen, a proper amount of APS (5 wt%, with respect to NaAlg) was introduced into the solution to generate alginate radicals. Ten minutes later, the mixture solution of 70% neutralized AA (7 mL), AAm (2 g), and MBA (0.048 wt%, with respect to monomers) was charged into the flask dropwise. Thereafter, the temperature was raised to 70 °C and kept at

151 this condition for 3 h to complete the polymerization. The obtained product was washed with
152 fresh ethanol to remove unreacted species, and then extracted gel was dried in a vacuum oven
153 at 70 °C for 24 h. The dried gels were milled and sifted through 40–80 mesh sieves for
154 further experiments. For comparison, a control hydrogel sample (NaAlg-g-poly(AA-co-AAm
155 (SH)), without adding RHA, was also prepared similar to the above described method.

157 **2.4. Characterizations**

158 The chemical structure of NaAlg, RHA, SH, and SH/RHA superabsorbent nanocomposite
159 was characterized using a Bruker Tensor 27 FTIR spectrophotometer with KBr pellets
160 operating in the wavenumber range of 400–4000 cm⁻¹. To evaluate the thermal stability of the
161 prepared hydrogels, thermogravimetric analysis (TGA) was performed using a thermal
162 gravimetric analyzer (TGA/DSC-1, Mettler Toledo) at temperature range of 25 to 750 °C
163 with a heating rate of 10 °C/min under nitrogen atmosphere. The surface morphology of
164 RHA, SH, and SH/RHA superabsorbent nanocomposite was investigated through a field
165 emission scanning electron microscope (FE-SEM) system (MIRA3 FEG-SEM, Tescan,
166 Czech) coupled with an Energy Dispersive X-ray analyzer (EDX) (Tescan, Czech, model
167 SAMX). Further studies on the morphology of SH/RHA superabsorbent nanocomposite were
168 performed through transmission electron microscope (TEM) analysis, which was
169 accomplished using a LEO 906 (Zeiss, Germany) TEM instrument.

171 **2.5. Evaluation on properties**

172 **2.5.1. Measurement of swelling kinetic**

173 To study swelling kinetic of the hydrogels, a pre-weighted dry hydrogel sample (W_d) was
174 immersed entirely in 100 mL distilled water and allowed to soak at room temperature. At
175 certain time intervals, the swollen hydrogel sample was taken out from the aqueous solution,

and after filtering and draining by a 100–mesh screen, it was weighed accurately (W_t). These measurement processes were continued until swollen hydrogel sample reached to a constant weight (equilibrium swelling weight (W_{eq})). The swelling capacity (Q_t) and equilibrium swelling capacity (Q_{eq}) were calculated using the following equations:

$$Q_t (g \cdot g^{-1}) = \frac{W_t - W_d}{W_d} \quad (1)$$

$$Q_{eq} (g \cdot g^{-1}) = \frac{W_{eq} - W_d}{W_d} \quad (2)$$

2.5.2. Measurement of water absorbency under load (AUL)

Water absorption capacity of the hydrogel samples in 0.9 wt% NaCl aqueous solution under different loads was measured as follows. First, a porous sintered glass filter plate ($d = 80$ mm, $h = 7$ mm) was placed in a petri dish ($d = 118$ mm, $h = 12$ mm), and then a pre-weighted dry hydrogel sample (0.1 g, 40-80 mesh) was put uniformly onto the wire cloth (100 mesh) located on the surface of sintered glass filter plate. Then, a glass cylinder ($d = 60$ mm, $h = 50$ mm) was placed onto the wire cloth so that it could surround hydrogel particles. Thereafter, a cylindrical solid load (Teflon, $d = 60$ mm, variable height) was passed through the glass cylinder and put on the dry hydrogel particles to exert different loads (0.3, 0.6, and 0.9 psi). Afterwards, 0.9 wt% NaCl aqueous solution was poured into the petri dish until the solution level reached to the height of sintered glass filter plate. To avoid any surface evaporation or possible change in saline solution concentration, petri dish and its other parts were covered properly. At given time intervals, the swollen hydrogel samples were weighed accurately, and then AUL was determined using the similar method as described previously.

2.5.3. Rheological analysis

The rheological properties of SH and SH/RHA hydrogel samples were investigated using a Anton Paar rheometer (MCR301, Germany) at 25 °C equipped with a plate-plate geometry (plates diameter of 25 mm and gap of 1 mm). A strain sweep test was first conducted on the hydrogel samples at a constant frequency of $\omega = 10$ Hz to determine the linear viscoelastic (LVE) region, where storage modulus (G') and loss modulus (G'') are independent of the strain amplitude. Then, the frequency sweep tests were done at a constant strain ($\gamma = 0.5$) to study viscoelastic behavior of the hydrogel samples in the LVE region over a wide range of angular frequencies (0.1 to 100 Hz).

