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Superabsorbent composites based on rice husk for agricultural applications: Swelling behavior, biodegradability in soil and drought alleviation

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Abstract Low-cost composites with high water absorption capacity were prepared by free radical copolymerization of acrylic acid (AA), acrylamide (AM) and gelatin in aqueous media using N,N' methylene bis-acrylamide (MBA) as crosslinker, potassium persulfate (KPS) as initiator and rice husk (RH) as a filler. The composites were characterized by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The effects of different parameters such as the alkaline treatment on the rice husk, the media pH and salinity and the composition of the composites on their water absorption capacity were investigated. The water retention and biodegradation tests in soil were also carried out. The optimized composite containing treated RH showed a maximum water uptake value of 825 g·g^{-1} in distilled water and good resistance in saline solutions and in the pH range of 6–10. Positive effects on the soil water retention were obtained after 30 days samples of soil containing 1 wt% of superabsorbent composites still contained about 7% of the initial absorbed water. Growth attributes, photosynthetic pigments and nodulation traits of droughted peanut were improved by 60 kg·ha^{-1} dosage of SAC. On the basis of the good results of water retention and controlled biodegradability in

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the soil, the developed composites have the potential to be used in agriculture for better water management, with relevant environmental benefits.

1. Introduction

Superabsorbent polymers (SAPs) are the most commercially successful products of the hydrogel family [1]. SAPs are reported as loosely cross-linked 3D hydrophilic polymeric networks that can swell, absorb and retain huge amounts of water or other biological fluids [2], and the absorbed fluid is hardly removed also under some pressure [3]. They are widely used in sanitary products, such as sanitary napkins and disposable diapers, and also in a variety of other fields. The traditional SAPs, employed in such applications, are based on expensive fully petroleum-based non-degradable polymers [4] including partial neutralization products of cross-linked polyacrylic acids, partial hydrolysis products of starch–acrylonitrile copolymers, starch–acrylic acid graft copolymers [5]. Bu these polymers have poor degradability and remain semi-permanently in water or soil. This means that conventional high-cost SAPs can have negative effects on the environment and living organisms. Consequently, the biodegradability of the SAPs is an important focus of the research in this field given the current attention towards environmental protection issues [5]. Some works reported studies on the biodegradability of superabsorbent hydrogels [6-8].

Taking into account the water imbibing properties of SAPs, their application in the agricultural field has been investigated to reduce irrigation frequency and compaction tendency and to increase the soil aeration and microbial activity [9] Mainly polyelectrolyte gels composed of acrylamide (AM), acrylic acid (AA) and potassium acrylate have been investigated for agricultural applications in arid areas [10]. The particles of SAP act as small water reservoirs in the soil from which the water is removed based on the root demand due to the difference in osmotic pressure. Numerous works have been reported [10] on the positive effects of SAPs on soil water retention and on the growth indices of plants under reduced irrigation regimes.

Therefore, the use of biodegradable SAPs in agriculture could represent a solution to the problem of water management, especially in arid areas, poor in this resource, as in Egypt. In addition, in order to make the use of SAPs in agriculture economically sustainable, the development of superabsorbent composites (SACs) based on low-cost natural fillers can be investigated [11]. For example, rice husk (RH) from the rice milling can be an appropriate low-cost filler of the SACs due to its hydrophilic properties and biodegradability. RH is an agricultural waste material, available in huge amounts and at low-cost in Egypt. Nearly all of the rice husk is burnt or dumped in open fields, only a small amount is used as fuel for boilers, electricity generation and bulking agents for composting of animal manure [12,13]. Consequently, the addition of low-cost natural fillers such as rice husk, an available low-cost agricultural waste in numerous rice-producing countries as Egypt and Italy, can decrease the final cost of the SACs

and it can represent a valuable valorization of this agricultural waste.

In addition, the use of catalyst, in small quantities, in the preparation of the superabsorbent composites can permit to operate in open systems (without the need for a reflux condenser or an inert atmosphere) and to reduce the reaction time in a few minutes, lowering production costs and therefore the final cost of resultant SACs.

In this work, SACs were prepared by free radical copolymerization of acrylic acid (AA), acrylamide (AM) and gelatin in aqueous media using N,N' methylene bis-acrylamide (MBA) as crosslinker, potassium persulfate (KPS) as initiator, N,N,N',N' tetra methyl ethylene diamine (TEMED) as catalyst and untreated/treated RH as filler. TEMED is an essential catalyst for polyacrylamide gel polymerization, but, to the best of our knowledge, it has not been previously used in the preparation of superabsorbent composites as done in this work. The use of this catalyst, even in small quantities, permits to produce composites in open systems (without the need for a reflux condenser or an inert atmosphere) and to reduce the reaction time in a few minutes, lowering production costs and therefore the final cost of resultant SACs.

The properties of the developed composites were evaluated by Fourier transforms infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The swelling behavior was investigated in distilled water, in different saline solutions and at different pH values.

In view of their potential application in the agricultural field, water retention and biodegradability tests in soil were also carried out. Furthermore, the possible application of the water-holding SAC in the alleviation of drought stress consequences on the growth, pigmentation and root nodulation of peanut plants was investigated.

2. Materials and methods

2.1. Materials

Acrylic acid (AA), purchased from ACROS Organics™ (Germany), and acrylamide (AM), from Sigma Aldrich® (Germany), were used as monomers for the graft copolymerization. N,N' methylene bis-acrylamide (MBA) and gelatin (from ACROS Organics™, Germany) were used as crosslinker and biopolymer backbone, respectively. N,N, N',N' Tetra methyl ethylene diamine (TEMED) and potassium persulfate (KPS), used as catalyst and radical initiator, respectively, sodium hydroxide, potassium hydroxide, sodium chloride, calcium chloride, ferric chloride and ethanol were purchased from ACROS Organics™ (Germany). All the materials were of analytical grade and were used as purchased. Rice hush (RH) derived from rice of species *Oryza sativa* L., cultivated in the Nile Delta, was kindly supplied by a rice mill at El-Mahalla El-Kobra (Egypt).

2.2. Rice husk treatment

To remove lignin and hemicelluloses, the rice husk was treated chemically according to the procedure reported by Ndazi et al. [14]: 100 g of rice husk was soaked in 1 L of 8% NaOH for 24 h, then washed with distilled water up to neutral pH and then dried at 80 °C for 24 h. The dried untreated and treated RH was crushed and sieved by 60 mesh sieve.

2.3. Preparation of superabsorbent composites

Samples containing different amounts of untreated/treated RH, gelatin, AA, AM, MBA and KPS were prepared in order to evaluate the effect of each component on the water absorption capacity of the produced SACs.

Different quantities of gelatin were completely dissolved in distilled water (7–26 wt%) at 50 °C into a 250 mL beaker placed on a hot plate with a magnetic stirring bar (750 rpm). Afterward, a known amount (from 0 to 29 wt%) of untreated/treated RH was added until homogenizing to obtain different concentrations (11–32 wt%) in the final SAC; then, a solution of AA (previously neutralized with KOH with a 70% neutralization degree), AM and N,N' methylene bis-acrylamide was added to the reaction mixture followed by addition of initiator (KPS) and catalyst (TEMED) (50 µL/10 g final composite). Finally, the mixture was heated to 70 °C and kept at this temperature for 5–10 min to complete polymerization. The resultant jell-like product was washed with ethanol to remove any impurities. Then, it was dried at 70 °C in a vacuum oven until to constant weight, milled and sieved to obtain a powder with particle sizes in the range of 60–80 mesh (0.2–0.25 mm). Hydrogels of fine particles having high specific surface area show high swelling rate and re-swellability as reported in the study carried out by Abdallah [15] on the effect of hydrogel particle size on water retention properties and availability under water stress. The study showed that hydrogels of small particles (0.8–1.0 mm) had a higher swelling rate and re-swellability compared with the medium (1.0–2.0 mm) and large-grained (2–4 mm) hydrogels. In addition, the water stored in the hydrogel of small particles resulted more readily available for plant roots.

