Synthesis and swelling behavior of environmentally friendly starch-based superabsorbent hydrogels reinforced with natural char nano/micro particles

Elaheh Motamedi\textsuperscript{b,*}, Babak Motesharezedeh\textsuperscript{b}, Ahmad Shirinfekr\textsuperscript{c}, Seyed Mahmood Samard\textsuperscript{d}

\textsuperscript{a} Department of Nanotechnology, Agricultural Biotechnology Research Institute of Iran (ABRII), Agricultural Research, Education and Extension Organization (AREEO), Karaj, Iran
\textsuperscript{b} Soil Science Department, College of Agriculture and Natural Resources, University of Tehran, Karaj, Iran
\textsuperscript{c} Tea Research Center, Horticultural Sciences Research Institute, Agricultural Research, Education and Extension Organization (AREEO), Lahijan, Iran
\textsuperscript{d} Department of Soil Biology, Soil and Water Research Institute, Agricultural Research, Education and Extension Organization (AREEO), Karaj, Iran

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\textbf{ABSTRACT}

Herein, the proficiency of natural char (NC) as cost-effective and biocompatible filler for the synthesis of high-performance starch-based superabsorbent composites was evaluated. To this goal, NC powder, ball-milled natural char (BMNCs) and chemically modified NC nanoparticles (NCNPs) were synthesized and then utilized as fillers for preparation of starch-g-poly(acrylic acid-co-acrylamide) superabsorbent composites. The morphology and surface functionalities of the as-synthesized fillers and their composites were scrutinized using FTIR, FESEM, elemental mapping, AFM, Boehm titration and TGA analyses. The results proved that the composite performance was controlled by the filler's properties (i.e., morphology, size, surface chemistry and functionalities) and NCNPs with the smallest particle sizes (14.8 ± 3.0 nm) and the highest oxygen functionalities was selected as the best filler candidates. Coexistence of the physical and covalent cross-linkage in the NCNPs/Hydrogel nanocomposite could be proposed as a reason for its two-fold water absorptivity (389.9 g/g) in comparison with the neat hydrogel (202.1 g/g). However, the addition of NC and BMNC in the polymer matrix could not significantly improve the water absorption performance of the composite. Absorbency under load (AUL) results showed that the gel strength of samples displayed the following descending order of NCNPs/Hydrogel > BMNC/Hydrogel > NC/Hydrogel > neat hydrogel > commercial hydrogel. All synthesized starch-based superabsorbent (nano)composites showed a Fickian water diffusion mechanism and pseudo-second-order swelling kinetic model. Moreover, after 14 days, NCNPs/Hydrogel nanocomposite showed three-fold water-retention (%) capability compared with the neat hydrogel (23.1 % vs. 7.1 %, respectively).

1. Introduction

Superabsorbent polymers (SAPs) are cross-linked polymeric networks with three dimensions and the ability to absorb and conserve a large amount of aqueous solutions [1–4]. While the term of SAP is commonly replaced by hydrogels in the literature, there is a clear distinction between these two terminologies. Generally, SAPs have larger water absorption capacity (1000–100000 %, 10–1000 g/g) compared to the regular hydrogels (100 %, 1 g/g) [5,6]. In the last two decades, biocompatibility, biodegradability, non-toxicity, abundance, and low cost of natural polymers make them appropriate candidates for the fabrication of the natural-based polymeric hydrogels [7–9]. In particular, starch as one of the most available and inexpensive polysaccharides with numerous hydroxyl functionalities, have been widely utilized for design of novel semi-interpenetrating (semi-IPN) hydrogels for specific environmental, agricultural and medical uses [10–15]. In spite of extensive studies conducted so far on the synthesis of starch-based hydrogels, it still requires more practical investigations for their economic production with superior properties like high swelling rate and capacity, appropriate water retention ability, sufficient mechanical strength and thermal stability as well as biodegradability [2,16,17].

On the other hand, incorporation of micro/nano-fillers in the matrix of polymers has been reported as an efficient strategy to improve properties of synthesized hydrogel composites [18–21]. In fact, a combination of synergistic benefits of starch-based hydrogels and inorganic nanoparticles can result in the fabrication of reinforced novel superabsorbent nano-biocomposites with the boosted mechanical, barrier, thermal and swelling characteristics [18,22]. The favorable interfacial polymer-filler interactions (i.e., hydrogen bondings, Van der Waals forces, electrostatic interactions, hydrophobic associations)
cause the formation of physical cross-links in the network of polymer nanocomposites which have been considered as one of the main proposed explanations for reinforcement mechanism [23]. To date, various nanomaterials such as clay, silica, graphene, nanocellulose, carbon nanotubes, biochar, metals and metal oxides have been applied to produce high-performance starch-based hydrogel nanocomposites [24–33].