2.5.4. Deswelling kinetics in saline solutions

To study deswelling kinetic of the hydrogel samples, pre-determined amount of dried hydrogel sample was first soaked in distilled water, and allowed to reach own equilibrium swelling capacity. Thereafter, the swollen hydrogel sample was removed from the aqueous solution, and after removing excess surface water with filter paper, it was immersed in 0.1 M saline solutions of NaCl, CaCl₂, and FeCl₃. At given time intervals, hydrogel sample was separated from saline solution by a filter paper, and then it was weighed to determine the swelling capacity according to the previously described method.

2.5.5. Swelling behavior in pH solutions

To asses swelling behavior of the hydrogel samples in various pHs, different pH solutions ranging from 2 to 12 were prepared by diluting aqueous solutions of NaOH (0.1 M) and HCl (0.1 M). The equilibrium swelling capacity of the hydrogel samples at each pH value was calculated by the method mentioned earlier (see section 2.5.1). Also, the pH-dependent swelling reversibility of hydrogels was evaluated in basic (pH = 8) and acidic (pH = 2)

aqueous solutions. For this purpose, the pre-weighted dry hydrogel sample was first immersed in basic ($\text{pH} = 8$) aqueous solution, and allowed to swell at room temperature. The swollen hydrogel sample was withdrawn from the basic solution at different time intervals and after excess surface water was wiped off with filter paper, it was weighed to determine swelling capacity. These measurements were continued until swollen hydrogel sample reached to own equilibrium swelling capacity. Thereafter, the swollen hydrogel sample equilibrated in the basic solution was transferred into acidic ($\text{pH} = 2$) aqueous solution. The swelling capacity measurements were the same as the procedure performed in basic solution. The swelling/deswelling cycle (swelling in basic solution and deswelling in acidic solution) was carried out for three times in which the time interval between two consecutive cycles was 30 min.

2.5.6. Evaluation of reswelling capability

Reswelling capability of the hydrogel samples was examined through the measurement of their equilibrium swelling capacity loss during sequential swelling/drying cycles. For this purpose, pre-weighted dry hydrogel sample was first immersed in excess distilled water and allowed to swell until it reached to own equilibrium swelling capacity. Then, the swollen hydrogel sample was removed from the aqueous solution and after weighing, it was dried to a constant weight in a vacuum oven at $80\text{ }^{\circ}\text{C}$. The dried hydrogel sample was soaked again in distilled water to determine its equilibrium swelling capacity. These swelling/drying cycles were continued for five times, and finally equilibrium swelling capacity losses were measured for each hydrogel sample.

2.5.7. Water retention behavior

To investigate the water retention behavior of hydrogel samples under constant temperature, the pre-weighted swollen hydrogel sample (W_{eq}) equilibrated in distilled water was placed in a vacuum oven at 80 °C. The swollen hydrogel was weighed every 1 h (W_t), and then the percentage water retention (WR%) was calculated using the equation 3.

$$WR\% = \frac{W_t - W_d}{W_{eq} - W_d} \quad (3)$$

Where W_d is the dry weight of hydrogel sample before swelling.

3. Results and discussion

3.1. Synthesis mechanism of superabsorbent nanocomposite

Graft copolymerization of AA and AAm monomers onto the backbone of alginate chains was performed by free radical polymerization technique in an aqueous medium containing an initiator (APS), a crosslinking agent (MBA), and filler (RHA) (Scheme 1). First, the sulfate anion radicals produced by thermal dissociation of APS molecules, abstract hydrogen atoms from the functional groups of NaAlg chains to form alkoxy radicals. These macro radicals act as free radical donor centers to the nearest monomers, resulting in chain initiation process. As the grafted chains grow, free radicals on the graft copolymers can be coupled together (self-crosslinking) or with the end vinyl groups of MBA molecules, causing formation of crosslinked structure. At the same time, RHA which may act as physical crosslinking agent builds the final hydrogel network (Cândido, Leitão, Ricardo, Feitosa, Muniz & Rodrigues, 2012; Rashidzadeh, Olad, Salari & Reyhanitabar, 2014).