2.4. Characterization

In order to evaluate the evidence of grafting and to determine the functional groups of the grafted samples, the dried SACs were characterized by FT-IR spectrophotometer (Jasco-4100 LE), operating in the region 400–4000 cm^{-1}. The samples were blended with KBr powder and pressed into tablets before the IR spectrum acquisition.

The morphology of the composites was evaluated by scanning electron microscopy (SEM) using a SEM JEOL JSM-6360 (JEOL, Tokyo, Japan). The composites were not subjected to any pretreatment before the SEM analysis but only coated with a homogeneous layer (5–6 nm thickness) of Au by a SEM coating device (Edward Spotter Coater) to induce electroconductivity.

Thermal gravimetric analysis (TGA) of the samples was performed by a Thermogravimetric Analyzer, TGA-50 (Shimadzu Corporation) with a heating rate of 10 °C/min under N$_2$ flow at 10 mL/min in the temperature range of 25–800 °C.

2.5. Swelling of SACs

In order to evaluate the water absorption capacity of the produced SACs, the swelling ratio was evaluated as follows. About 0.1 g of composite powder was placed in distilled water or saline solutions at room temperature and was kept in the medium until to reach the swelling equilibrium (24 h). Solutions of NaCl, CaCl$_2$, and FeCl$_3$, at concentrations from 25 to 200 mmol/L, were used to investigate the ion effect on the SAC absorption capacity. In addition, aqueous solutions at different pH (from 2 to 12) were used to test the effect of the media pH on the swelling ratio. The pH values of the solution were adjusted by adding HCl or NaOH to distilled water.

Swollen samples were then separated from the different investigated solutions by filtering over a 60-mesh screen for 30 min without blotting and, then, they were weighted. The swelling ratio (SR) of SACs was calculated by the following equation:

$$SR(g \cdot g^{-1}) = \frac{w_2 - w_1}{w_1} \tag{1}$$

where w_1 and w_2 are the weight of the initial dried sample and of the swollen sample, respectively.

2.6. Water retention in soil

Different amounts (0.25, 0.5, 0.75 and 1 g) of dried composite powder were well-mixed with 100 g of air-dried sandy loam soil and the mixture was placed in a 500 mL glass beaker, then 100 g of tap water was slowly added into the beaker. The weight of the beaker, including the soil and the sample, was measured and marked as W_0. A control experiment without the superabsorbent composite sample was also carried out. The beakers were maintained at room temperature and weighed daily (W_i) for 30 days. The water retention (WR) in the soil over time was calculated by the following equation:

$$WR(\%) = \frac{W_i}{W_0} \cdot 100 \tag{2}$$

2.7. Soil burial degradation

The biodegradability of the SACs was evaluated by monitoring the weight loss of the samples in soil over time, following the procedure by Wang et al. [16]. Dried gel samples were weighed (1 g) and then buried in the soil at a depth of 15 cm for 150 days. The soil was maintained at 20 wt% moisture. The buried samples were dug out at certain time intervals, washed with distilled water, dried under vacuum at 60 ± 2 °C for 24 h, and then conditionate in a desiccator for at least a day. Finally, the samples were weighed to determine the percentage residual weight (RW):

$$RW(\%) = \frac{w_t}{w_0} \cdot 100 \tag{3}$$

where w_0 is the initial dry weight, w_t is the weight (after dried) at time t.

2.8. Pot experiment

In the greenhouse of the Faculty of Science, Tanta University (Egypt), a pot investigation was conducted in the period from 18 May to 7 July 2019 to estimate the peanut performance (*Arachis hypogaea* L. cv. Giza 5) under water deficiency conditions, in presence or absence of the superabsorbent composites (gelatin-g-p (AA-co-AM)/RH). The soil used for this experiment possessed a sandy texture, slightly alkaline (pH = 7.02), EC of 2.4 mS cm^{-1} and bulk density 1.63 g cm^{-3}. The elemental analyses of the soil revealed the following values: N = 0.39 wt%, P = 1.3 wt%, K = 14.0 wt%, Mg = 17.8 wt%, Na = 10.3 wt%, Cl = 5.7 wt%, total CO$_3$ = 16.21 wt% and active CO$_3$ = 5.34 mg kg^{-1} soil. The soil (12 kg) was put in plastic pots (35 cm width × 25 cm depth). Pots were separated into two groups, the 1st group comprised 8 pots containing SAP-free soil, used as control. The 2nd group comprised 16 pots containing soil mixed with the SAC with the highest swelling percentage (69.0 wt% AA, 11.7 wt% AM, 6.0 wt% gelatin, 11.7 wt% RH, 0.6 wt% MBA and 1.0 wt% KPS). The pots with SAC were then divided into 4 subgroups (4 pots each) having different SAC dosage: 15, 30, 60 and 90 kg·ha^{-1} equivalent.

In all pots, a number of 5 seeds were sown and watered with the full field capacity (FC = 90%). Pots were arranged in a completely randomized block (CRB) design and the 1st group was subdivided into 2 subgroups (4 each), with the 1st subgroup received 90% FC and the 2nd received 40% FC water. However, all pots of the 2nd main group (containing the SAC) just received water of 40% FC on the 4th day of seed sowing. After full seedling establishment (8 days), each pot was thinned into 3 uniform individuals. Pots were irrigated according to the corresponding FC once every 5 days. The plants were left to grow under controlled growth conditions (32/23 ± 2 °C, photoperiod of 12 h and relative humidity of 65 ± 3%) till the age of 50 days. Nitrogen and phosphate fertilizers were applied (kg·ha^{-1}) as recommended by the Ministry of Agriculture and Land Reclamation of Egypt.

Plants were harvested after 50 days of growth, washed several times under tap water, then washed once with distilled water. Plants were separated into shoots and roots, their lengths were measured then their fresh weight (*FW*) was recorded. All samples were then allowed to dry in an air-forced oven at 70 °C till constant weight and the dry weight (*DW*) was attained. Water content (*WC*) was calculated by the Eq. (4):

$$WC(\%) = \frac{FW - DW}{FW} \cdot 100 \qquad (4)$$

Photosynthetic pigments (Chl a, Chl b and carotenoids) were extracted from fresh leaves in 80% cold aqueous acetone by means of pre-chilled mortar and pestle. Samples were centrifuged and the pigment fractions were assayed spectrophotometrically and expressed as mg g^{-1} FM [17].

The number of nodules/plant was calculated in fresh root samples, then the nodules were separated and dried at 70 °C for 5 days, then their dry weight was reported. Leghaemoglobin content in peanut roots was estimated as described by Chouhan et al. [18]. Peanut fresh nodules (0.1 g) were homogenized in 4 mL of 50 mM phosphate buffer (pH 6.5), followed by centrifuged at 10′000 rpm for 25 min. The cleared super-

natant was combined with an equal amount of alkaline pyridine reagent and divided into two equal parts. For the reduction of hemechrome in the filtrate, few crystals of sodium dithionate were added to one part and for the oxidation of hemechromein the other part, an equal volume of 5 mM potassium hexacynoferrate was added. Absorbance readings were taken at 556 nm (for reduced samples) and 539 nm (for oxidized samples) and the content of leghemoglobin was calculated as described by Chouhan et al. [18].

The studies were conducted in triplicate in the case of pot experiment and the data were represented as mean ± standard deviation (SD). Using CoStat software, differences between treatments were investigated and analysis of variance (ANOVA) was performed with Duncan's test at 5% probability level.