3.2. FTIR spectra analysis

FTIR spectra of NaAlg, RHA, SH, and SH/RHA have been depicted in Fig. 1(a). The FTIR spectrum of NaAlg shows absorption bands at 892 cm^{-1} and 943 cm^{-1} , which are related to the stretching vibration of Na–O bonds. The peaks at 1031 cm^{-1} and 1095 cm^{-1} are assigned to the stretching vibration of alcoholic (–C–OH) groups of polysaccharide structure of NaAlg. Also, the absorption bands at 1651 cm^{-1} and 1415 cm^{-1} are corresponded to asymmetric and symmetric stretching vibrations of carboxylate (COO^-) groups, respectively. Moreover, the broad peak observed at 3314 cm^{-1} is due to the hydroxyl (O–H) stretching vibration mode (Samanta & Ray, 2014; Shi, Wang, Kang & Wang, 2012; Yang, Ma, Guo & Zhang, 2014). As shown in FTIR spectrum of RHA, the peaks appeared at 469 cm^{-1} , 802 cm^{-1} , and 1101 cm^{-1} are attributed to the bending vibration and symmetric and asymmetric stretching vibrations of Si–O–Si bonds, respectively (Cândido et al., 2013). Also, the bands at 1651 cm^{-1} and 3619 cm^{-1} are ascribed to O–H stretching vibrations of silanol groups (Chandrasekhar, Pramada & Praveen, 2005). For SH and SH/RHA, the absorption peaks emerged respectively at 1649 cm^{-1} and 1672 cm^{-1} are related to the overlapped stretching vibration of carboxamide and bending vibration of N–H in amide group. Also, the asymmetric stretching modes of carboxylate anions in FTIR spectra of SH and SH/RHA appeared at 1545 cm^{-1} and 1556 cm^{-1} , respectively, while their symmetric stretching modes were found at 1461 cm^{-1} , 1417 cm^{-1} , and 1458 cm^{-1} , and 1390 cm^{-1} wavenumbers, respectively. Moreover, the stretching vibration modes of C–N group in FTIR spectra of SH and SH/RHA were observed at 1358 cm^{-1} and 1328 cm^{-1} , respectively. Additionally, overlapped absorption bands of O–H and N–H groups are identified by broad and intense peaks between 3400 cm^{-1} and 3600 cm^{-1} (Marandi, Mahdavinia & Ghafary, 2011; Yang, Ma, Guo & Zhang, 2014). According to the FTIR spectra of SH and SH/RHA, it can be obviously perceived that the characteristic absorption bands of alcoholic groups of NaAlg chains have been weakened after reaction. Also,

comparing with the FTIR spectrum of NaAlg, the strong peak at 3314 cm^{-1} for hydroxyl stretching vibration has shifted to 3444 cm^{-1} and 3619 cm^{-1} in the FTIR spectra of SH and SH/RHA, respectively. Moreover, characteristic absorption bands of Na–O group in NaAlg have been disappeared in the FTIR spectra of SH and SH/RHA. These results imply that hydroxyl groups of NaAlg chains have participated in grafting reaction with acrylate-based monomers. In comparison with FTIR spectrum of RHA, SH/RHA showed all characteristic peaks associated with RHA with variations in intensity and wavenumbers, confirming the nanocomposite formation. However, the intensity of the characteristic absorption band of Si–O–Si groups of RHA (1101 cm^{-1}) has been decreased in FTIR spectrum of SH/RHA. Also, characteristic peak of silanol groups of RHA (3619 cm^{-1}) has been appeared with higher intensity in FTIR spectrum of SH/RHA. The observed phenomenons can be interpreted as follows. The strong hydrogen-bonding interactions among functional groups of hydrogel and oxygen atoms of Si–O–Si groups of incorporated RHA diminished –Si–O– bond strength. Therefore, the weak stretching vibration of Si–O–Si bonds induced a peak with lower intensity in FTIR spectrum of SH/RHA. In the case of silanol groups of RHA (3619 cm^{-1}), in spite of strong hydrogen-bonding interactions among them and functional groups of hydrogel, overlapping more intense absorption bands of O–H and N–H groups of hydrogel with their absorption band made a relatively sharp peak in FTIR spectrum of SH/RHA. Taken together, it can be concluded that graft copolymerization among NaAlg, AA, and AAm as well as incorporation of RHA into SH matrix has been performed successfully.

3.3. Thermogravimetric analysis

Fig. 1(b) and (c) show the TGA and differential TGA (DTG) curves of SH and SH/RHA hydrogel nanocomposite sample (with 15 wt% RHA), respectively. As can be seen from Fig.

1(b) and (c), both hydrogel samples exhibit four-stage decomposition process. The first stage between temperature 50 °C and 110 °C accompanied by a minor weight loss is related to the water evaporation of samples. In continue, dehydration of saccharide rings and breaking of C–O–C bonds in the NaAlg chains were performed within the temperature range of 110–248 °C, which is identified as second degradation stage (Hua & Wang, 2009). The maximum decomposition rate at first and second degradation stages for SH and SH/RHA occurred at 90 °C, 239 °C, and 98 °C and 243 °C, respectively. These results imply that SH/RHA possesses greater thermal stability and higher moisture preserving capability compared with the neat hydrogel sample. The sharp weight loss of SH and SH/RHA respectively within temperature range of 333–402 °C and 340–412 °C is due to the thermal decomposition of the carboxyl and amide side groups of the copolymers, which is associated with the emission of ammonia and other gases (Su, Zhang, Xu, Wang, Song & Wang, 2008; Zhang & Wang, 2007). The maximum degradation temperature ($T_{\max}$) for SH and SH/RHA samples was found to be 440 °C and 448 °C, respectively. The largest weight loss at these temperatures can be attributed to the formation of anhydride by association of the two neighboring carboxylic groups on the polymer chains and elimination of water molecule, breakage of copolymer chains, and destruction of the crosslinked network structure (Huang, Lu & Xiao, 2007). The SH/RHA sample demonstrated a lower weight loss within the temperature range of 30–742 °C compared with the SH sample. Also, the char yield of SH and SH/RHA at 742 °C was about 40.54% and 49.52%, respectively. These results indicated that incorporation of RHA into hydrogel matrix can significantly improve thermal stability of the hydrogel sample. These findings were in good agreement with the results obtained by other researchers (Cândido et al., 2013).

Fig. 1. FTIR spectra of NaAlg, SH, SH/RHA, RHA (a), TGA (b), and DTG curves (c) of SH, and SH/RHA samples.

3.4. Morphological analysis

Morphology of the prepared materials was studied using TEM and FE-SEM techniques (Fig. 2). Fig. 2(a) and (b) show SEM images of RHA. According to Fig. 2(a), RHA shows almost homogeneous distribution of silica particles with dimensions lower than 100 nm. From Fig. 2(b) it can be inferred that RHA possesses more pores (depicted by arrow signs), which have been distributed within the ash. Therefore, the obtained silica is a highly porous material with a large internal surface area. SEM images of SH (Fig. 2(c) and (d)) exhibit that it has relatively smooth surface with low porosity, which can be associated with the lower water uptake capacity. According to SEM images of SH/RHA (Fig. 2(e) and (f)), in the presence of RHA, polymeric matrix of hydrogel presented spherical-like structures with dimensions lower than 100 nm. Moreover, as evident in Fig. 2(g), SH/RHA has interlaced structure with high porosity, resulting from the physical crosslinking effect of the incorporated RHA. The irregular porous structure on the surface of SH/RHA (Fig. 2(g)) is attributed to the inhomogeneous distribution of silica nanoparticles within hydrogel network, which can be obviously seen from element mapping analysis of SH/RHA (Fig. 2(h)). This phenomenon causes generation of regions with different physical crosslinking densities within hydrogel network, which in turn each of them forms pores with various shapes and sizes. To further characterize the morphology of SH/RHA, TEM analysis was also carried out (Fig. 2(i) and (j)). As shown in Fig. 2(i), silica nanoparticles emerged as opaque regions, which have been surrounded by irregular pores of hydrogel network. Fig. 2(j) shows translucent interconnected regions within hydrogel network, implying interlinked three-dimensional porous structure of SH/RHA superabsorbent nanocomposite.

Fig. 2. SEM micrographs of RHA (a) and (b), SH (c) and (d), SH/RHA superabsorbent nanocomposite (e-g), results of element mapping of the silica nanoparticles on the surface of SH/RHA (h), and TEM images of SH/RHA (i) and (j).

3.5. Swelling kinetic studies

To investigate the effect of RHA on the swelling capacity and swelling kinetic of the synthesized hydrogels, swelling kinetic measurements were performed in distilled water as swelling medium. As shown in Fig. 3(a) for SH and SH/RHA samples, the swelling kinetics follow a similar trend. The swelling capacity of both hydrogel samples increased quickly during the initial time periods after immersion, and then a slower swelling process occurred until the equilibrium swelling capacity was achieved. From Fig. 3(a) it can be seen that, diffusion of water molecules into hydrogel network of SH/RHA at initial time periods occurs with faster rate than that of SH. This can be attributed to the porous structure of SH/RHA, which enhances the contact surface area, and thus induces higher swelling rate. In continue, three-dimensional interlinked porous channels within SH/RHA network hinder penetration of water molecules into hydrogel network, prolong required time to reach equilibrium swelling capacity, and therefore reduce water absorption rate compared with SH sample. This

phenomenon can be obviously seen from swelling kinetic curves, in which SH/RHA took longer time (9470 min) to reach own equilibrium swelling capacity, while equilibrium water absorption capacity of SH was achieved within 2930 min. The equilibrium swelling capacity of SH sample was 830 g.g^{-1} , while SH/RHA sample presented higher water absorption capacity of 1070 g.g^{-1} at equilibrium state. This is due to the higher electrostatic repulsive forces between carboxylate groups of hydrogel matrix and negative surface charges of SiO_2 nanoparticles, which resulted in an expanded hydrogel network and larger swelling capacity (Cândido et al., 2013). The equilibrium swelling capacity of SH/RHA superabsorbent nanocomposite developed in the present study was greater than that of other alginate-based hydrogel composites reported in the literature (Hua & Wang, 2009; Rashidzadeh, Olad, Salari & Reyhanitabar, 2014; Wang & Wang, 2010).