3. Results and discussion

3.1. Characterization

3.1.1. FT-IR analysis

Fig. 1 shows the FT-IR spectra of alkali-treated RH, gelatin and a SAC sample containing gelatin-g-p (AA-co-AM)/RH (11.6 wt% RH, 11.6 wt% AM, 6 wt% gelatin, 70 wt% AA, 1 wt% KPS, 0.07 wt% MBA). FT-IR spectrum of alkali-treated rice husk shows absorption bands at 3454 cm^{-1} (attributed to O–H-stretching), 2925 cm^{-1} (–CH$_2$-stretching) and 1053, 1157 cm^{-1} (β$_{1, 4}$-glycosidic bond), characteristic of the cellulosic structures. The spectrum of gelatin presents bands at 3457 cm^{-1} (overlapped N–H and O–H-stretching), 2925 cm^{-1} (saturated C–H stretching) and 1630 cm^{-1} (carboxamide). The comparison between the spectra of treated RH and the prepared SAC revealed some differences that suggested changes in the composition of treated RH during the graft copolymerization reaction. The absorption peak observed for RH between 1053 and 1157 cm^{-1}, attributable to C–O–C bond, was more marked than that in the spectrum of the SAC. This suggested that part of the C–O–C bonds in the treated RH were broken. The absorption peak at 3455 cm^{-1} (O–H-stretching) was higher in the spectrum of the SAC than that of treated RH, showing that after the reaction part of OH-groups were grafted on the carbon chain of RH cellulose with an increase of –COOH groups.

In the spectrum of the prepared SAC, the band at 3449 cm^{-1} is attributable to the –N–H stretching vibration of the acrylamide unit, overlapped with the O–H stretching band that is present in the cellulose and acrylate units. The peaks at around 2928 cm^{-1} were ascribed to the C–H absorption band that may occur in the methyl and methylene groups of copolymer AA-co-AM and cellulose. The observed band at 1640 cm^{-1} could be due to the shift of the C═O stretching vibration of carboxylate, caused by the overlapping of amide group (–CONH$_2$). The peak at 1570 cm^{-1}, corresponded to the asymmetric –COO– stretching as confirmed also by the peaks at 1450 and 1409 cm^{-1} due to the symmetric stretching mode of the carboxylate anion, indicated the presence of copolymer AA-co-AM into the graft-copolymer composite. The absorption at 1078 cm^{-1} could be due to the β 1,4-glycosidic bond of RH, and the peak at 1450 cm^{-1} to the skeletal C═C stretching in the aromatic rings. Both these peaks revealed the existence of cellulose in the composite. In addi-
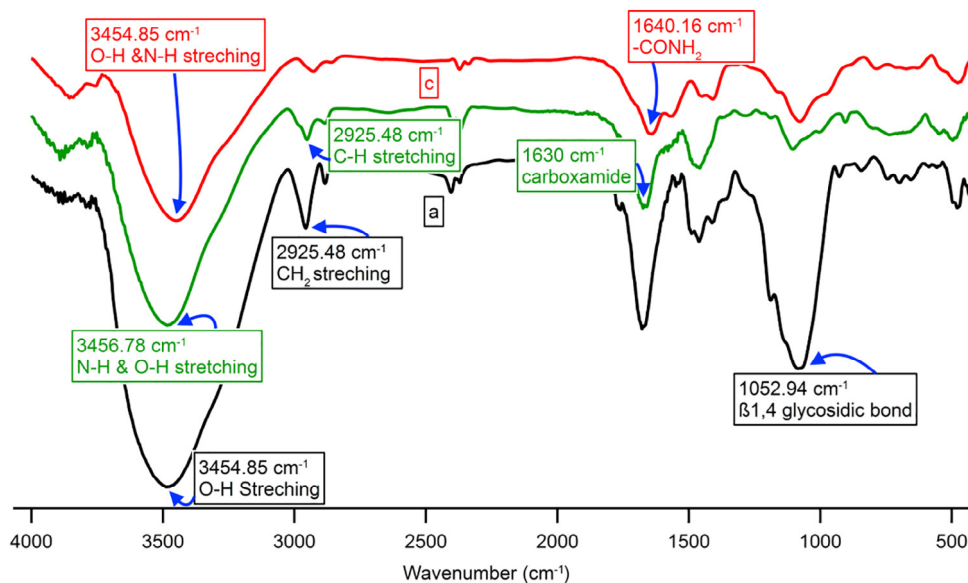
Fig. 1 FT-IR spectra of (a) alkali treated RH, (b) gelatin and (c) gelatin-g-p (AA-co-AM)/rice husk composite.

tion, the bands at 1450 and 1168 cm^{-1} may be attributed to the –C–O– and –O–H coupling interactions of the –COOH and C–N stretching vibrations. The absorption peak at 1640 cm^{-1} could be due to carboxamide, indicating that these functional groups were grafted in the treated RH after graft copolymerization. The FT-IR spectra (Fig. 1) proved that the AA and AM monomeric units were incorporated into the copolymer AA-co-AM chains and the copolymer chains were successfully grafted onto the macromolecular cellulose chains of treated RH. The obtained FT-IR results are in agreement with several previous works concerning SAPs based on copolymers AA-co-AM-co-AMPS (2-acrylamido-2-methyl-1-propanesulfonic acid) onto sodium carboxymethyl cellulose (CMC) and montmorillonite (MMT) [6], gelatin-g-poly(AA-co-itaconic acid) [19] and AA-co-AM-co-DMDAAC (dimethyl diallyl ammonium chloride) onto pretreatment wheat straw [20].

3.1.2. Morphology

Water absorbance and retention rate of the superabsorbent hydrogels markedly depend on their porosity and mean pore size. Hence, the microstructure morphology of the prepared SACs is one of the most important properties to consider. Figs. 2 and 3 shows some SEM images of gelatin-g-p(AA-co-AM)/untreated RH and gelatin-g-P(AA-co-AM)/treated RH, respectively. The surfaces were coarse, undulant and highly porous. This morphology is suitable for the penetration of water into the polymer network. The internal structure was also highly porous; the pores were numerous with uniform size and interconnected. The washing with ethanol and the subsequent drying leads to the development of the highly porous structure of the final composite. The presence of the porous microstructure beside large pores above causes large amounts of water to be absorbed and a high swelling rate of the superabsorbent composite [21]. Due to the presence of rice husk cellulose in the composite, there is an increase in the hydrophilic groups in the composite which facilitates and accelerates the diffusion of liquids through the composite [2].

3.1.3. Thermogravimetric analysis

Fig. 4 shows the thermogravimetric curves of gelatin-g-P(AA-co-AM), gelatin-g-P(AA-co-AM)/treated RH, gelatin-g-P (AA-co-AM)/untreated RH composites. The operating conditions used to produce these SACs were the following: copolymerization temperature of 70 °C; weight ratio of treated or untreated RH to AM 1:1 (11.6 wt% on the total weight of each component); weight percentages of the other components gelatin/AA/initiator/crosslinker in the feed were 6/70/1/0.07 wt%, respectively, on total weight. The thermograms of the SACs showed four thermal degradation steps. The fist weight loss (around 10%), in the range of 50–100 °C, is attributable to the loss of residual moisture due to their high-water absorbency. The subsequent minor weight loss of about 8% from 100 to 250 °C is ascribed to the dehydration of saccharide rings and the breaking of C–O–C bonds in the chain of cellulose of both treated and untreated RH [22]. The relevant weight loss of about 43% for gelatin-g-P(AA-co-AM), 40% for gelatin-g-P(AA-co-AM)/treated RH and 42% for gelatin-g-P (AA-co-AM)/untreated RH in the range 250–500 °C is attributable to the thermal decomposition of the carboxylate and amide side-groups of the copolymers and MBA in the network, leading to the evolution of ammonia, CO_2 and other gases from the polymeric backbone [23-25] and also to the degradation of the protein chains [25,26]. The temperature at which the maximum degradation rate occurs, T_{max}, was at 441 °C corresponding to a weight loss is about 50%. This maximum degradation rate can be due to various concomitant phenomena as the elimination of the water molecule from the two adjacent carboxylic groups of the polymer chains with the formation of anhydride, main-chain scission and destruction of crosslinked 3D network structure [27].