To evaluate swelling kinetics of the prepared hydrogel samples, the experimental swelling data were assessed by the following pseudo-second order swelling kinetic model (Eq. 4).

$$t/W = A + Bt \quad (4)$$

$$A = \frac{1}{k_s W_\infty^2} \quad (5)$$

$$B = 1/W_\infty \quad (6)$$

Where $W \text{ (g.g}^{-1}\text{)}$ is the swelling capacity at time $t \text{ (min)}$; the $A \text{ parameter (g.min.g}^{-1}\text{)}$ attributes to an initial swelling rate $[(dW/dt)_0]$ of the hydrogel; $k_s \text{ (g.g}^{-1}\text{.min}^{-1}\text{)}$ is the constant rate of swelling; $W_\infty \text{ (g.g}^{-1}\text{)}$ is the theoretical equilibrium water absorption capacity (Rashidzadeh, Olad & Reyhanitabar, 2015). The plot of t/W versus t (Fig. 3(b)) gives straight lines with good linear correlation coefficients, indicating that the swelling kinetics of

hydrogel samples have better compliance with pseudo-second order model. The W_{∞} and k_s were determined through the slope and intercept of the plotted straight lines, respectively, and were collected in Table 1. According to the results, the theoretical equilibrium swelling capacity (W_{∞}) for SH and SH/RHA was obtained as 833.3 ($\text{g}\cdot\text{g}^{-1}$) and 1111.11 ($\text{g}\cdot\text{g}^{-1}$), respectively, which were close to those experimental values. Moreover, the swelling rate constant of SH was higher than that of SH/RHA. This is due to the three-dimensional interlinked porous structure of SH/RHA sample, which retards the diffusion of aqueous solutions into hydrogel network, extends the time to reach equilibrium swelling capacity, and consequently reduces the swelling rate.

In order to determine water diffusion mechanism of hydrogel samples, the swelling data obtained from the first 60% of the fractional water uptake were fitted with the following equation (Karadağ, Üzümlü & Saraydın, 2005):

$$W_t/W_{\infty} = kt^n \quad (7)$$

Where W_t and W_{∞} correspond to the water uptake capacity at time t (min) and at equilibrium, respectively. The k is proportionality constant, and n determines the diffusion mechanism of water molecules. For swellable hydrogel systems, when $n < 0.5$, the diffusion mechanism is Fickian diffusion type. For non-Fickian (anomalous diffusion) type, n is between 0.5 and 1.0, and for case-II diffusion mechanism (relaxation-controlled transport) n is 1.0. Also, for supercase II diffusion, n is greater than 1.0 (Kaşgöz & Durmus, 2008). The plot of $\ln(W_t/W_{\infty})$ versus $\ln(t)$ for SH and SH/RHA samples (Fig. 3(c)) gives straight lines that the values of n and k can be calculated from their slope and intercept, respectively. The values of n and k for both hydrogel samples have been given in Table 1. As shown in Table 1, the

value of n for SH and SH/RHA samples was 0.785 and 0.842, respectively. Therefore, the water transport mechanism in both hydrogel samples was non-Fickian diffusion type.

In order to further characterize the hydrogel behavior in distilled water, diffusion coefficient in the gel phase of hydrogel samples was determined by the short time approximation method. This method is used for the first 60% of equilibrium swelling capacity. The diffusion coefficients of SH and SH/RHA samples were calculated using the following equation:

$$W_t/W_\infty = 4(Dt/\pi r^2)^{1/2} - \pi(Dt/\pi r^2) - \pi/3 (Dt/\pi r^2)^{3/2} \quad (8)$$

Where D is diffusion coefficient ($\text{cm}^2 \cdot \text{min}^{-1}$), t is the immersion time (min), and r is the radius (cm) of the hydrogel sample. By comparing Eq. 7 with Eq. 8 and assuming $n = 0.5$, it can be concluded that (Singh & Singhal, 2012):

$$k = 4(D/\pi r^2)^{1/2} \quad (9)$$

$$W_t/W_\infty = 4(Dt/\pi r^2)^{1/2} \quad (10)$$

The W_t/W_∞ versus $t^{1/2}$ was plotted for hydrogel samples (Fig. 3(d)), and the values of D were determined from the slope of the lines, and listed in Table 1. It can be seen that the diffusion coefficient (D) value for SH ($0.476 \times 10^{-7} \text{ cm}^2 \cdot \text{min}^{-1}$) is greater than that of SH/RHA ($0.379 \times 10^{-7} \text{ cm}^2 \cdot \text{min}^{-1}$), indicating the faster diffusion rate of water molecules in SH sample. The lower water diffusion rate in SH/RHA sample is attributable to three-dimensional interlinked channels within its network made by incorporated RHA. These structures hinder penetration of water molecules into hydrogel network, prolong required time to reach equilibrium swelling capacity, and thus reduce water diffusion rate.

Water sorption rate constant of hydrogels is another important parameter that determines their diffusional characteristics, and can be calculated from the following water sorption equation (first order swelling kinetic model):

$$W_t = W_\infty (1 - e^{-k_w t}) \quad (11)$$

Where t is sorption time (min), k_w (min^{-1}) is water sorption rate constant, and W_t and W_∞ are the water absorption capacity at time t and equilibrium water absorption capacity, respectively (Karadağ, Saraydin & Güven, 2004). The plots of $-\ln(1 - W_t/W_\infty)$ versus t for hydrogel samples have been shown in Fig. 3(e). The values of k_w were calculated from the slope of the plots, and provided in Table 1. The results indicated that the water sorption rate constant of SH (0.0025 min^{-1}) is higher than that of SH/RHA (0.0017 min^{-1}). These results were in good agreement with those previously obtained for SH and SH/RHA samples by pseudo-second order swelling kinetic model. Nevertheless, the plotted straight lines in pseudo-second order swelling kinetic model possess good linear correlation coefficient compared with those lines in first order one. Therefore, the swelling kinetic of both hydrogel samples can be justified as well by pseudo-second order swelling kinetic model.

Table 1. Swelling kinetic parameters of SH and SH/RHA samples in distilled water.

Hydrogel	Swelling kinetic parameters					
	k_s ($\text{g} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$)	W_∞ ($\text{g} \cdot \text{g}^{-1}$)	k	n	D ($\text{cm}^2 \cdot \text{min}^{-1}$)	k_w (min^{-1})
SH	3.92×10^{-6}	833.3	0.0059	0.785	0.476×10^{-7}	0.0025
SH/RHA	2.15×10^{-6}	1111.11	0.0037	0.842	0.379×10^{-7}	0.0017

Fig. 3. Swelling kinetic curves of SH and SH/RHA in distilled water (a), plots of t/W versus t (b), plots of $\ln(W_t/W_\infty)$ versus $\ln(t)$ (c), plots of W_t/W_∞ versus $t^{1/2}$ (d), and plots of $-\ln(1 - W_t/W_\infty)$ versus t for SH and SH/RHA hydrogel samples (e).

3.6. Swelling behavior under load

Water absorbency of a hydrogel sample under load is an important characteristic, which severely affects its potential application in soil medium. To determine water absorption capacity of the hydrogel samples at various loads, swelling kinetics of SH and SH/RHA were assessed in NaCl aqueous solution (0.9 wt%) as swelling medium under different pressures (0.3, 0.6, and 0.9 psi) (Fig. 4(a) and (b)). As shown in Fig. 4(a) and (b), swelling capacity of both hydrogel samples increases rapidly at the beginning times of the test, and continuously its value rises gradually until equilibrium swelling capacity is achieved. In the case of SH (Fig. 4(a)), the maximum value of AUL was achieved within 145 min for each pressure, and this value remained unchanged with prolonging solution contact time. In contrast, SH/RHA (Fig. 4(b)) reached to own maximum value of AUL after 265 min at all pressures, demonstrating its lower swelling rate compared with SH. According to Fig. 4(a) and (b), the equilibrium swelling capacity of SH and SH/RHA at pressures of 0.3, 0.6, and 0.9 psi was 50.14, 42.21, 35.89 g.g⁻¹, and 101.1, 88.1, and 80.8 g.g⁻¹, respectively. These results indicate that the values of AUL for SH/RHA are greater than that of SH at all pressures. This is due to the effective role of incorporated RHA in SH/RHA, which makes strong electrostatic repulsive forces with carboxylate groups of hydrogel, expands hydrogel network, and thus enhances swelling capacity. Also, it can be observed that the value of AUL decreases with increasing the amount of the applied load. This phenomenon is consistent with the fact that higher applied pressure induces greater depletion of absorbed water, and so lower swelling capacity.

3.7. Rheological studies

To make a comparative measure of the gel strength of SH and SH/RHA samples as well as evaluating their gel properties, rheological analysis was executed by recording mechanical

responses of hydrogel samples within angular frequency range of 0.1-100 Hz. Hydrogel samples were first subjected to a strain sweep tests at constant frequency ($\omega = 10$ Hz) to determine LVE region in which G' (storage modulus) and G'' (loss modulus) are independent of the applied strain (Fig. 4(c)). According to Fig. 4(c), below 0.5% deformation, G' and G'' values were independent of the applied strain, indicating the LVE region. Thus, the strain amplitude was determined as 0.5%. The G' and G'' of SH and SH/RHA samples as a function of oscillatory frequencies between 0.1 and 100 Hz have been depicted in Fig. 4(d). As shown in Fig. 4(d), both G' and G'' values of hydrogel samples present an almost increasing trend in the whole frequency range. However, G' values of hydrogel samples exhibit a relatively plateau region in the frequency range of 0.63-25.1 Hz, implying frequency-independent characteristic of storage modulus of synthesized hydrogels. According to the results, in the present hydrogel systems, G' values were considerably greater than that of G'' in all frequency range. This indicates that the elastic response of the hydrogels is significantly stronger than that of their viscous response. Therefore, the synthesized hydrogel samples possessed stable three-dimensional network structure with good mechanical rigidity. Moreover, G' values of SH/RHA were higher than that of SH throughout the whole frequency range, indicating the stiffest hydrogel network of SH/RHA. Besides, G'' value of SH sample demonstrated 42.66% loss at the end frequency of 100 Hz compared with its value at 0.1 Hz. In contrast, SH/RHA showed higher loss of 52.44% in own G'' value as frequency was altered from 0.1 to 100 Hz. These findings revealed that SH/RHA has higher gel strength compared with the neat hydrogel sample (SH). The reason for this phenomenon can be attributed to the additional physical crosslinking points within SH/RHA made by incorporated RHA. These physical crosslinkages hold polymeric chains together tightly, and thus build a firm hydrogel network with higher gel strength.