The last degradation stage might be due to the elimination of SO_2 molecule from the pendant chain attached to the polymeric backbone. The SAC with alkali-treated RH showed a higher decomposition temperature range compared to SAC without RH and with untreated RH. The higher temperature
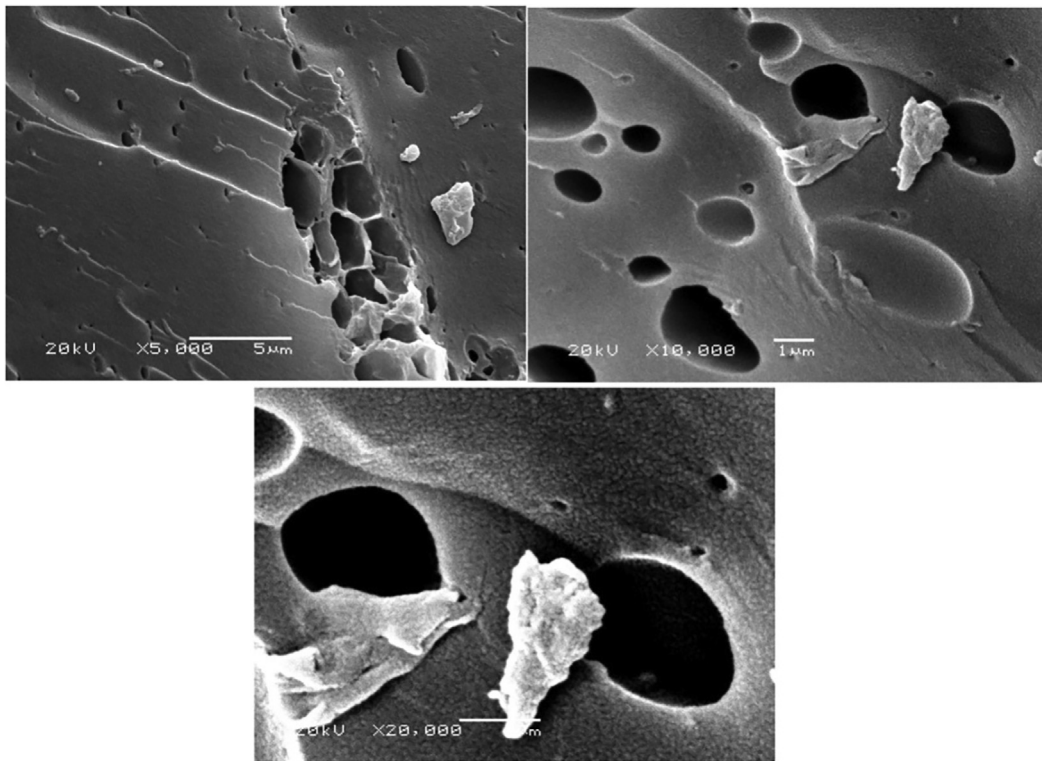
Fig. 2 SEM photographs of gelatin-g-P(AA-*co*-AM)/untreated RH (X 5000, X 10000, X 20000).
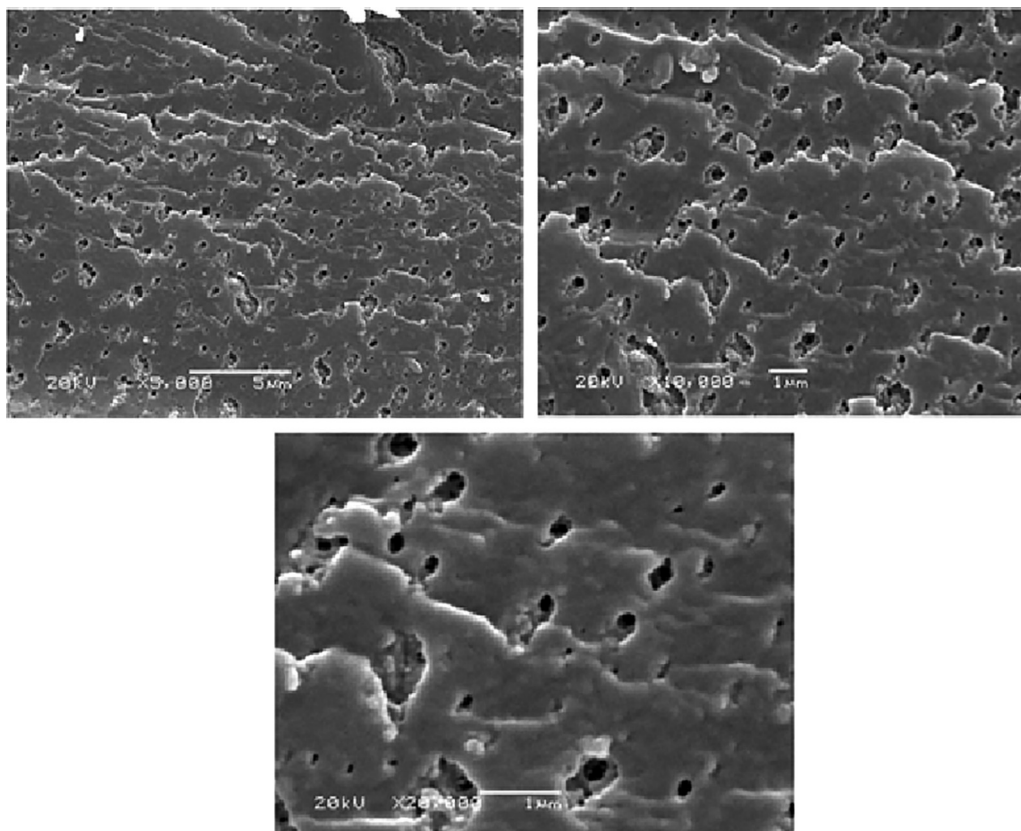

Fig. 3 SEM photographs of gelatin-g-P(AA-co-AM)/treated RH composite (X 5000, X 10000, X 20000).
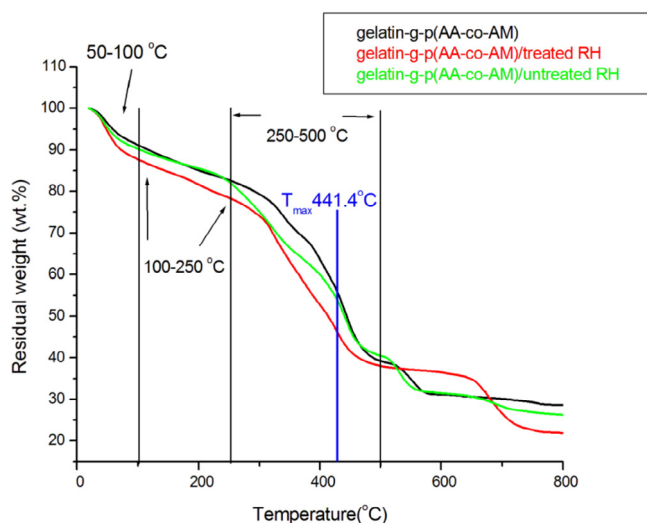
Fig. 4 TGA curves of (a) gelatin-g-P(AA-co-AM), (b) gelatin-g-P (AA-co-AM) /treated RH and (c) gelatin-g-P(AA-co-AM)/untreated RH composites.

step (T > 600 °C) can be due to the decomposition of the thermally more stable structures due to crosslinking reactions produced during heating [25]. Cross-linking reactions may occur between hydroxyl groups and carboxylic acid formed by the chain scission, as in the case of polyamides [28]. The properties of RH in the SAC polymeric network may be the main reason for the difference in TGA results.

3.2. Swelling of SACs

3.2.1. Effect of untreated and treated RH addition

The effect of both natural and treated rice husk on water absorbency of the prepared composites was investigated varying the quantity of RH from 0 to 29 wt% on the total weight. The reaction conditions used were the following: reaction temperature of 70 °C; content of AA, KPS, MBA were 98.5, 1.4, 0.098 wt%, respectively, on RH-free total weight. Fig. 5a shows the effect of untreated RH content on the water absorbency of SACs. The results reported in Fig. 5 are average values of three replicates with the relative error bars. When 8 wt% of RH was added to the composite the water uptake capacity reached its maximum value of 350 g·g^{-1} and then, increasing the RH content, decreased. This behavior can be explained as follows. Firstly, with the addition of untreated RH, there are many active groups, including –OH, –CHO, on the surface of cellulose (RH) that make the composite more hydrophilic. Besides, these active groups could be involved in the copolymerization reaction as well as in the creation of a tridimensional network that, consequently, prevents the polymeric chains from twisting and weaken the hydrogen bonding interactions among the hydrophilic groups. All this leads to an increase in the water absorption capacity as observed. As the RH content increased above 8 wt%, RH shows a typical behavior of inert filler [29] that increases the crosslinking density narrowing the network voids of the hydrogel with consequent reduction of the water absorption capacity. Furthermore, the excess of RH can physically obstruct the voids of the network.

With the addition of alkali-treated RH the water absorbency of the composite increased compared with untreated RH as shown in Fig. 5a. As reported by Ndazi et al. [14], alkali treatment of rice husk with 8 wt% NaOH solution markedly reduces its content of lignin and hemicellulose by 96 and 74%, respectively, and increases the α-cellulose content by 400%. As well-known, the polysaccharide components of plant cell walls are highly hydrophilic whereas the lignin is hydrophobic. Consequently, an increase of the cellulose content in the treated RH, at the expense of reducing the lignin content, improved the hydrophilic properties of the prepared composite (Fig. 5a). Although the composite with 14 wt% of treated RH was not the one with the highest water absorption capacity, this composite was selected for the subsequent investigations on the effect of gelatin content because it represents a good compromise between composite cost and good swelling properties (about 300 g·g^{-1}).

3.2.2. Effect of gelatin content

Effect of gelatin content on water absorbency of the prepared composites was investigated varying the quantity of gelatin from 0 to 26 wt% on the total weight. The reaction conditions used were the following: reaction temperature of 70 °C; weight percentages of treated RH, AA, KPS, MBA, were 14.0, 84.6, 1.3, 0.084 wt%, respectively, on gelatin-free total weight.

Gelatin is a heterogeneous mixture of water-soluble proteins of high average molecular weights, produced by partial hydrolysis of collagen. It has different functional groups in side chains as –COOH, -SH, –OH, –CONH- and –NH$_2$.

As shown in Fig. 5b, swelling of the composite (gelatin, AA (70% neutralized) and RH) increased and reached the maximum value of 552 g·g^{-1} with the addition of gelatin at 6.5 wt% and decreased as gelatin content increased.

This behavior may be attributed to: i) the availability of more grafting sites for initiation of graft copolymerization at higher gelatin concentration; ii) greater availability of monomer in the vicinity of the chain propagating sites of gelatin macro radicals; and iii) increase the hydrophilicity of the hydrogel originated from higher AA content that increases the affinity with water. With the further increase of gelatin concentration, the increase of the reaction medium viscosity reduces the movements of gelatin macro radicals and favors preferentially the homo-polymerization respect to the graft copolymerization reducing the grafting ratio and the swelling capacity. Besides, deactivation of the macro radical growing chains (e.g., by transfer reactions, combination and/or interaction with the primary radicals) could occur soon after their formation [30]. Similar observations were reported also by Hosseinzadeh et al. [31].

3.2.3. Effect of acrylamide content

AM is a non-ionic monomer with a good salt resistance. Meanwhile, AA, being an ionic monomer, has a better water adsorption capability. When AM and AA copolymerized onto cellulose backbone, the absorbency increases in both deionized water and saline solutions. This phenomenon may be explained by the combined effect of –CONH$_2$ and –COO– groups. However, the –COO– group has higher hydrophilicity than –CONH$_2$ [32]. As reported in a previous study [33], the combined absorbent effect of –CONH, –COONa and –COOH groups is superior to that of single groups. When a suitable
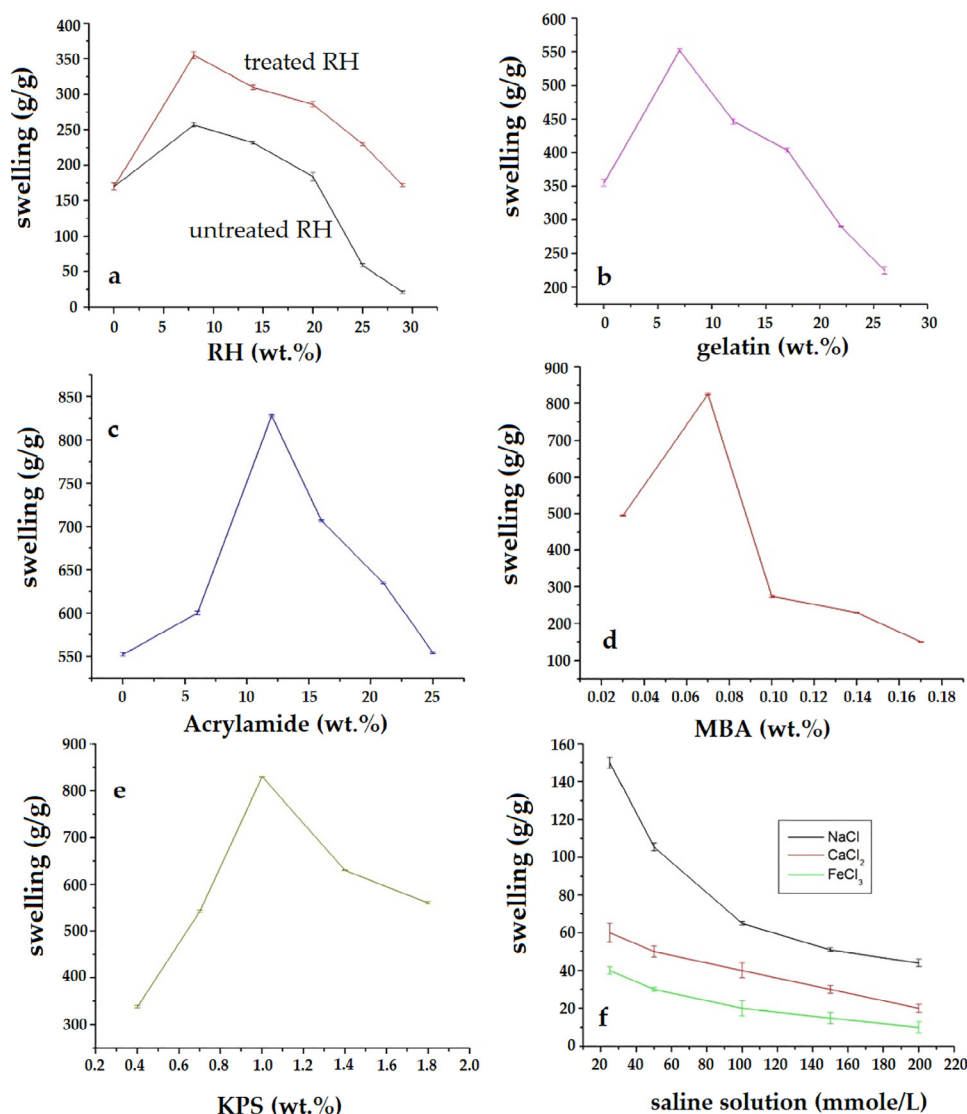
Fig. 5 Effect of (a) untreated/treated RH content, (b) gelatin content, (c) acrylamide content, (d) crosslinker content, (e) initiator content and (f) saline solutions on SAC water absorbency.

ratio of –CONH, –COONa and –COOH groups on the composite cooperate, the water absorbent ability increases and the repulsion between ions is reduced. The correlation between the AM content and water absorbency of the prepared SAC containing 11.6 wt% treated RH after gelatin addition was investigated by varying the AM concentration up to 25 wt%. The other operating conditions were the followings: reaction temperature, 70 °C; concentrations of gelatin, treated RH, AA, KPS/ MBA were 6.6, 13.2, 79.0, 1.2, 0.079 wt%, respectively, on AM-free total weight.