Fig. 4. Water absorbency under load (AUL) for SH (a) and SH/RHA (b) as a function of time in 0.9 wt% NaCl aqueous solution at different pressures (0.3 psi, 0.6 psi, and 0.9 psi), strain dependence of the storage modulus (G') and loss modulus (G'') at a constant angular frequency ($\omega = 10$ Hz) (c), and frequency dependence of storage modulus (G') and loss modulus (G'') at a constant strain (0.5%) for SH and SH/RHA samples (d).

3.8. pH-dependent swelling behavior

Fig. 5(a) depicts swelling behavior of SH and SH/RHA superabsorbent nanocomposite in aqueous solutions with different pH values. As shown in Fig. 5(a), swelling capacity of both hydrogels increases drastically as pH values rising from 2 to 5 until it remains almost

constant in the pH range of 5-7. In continue, water absorption capacity decreases severely with further increase in pH values up to 12. These changes evident in swelling capacity against different pH values can be justified as follows. In acidic medium ($\text{pH} < 5$), carboxylate groups ($-\text{COO}^-$) in the hydrogel matrix are transformed into carboxylic acid groups ($-\text{COOH}$). At this condition, the hydrogen-bonding interactions among carboxylic acid groups are strengthened. These strong interactions act as additional crosslinking points (physical crosslinkages) induce an increase in physical crosslinking density of hydrogel sample. Thus, the hydrogel network tends to shrink and swelling capacity decreases. At higher pHs ($5 < \text{pH} < 9$), due to the decreased effect of H^+ , hydrogen-bonding interactions are broken. Besides, dissociation of the carboxylic acid groups ($-\text{COOH} \rightarrow -\text{COO}^- + \text{H}^+$) causes the reinforcement of anion-anion repulsions among carboxylate groups, which in turn makes hydrogel swell further (El-Hamshary, 2007). However, the swelling capacity loss in highly basic solutions ($\text{pH} > 9$) is attributed to the shielding effect of Na^+ counterions on the carboxylate anions, which prevents the effective anion-anion repulsions among carboxylate groups. Therefore, the hydrogel sample underwents shielding effect-induced shrinkage and so swelling capacity decreases (Spagnol, Rodrigues, Pereira, Fajardo, Rubira & Muniz, 2012).

The pH-dependent swelling reversibility of SH and SH/RHA hydrogel samples was also tested in aqueous solutions with pHs 2 and 8 (Fig. 5(b)). As can be seen from Fig. 5(b), at $\text{pH} = 8$, due to the electrostatic repulsive forces among carboxylate anions, the swelling capacity of hydrogels is increased quickly. The increasing trend of swelling capacity throughout the swelling process at this pH value is defined as switch on. In contrast, at $\text{pH} = 2$, due to the protonation of carboxylate groups, the swelling capacity of both hydrogels is decreased, sharply. The decreasing trend of swelling capacity of the hydrogel samples is also identified by switch Off term. After three swelling/deswelling cycles, maximum equilibrium swelling capacity of SH/RHA sample showed lower loss compared with the SH sample. This indicates

that SH/RHA superabsorbent nanocomposite possesses excellent pH-dependent swelling reversibility behavior. This intriguing reversible swelling/deswelling (On-Off switching) behavior at different pH values is an implication of better pH-sensitive system, which is more advantageous for controlled drug delivery applications.

3.9. Deswelling kinetic studies in saline solutions

The deswelling kinetics of the swollen SH and SH/RHA samples in 0.1 M aqueous solutions of NaCl, CaCl₂, and FeCl₃ have been depicted in Fig. 5(c) and (d), respectively. As shown in Fig. 5(c) and (d), swelling capacity of the swollen hydrogel samples decreases rapidly as they were transferred into saline solutions. Moreover, it is obvious that deswelling rate of swollen hydrogels in saline solutions is in the order of FeCl₃ > CaCl₂ > NaCl. The observed trend is attributed to the complexation ability of multivalent cationic solutions. On the other hand, ionic crosslinking points within hydrogel network, generated by complexation of carboxylate and carboxamide groups with multivalent cations, cause an increase in the crosslinking density of hydrogel. Therefore, hydrogel network shrinks and swelling capacity decreases. Besides, the higher cation charge induces a greater crosslinking extent within hydrogel network and so brings faster deswelling rate for swollen hydrogels (Shi, Wang & Wang, 2011). According to the deswelling kinetics of SH and SH/RHA samples, it can be observed that SH/RHA has a slower deswelling rate and higher equilibrium water retention in all saline solutions. The equilibrium water retention of SH and SH/RHA in 0.1 M aqueous solutions of NaCl, CaCl₂, and FeCl₃ was about 10.29%, 3.49%, 0.568%, and 25.21%, 10.14%, and 1.95%, respectively. The highly porous structure of SH/RHA with interlinked channels prevents the fast discharging of water molecules, retards quick shrinking of hydrogel network, and thus improves its deswelling resistance in saline solutions. Furthermore, strong hydrogen-bonding interactions among silanol groups of RHA and absorbed water molecules

in SH/RHA hydrogel network not only enhance its water uptake capacity but also suppress water molecules from easily releasing (Cândido et al., 2013). As a result, SH/RHA superabsorbent nanocomposite with excellent deswelling property in saline solutions can be used as an efficient irrigation system in agricultural and horticultural applications.