Fig. 5c shows that the water absorbency increased with increasing AM content and reached the maximum value of 825 g·g^{-1} at 11.6 wt% AM and, then, decreased. Firstly, when the AM monomer content increased, the grafting rate increased and the branching chain grafted into the cellulose became long, favoring the formation of the ideal network structure of the composite with a consequent increase of the water absorption capacity. The highest water absorbency was obtained with the molar ratio of AM:AA of 1:6. When the

ratio AM:AA further increased; the water absorbency decreased. This may be due to the ionic groups of AA (–COOH) that are more solvated than the non-ionic groups of AM (–CONH) in an aqueous medium. In conclusion, the optimal molar ratio AM:AM was 1:6. Similar results were reported in a study on crosslinked acrylic acid and acrylamide copolymers [34].

3.2.4. Effect of crosslinker content
The crosslinking ratio strongly influences the swelling properties of superabsorbent polymers. To study the effect of crosslinker content on the water absorbency of the prepared composites, the MBA content was varied from 0.03 to 0.17 wt%. The reaction conditions of the prepared samples were the following: reaction temperature 70 °C; concentrations of gelatin, treated RH, AM, AA and KPS were 6.0, 11.6, 11.6, 70, 1 wt%, respectively, on MBA-free basis. As shown in Fig. 5d, the swelling increased from 495 to 825 g·g^{-1} when the MBA content increased from 0.03 to 0.07 wt%, while it

decreased with a further its increase. When the crosslinker content is below 0.07 wt%, the superabsorbent composite network is not well-formed and the resulted hydrophilic polymer chains would dissolve in an aqueous medium. This inefficient formation of the composite network might be due to the scarcity of crosslink points and the water molecules cannot be held with a consequent decrease in the water absorbency. On the other hand, the excess of crosslinker causes high crosslinking density with consequent reduction of the voids into the 3-D network. This leads to reducing the water content retained in the hydrogel network. Similar results were previously reported [35,36] and in accordance with the Flory's network theory [37].

3.2.5. Effect of initiator content

The effect of the KPS content on the water absorbency of the prepared SACs containing 11.6 wt% treated RH was studied by varying the KPS concentration from 0.4 to 1.8 wt%. The other operating conditions used to prepare the SACs were the following: reaction temperature, 70 °C; content of gelatin, treated RH, AM, AA, MBA was 6.1, 11.7, 11.7, 70.5, 0.07 wt %, respectively, on KPS-free basis.

As shown in Fig. 5e, the water absorbency increased with increasing the KPS content until reaching a maximum value of 825 $g \cdot g^{-1}$ at 1 wt% KPS and, with a further increase in KPS, the water absorbency decreased. This trend may be explained by the fact that at low KPS concentration, there was a shortage of active centers that led to an insufficient crosslinking degree with consequent decrease of water absorbency due to the formation of homopolymers, soluble in the reaction medium (water). With increasing the KPS content, the grafting yield and, in turn, the absorbency of grafted polymer increased. However, an excess of KPS, above 1 wt%, generated more free radicals and this, consequently, accelerated the chain termination reactions via bimolecular collision with further increase of the crosslinking density. This phenomenon is referred to as ''self-crosslinking'' by Chen and Zhao [36]. In addition, the swelling loss at high concentrations of KPS can be also attributable to the free radical degradation of gelatin backbones by the sulfate radical-anions [31]. In conclusion, on the basis of the obtained results, the optimal KPS concentration was 1 wt%.

3.2.6. Effect of saline solution

The swelling ability of a superabsorbent in a salt solution has important application implications, especially in agriculture and horticulture. The external solution properties such as the charge number and ionic strength greatly influence the swelling ratio in combination with the nature of the polymer, e.g. the presence of hydrophilic groups and the percent of crosslinking (the elasticity of the network). The swelling loss in saline solutions compared to that in pure water is often attributed to a ''charge screening effect'' of the additional cations resulting in a non-perfect anion-anion electrostatic repulsion [38]. Consequently, the osmotic pressure, derived from the mobile ion concentration difference between the hydrogel network and the aqueous solution, decreases with the resultant reduction of water uptake [38]. The effect of saline solutions on the swelling was investigated using solutions of NaCl, CaCl$_2$ and FeCl$_3$ at various concentrations (25–200 mmol/L) and the SAC with higher swellability, having the following composition: 6.0 wt%

gelatin, 11.6% treated RH, 11.6 wt% AM, 70 wt% AA, 1 wt% KPS, 0.07 wt% MBA.

As shown in Fig. 5f, the swelling is strongly dependent on the ''type'' of salt added to the medium. For the same concentration, there was a decrease of the swelling and consequently of the water uptake in this order $Na^+ > Ca^{2+} > Fe^{3+}$. The absorbency decreased with the increase of the ionic strength of salt solution, as well expressed by Flory's equation [37] This can be attributed to the higher complexing ability of the multivalent cations with the anion's groups of grafted copolymers [16]. So, the water absorbency in the saline solutions for the prepared SACs decreased in order of NaCl > CaCl$_2$ > FeCl$_3$ [5].

As shown, the water absorbency decreased with increasing salt concentration. This is due to the decrease of the osmotic pressure: the more ionic strength the less difference in the concentration of movable ions between the hydrogel network and the external saline solution that led to the gel contraction with consequent reduction of water absorbency.

3.2.7. Effect of pH

Given the variability of the pH in the soil, the swellability of the prepared SACs was investigated in solutions at various pHs (from 2.0 to 12.0). Standard solutions of sodium hydroxide and hydrochloric acid were used to adjust the pH of the water. No buffer solutions were used, because the counter ions of the buffer solution decrease the swellability of the composite. The SAC with higher swellability, having the following composition: 6.0 wt% gelatin, 11.6% treated RH, 11.6 wt% AM, 70 wt% AA, 1 wt% KPS, 0.07 wt% MBA, was used.

As shown in Fig. 6, when the pH values increased from 2 to 10 the swellability increased then decreased to higher pHs. While it remained roughly constant in the pH range from 6.0 to 8.0. At very acidic conditions (pH < 4.0), most of –COO– groups were protonated to –COOH groups. In the swelling medium, the screening effect of the Cl$^-$ counter ion charge shielded ammonium cations and prevented an effective repulsion [16,37-39]. So, at acidic pHs, the composite was neutral
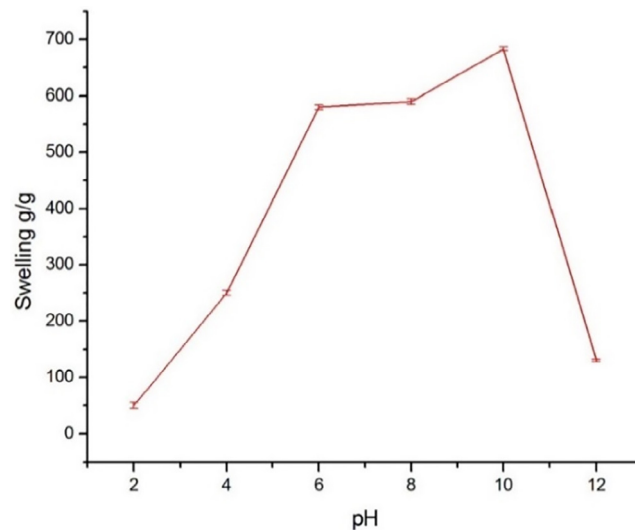

Fig. 6 Effect of pH on water absorbency.

and the flexibility of the polymeric network was reduced because the main anion–anion repulsive forces were eliminated, and, consequently, the equilibrium water absorbency largely decreased.

At higher pHs (pH > 4.0), carboxylic acid groups (–COOH) within the polymeric network were in form –COO– that attracted cations into the composite region to replace H^+ ions. This increased the concentration of the free ions inside the composite. Therefore, because of the ionic swelling pressure increase, the composite expanded and maximized the repulsion between the ionized poly carboxylate groups. The maximal water absorbency of the composite was reached at pH 10, when all the –COOH groups were in form – COO–. The increase of the anionic density in the composite led to high swelling capacity. The decrease of swelling above pH 10 can be attributable to the increase of the ionic strength in addition to the shielding effect (screening effect) [37]. At high pHs, the high concentration of Na^+ cations, derived from NaOH, shielded the –COO– groups and prevented the perfect anion–anion repulsion [40].

3.3. Water retention in soil

SAPs were successfully used as soil amendments in agriculture and horticultural applications to improve the physical properties of soils such as water-holding capacity and nutrient retention [1]. SAPs can also increase seed survival rates and accelerate the plant growth. Consequently, the water retention capacity of the SACs in soil is an important property in view of their application in agriculture. Fig. 7 shows the water retention in the soil over time at various SAC/soil dosages. In these tests the SAC having the following composition: gelatin/AA/AM/treated RH 6.0/70/11.6/11.6 wt% was used.

The results showed that the soil, without the superabsorbent, lose all of the absorbed water after 14 days, whereas for the soil containing 0.25, 0.5, 0.75 and 1 g of superabsorbent per 100 g of soil the absorbed water was totally lost after 17, 19, 22.5, 32 days, respectively. As expected, the higher the dosage of SAC/soil the lower the rate of water loss. When 1 g of superabsorbent was used per 100 g soil, about 6.5%
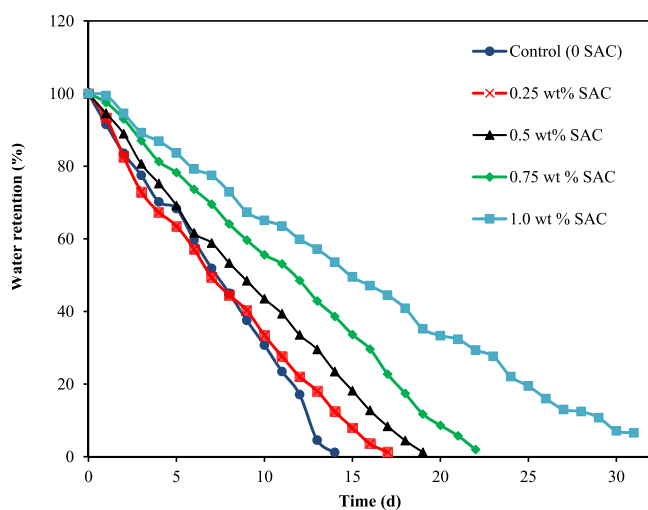
of the initial absorbed water was still present after 30 days. Therefore, the use of these SACs in soil can reduce the irrigation frequency given their good water retention capability.

3.4. Soil burial degradation

The biodegradability of the prepared SACs (gelatin/AA/AM/treated RH: 6.0/70/11.6/11.6 wt%) was investigated by soil-buried test over time and the average results are shown in Fig. 8.

As can be seen, a continuous weight loss of the sample over time was observed, and after 160 days (about 5 months) a total weight loss of about 60% was reached showing the good degradability in soil of the SAC prepared in this work.

3.5. Effect of SAC on peanut growth parameters

The growth rate of peanut shoot and root system was significantly influenced by water stress (50% FC) treatment, as well as the dosages of the applied SAC (15, 30, 60 and 90 kg·ha^{-1}) (Fig. 9). Shoot length, root depth and shoot and root water contents were drastically reduced (90.3, 34.62, 30.0 and 28.1, respectively) as affected by drought stress. Water-stress responsive mechanisms of the plant are profoundly varied from species to species depending on the extent and period of water stress, developmental stage, genetic elements of the species and the environmental factors [41]. Drought stress hampers plant growth by halting metabolic processes, loss of turgor, restriction of CO_2 assimilation, closure of stomata, increased production of active oxygen species [42], and deteriorating enzymatic activity, leaf expansion, ion balance and cellular division [43].

However, soil amendment with various SAC dosages efficiently improved the growth characteristics of water-stressed peanut. Growth increase was a function of the SAC dosage up to 60 kg·ha^{-1}, the growth rate of the stressed peanut improved by increasing SAC dosage from 15 to 60 kg·ha^{-1}, then it slightly declined by the highest dosage (90 kg·ha^{-1}). The augmentative role of SAC on the stressed peanut can be attributed to the consistent soil conditioning, limited production of oxygen radicals, increased leaf area [44], improved stomatal conductance and induced CO_2 fixation [45].
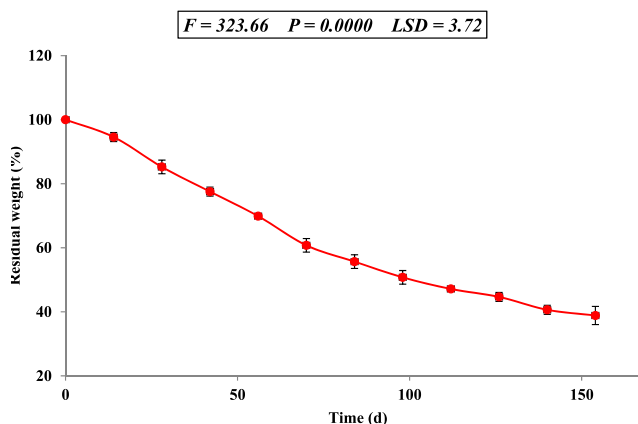

Fig. 7 Effect of superabsorbent composite content on the water retention in soil over the time.

Fig. 8 Soil burial degradation.