Fig. 5. Equilibrium water absorbency of SH and SH/RHA at different pH solutions (a), the On–Off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 2.0) of hydrogel samples (b), deswelling kinetic curves of SH (c), and SH/RHA (d) in 0.1 M aqueous solutions of NaCl, CaCl₂, and FeCl₃.

3.10. Reswelling capability studies

One of the most important characteristics of the hydrogels is reswelling capability, which influences their reusability in soil medium. The equilibrium swelling capacity of SH and SH/RHA samples at each consecutive swelling/drying cycles has been shown in Fig. 6(a). The equilibrium swelling capacity of SH was 806 g.g^{-1} and 321.5 g.g^{-1} on the 1th and 5th cycles, respectively, indicating swelling capacity loss of 60.11%. While, in the case of SH/RHA the equilibrium swelling capacity decreased from 1052 g.g^{-1} to 756.36 g.g^{-1} after five sequential swelling/drying cycles, indicating swelling capacity loss of 28.1%. These results can be justified as follows. The large pressure within SH network exerted by absorbed water molecules leads to the rupture of part of polymer chains segments. Hence, the structure of voids in the hydrogel network collapses gradually, resulting in the reduced swelling capacity. In the case of SH/RHA, the firm three-dimensional frameworks within hydrogel network, created by physical crosslinking effect of RHA, enable it to bear high pressure of absorbed water molecules. Thus, SH/RHA presents lower swelling capacity loss during swelling/drying cycles compared with the neat hydrogel sample. Consequently, the use of this hydrogel nanocomposite in soil can reduce irrigation frequencies, improve drought resistance of plants, and also can extend utilization periods of the hydrogels.

3.11. Water retention studies under constant temperature

Water retention behavior of SH and SH/RHA samples was studied through examining their swelling capacity loss under constant temperature (80°C), periodically (Fig. 6(b)). As shown in Fig. 6(b), SH loses own water more quickly than that of SH/RHA so that its absorbed water evaporated entirely after 6 h, while water retention capacity of SH/RHA was reached to 25% at that time interval. This may be attributed to the strong H-bonding interactions between water molecules and silanol groups of RHA in SH/RHA, which can delay

evaporation rate of absorbed water, and thus improve the water retention capability. As a result, incorporation of RHA into hydrogel matrix can not only enhance water absorption capacity but also can improve water retention capability of the superabsorbent nanocomposite.

Fig. 6. The equilibrium swelling capacity loss of SH and SH/RHA samples during consecutive swelling/drying cycles (a), and water retention behavior of hydrogel samples under constant temperature (80 °C) (b).

4. Conclusion

The superabsorbent nanocomposite NaAlg-graft-poly(AA-co-AAm)/RHA has been synthesized successfully by a radical polymerization in aqueous solution using APS as the initiator, MBA as the crosslinker, and RHA as the inorganic filler. FTIR results confirmed grafting of the acrylate monomers onto the alginate chains and also successful incorporation of RHA into hydrogel matrix. TGA analysis results revealed that incorporation of RHA into hydrogel network causes a substantial improvement in thermal stability of the superabsorbent nanocomposite. The introduction of RHA makes the hydrogel becomes highly porous, which can be clearly seen from SEM images. Moreover, in the presence of RHA, interlinked three-

dimensional channels were formed within superabsorbent nanocomposite network, as shown in TEM images. Superabsorbent nanocomposite showed higher equilibrium swelling capacity (1070 g.g⁻¹) compared with the neat hydrogel (830 g.g⁻¹). The swelling kinetic results indicated that the water transport mechanism of the hydrogels with and without RHA was non-Fickian diffusion type. Moreover, SH presented greater diffusion coefficient value compared with the SH/RHA, suggesting that SH possesses higher water diffusion rate. Swelling capacity measurements under load demonstrated that SH/RHA has greater water absorption capacity compared with SH at all exerted pressures. Rheological measurements revealed that both hydrogel samples have a stable crosslinked network structure with good mechanical integrity. In addition, SH/RHA showed higher gel strength compared with the neat hydrogel sample, which was due to the firm hydrogel network made by physical crosslinking effect of the incorporated RHA. The swelling behavior of the hydrogels was noticeably affected by different saline solutions, solution pH, and temperature. The SH/RHA showed excellent pH-dependent swelling reversibility behavior at different pH values. Also, it had excellent salt resistance property, good reswelling and water retention capability compared with the SH sample. These good characteristics indicated that the developed superabsorbent nanocomposite can be used as most suitable candidate for water management in agricultural and horticultural applications, particularly in arid and desert regions. An effective water management system will also ensure the feeding of plants with nutritional elements, resulting in the improved growth quality of plants.

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