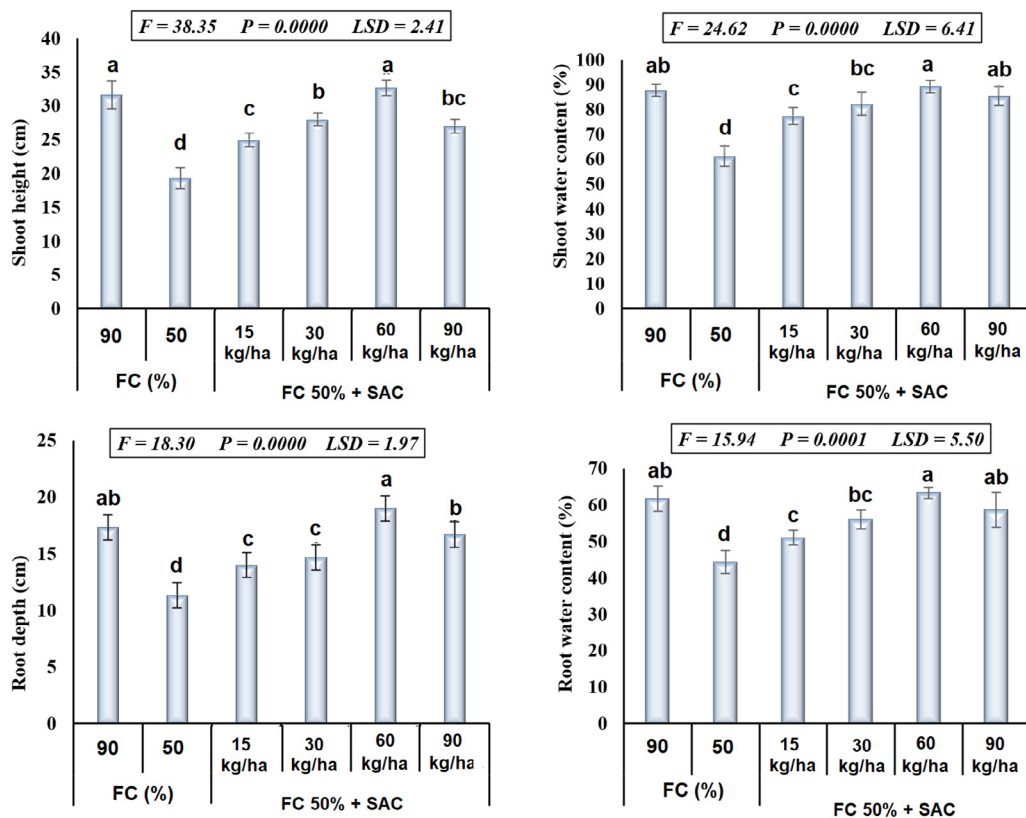**Fig. 9** Effect of SAC dosages on water-stressed peanut growth parameters. Different letters imply significant differences at 5% level.
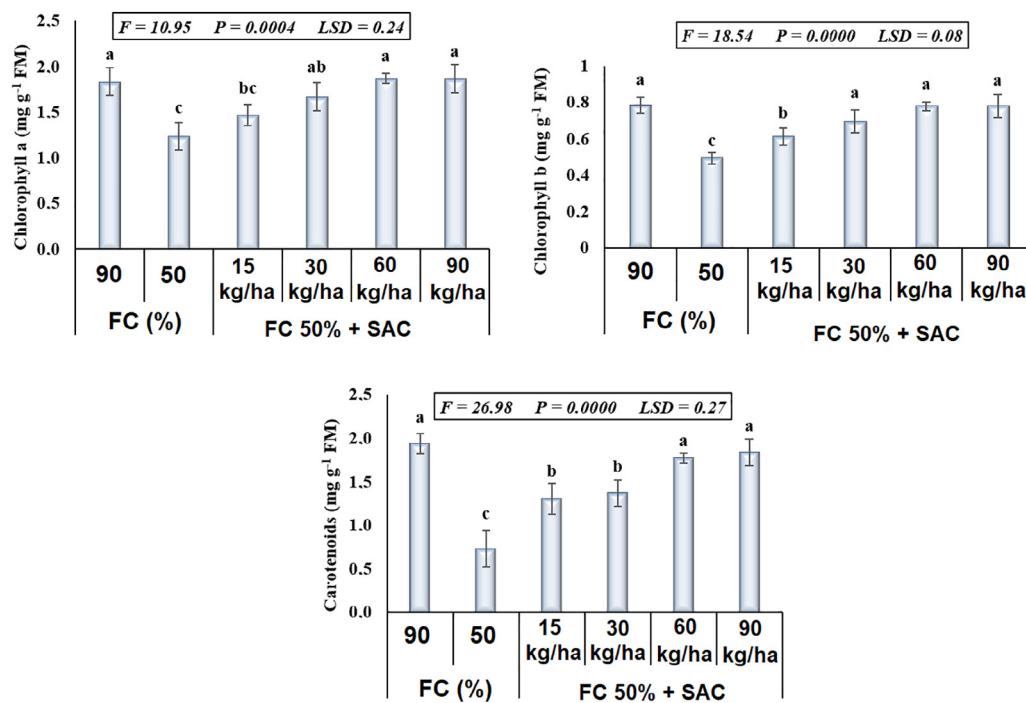

Fig. 10 Effect of SAC dosages on water-stressed peanut photosynthetic pigments. Different letters imply significant differences at 5% level.

3.6. Effect of SAC on peanut photosynthetic pigments

Fig. 10 indicates a substantial decrease in the photosynthetic pigment content (Chl a, Chl b and carotenoids) in peanut leaves due to water stress. However, soil manipulation with SAC retrieved the deleterious implications of water stress on peanut leaves photosynthetic pigments. The most noticeable increase in pigment content was achieved with the SAC dosage of 60 kg·ha^{-1}. Chlorophyll deterioration following drought exposure has been ascribed to increased chlorophyllase (chlorophyll degrading enzyme) activity, structural alternations in the chlorophyll molecule, disturbed lipid-protein complex in thylakoids membrane, disrupted light-harvesting protein complex and inhibition of Calvin cycle enzymes [46]. Furthermore, active oxygen species are not exempted from their destructive role in the breakdown of chlorophyll molecules. The enhanced chlorophyll content in the droughted plants by SAC was previously reported in maize [47,48] and wheat [49]. The positive role of SACs on the chlorophyll content of water-stressed plants was attributed to the ability of these polymers to bind and retain micronutrients together with water due to their high absorption potential, contributing to improved chlorophyll biosynthesis [50].

3.7. Effect of SAC on peanut root nodulation attributes

Fig. 11 shows that water stress decreased the number of nodules/plant, nodules dry weight and leghemoglobin content in peanut roots. Interestingly, soil conditioning with SAC had improved the nodulation attributes and leghemoglobin content in the droughted peanut plants. Root nodules are the site of symbiotic association of nitrogen-fixing microorganisms with the host plant. *Rhizobia* symbiosis with peanut increases soil fertility and improve the crop yield, as this symbiosis provides peanut with 70–90% of its nitrogen demand [51]. The decreased nodules number in plants subjected to drought stress was previously reported in common bean [52] and soybean [53]. The reduced number of nodules in plants experiencing drought stress has been attributed to the reduced photosynthates supply to the nodules by the host plant [54]. Also, reduced legheamoglobin in droughted plants was ascribed to reduced oxygen supply for symbiosis maintenance [55].

4. Conclusions

Novel biodegradable superabsorbent composites were prepared by grafting copolymerization of acrylic acid and acrylamide as monomers, gelatin as a biopolymer backbone and rice husk as filler using potassium persulfate as initiator and N,N' methylene bis-acrylamide as a crosslinker. The effect of the concentration of the various components was investigated to individuate the optimal SAC composition in terms of water absorption capacity in deionized water.

The optimized SAC containing 11.6 wt% of alkali-treated rice husk showed a maximum water absorbency value in distilled water of 825 g·g^{-1} and good salt resistance in a medium pH range of 6–10. The swelling behavior of the prepared SACs was significantly influenced by the nature of the external solution (salt type and concentration, pH). The effect of three cationic salt solutions on the swelling had the following order: $Na^+ > Ca^{+2} > Fe^{3+}$ showing that the prepared SACs swell much less in the presence of monovalent salt and can collapse in presence of multivalent ions. However, the uptake capacity in saline solutions was yet as high as 20–60 g·g^{-1} (i.e. 2000–6000%).

Water retention results indicated that soil containing 1 wt% of the optimized SAC can retain water for more than a month,

Fig. 11 Effect of SAC dosages on water-stressed peanut nodulation attributes. Different letters imply significant differences at 5% level.

halving the irrigation frequency. In addition, the SACs showed a controlled biodegradability in soil that guarantees their presence in the soil for a sufficiently long time (> 5 months).

The drought stress which represents a terrible threat for plants grown in arid regions could be controlled by conditioning the soil with ecological production SACs.

The good results obtained showed that the relatively low-cost prepared SACs have the potential to be used in agriculture as small water reservoirs and controlled water release systems, reducing the frequency of irrigation for a better water management.

CRediT authorship contribution statement

El-Refaie Kenawy: Conceptualization. **Maurizia Seggiani:** . **Ali Hosny:** . **Mohamed Rashad:** . **Patrizia Cinelli:** . **Khalil M. Saad-Allah:** . **Mohamed El-Sharnouby:** . **S. Shendy:** . **Mohamed M. Azaam:** .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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