Natural char (NC) referred to as organic particles, occurs in various coalification stages with char morphology which is found in all carbonate mudstones and/or coal seams in the world [34]. Industrial viability, along with cheap cost and environmental compatibility of NC [35], makes it a feasible and scalable additive candidate for reinforcing polymers. However, efficient incorporation of the raw NC particles in the polymeric architectures has been restricted because it doesn’t have proper surface functional groups for favorable interaction with ionic moieties (carboxyl, amide, hydroxyl groups) of the SAPs chains. In addition, the heterogeneous characteristic of raw NC particles (wide-ranging particle size and randomly distributed pores) [34] may also be considered as restrictive factors in the efficient production of its uniform hydrogel composites. Tackling these obstacles, surface chemical/physical modifications could be performed to produce engineered NC particles with uniform size and superior surface properties [35]. Specifically, modified NC particles are expected to act as both nanofillers and physical crosslinkers through the formation of hydrogen bonds between functional groups of hydrogel matrix and surface of NC particles [36]. In this sense, application of reinforced NC/starch-based hydrogel (nano)composites as agricultural superabsorbent are expected to result in eco-friendly and economic win-win effects for both improved soil water storage as well as a soil amendment. Regarding this, incorporation of biochar and carbon fibers in the superabsorbent polymer composites have been reported as a proper strategy not only for increase plant available water in soils but also for increase induce faster growth of plants [37,38].

Although different starch-based superabsorbent hydrogels reinforced with various inorganic nano/micro fillers have been reported so far [18,39–41]. However, the potential use of NC as cost-effective, bio-based and viable filler for reinforcing SAPs and producing environmentally friendly starch-based SAP hydrogels have not been reported yet. Therefore, as the first aim of the current study, the proficiency of two different methods (i.e. physical ball-milling vs. surface chemical oxidation) in the synthesis of modified NC particles was investigated. As the second aim, the novel NC nano/micro particles were profitably utilized to fabricate environmentally friendly NC/starch-g-poly(acrylic acid-co-acrylamide) superabsorbent composites with enhanced water absorbency, high water retention capacity, and improved thermal stability. The effect of particle size, surface chemistry and functionality of modified NC (nano)particles were further scrutinized. The favored physical interactions between chemically modified NC nanoparticles (NCPNs) and polymer matrix made novel bio-based SAP nanocomposite with superior water absorbency, which could be efficiently employed as a cost-effective and environmentally benign agricultural superabsorbent polymer.

2. Materials and methods

2.1. Materials

Sulfuric acid (H2SO4, 98 %, MW = 98.08), hydrogen peroxide (H2O2, 30 %, MW = 34.01) and potassium permanganate (KMnO4, MW = 158.03) were obtained from Sigma–Aldrich Co. Moreover, starch (corn starch (C6H10O5)n, practical grade), acrylamide (AAm, 98 %, MW = 71.08, CH2 = CHCONH2), acrylic acid (AA, 99 %, MW = 72.06, CH2 = CHCOOH), N,N-methylene bisacrylamide (MBA, 99 %, MW = 154.17, (CH2 = CHCONH2)CH2), ammonium persulfate (APS, 98 %, MW = 228.20, (NH4)2SO4), potassium hydroxide (KOH, 85 %, MW = 56.11) and methanol (CH3OH, 98 %, MW = 32.04), were purchased from Sigma and commercial hydrogel was kindly supplied by Bloorab company, Iran.

2.2. Characterizations

The samples were analyzed by field emission scanning electron microscopy (FESEM) equipped with a detector of back-scattered electrons (BSE) and elemental mapping (TESCAN MIRA II microscope; 20 kV accelerating voltage). Prior to FESEM imaging, the samples were coated with a thin layer of gold using a vacuum sputter coater. Fourier-transform infrared (FTIR) spectroscopy using KBr pellets with Thermo spectrometer (scan range of 400–4000 cm⁻¹), and atomic force microscopy (AFM) in non-contact mode (DF9550, DME Denmark, tip curvature below 10 nm) were employed for characterizing the as-synthesized samples. The samples were prepared for AFM analyses using drop-casting of their dilute suspensions (0.05 mg/mL) onto the mica substrate. Moreover, dynamic light scattering (DLS) (Nanoseries Zetasizer, Particle Metrix Co.), and thermogravimetric analysis (TGA, TA Instrument; model SDT Q600) in Ar atmosphere, from room temperature to 700 °C (10 °C/min) were utilized for the sample characterizations. Transmission electron microscopy (TEM) images were taken by the TEM Philips EM 208S instrument (100 kV accelerating voltage) affirming the nano-metric size of NCNPs. In addition, Boehm titration was used as a chemical method to calculate the oxygen surface groups on the as-synthesized samples [42,43]. This test is based on the fact that bases with various strengths (NaHCO3, Na2CO3, NaOH) could neutralize different acidic oxygen functionalities on the surface of carbon materials [42,43]. The strongest acidic groups (carboxylic groups) were neutralized with the weakest base (NaHCO3), both carboxylic and lactonic functionalities were neutralized with the Na2CO3, and finally, the strongest base (NaOH) neutralized all the carboxylic, lactonic and phenolic groups. The amount of each acidic functionality could be calculated by the difference between the uptake of each titrating base.

2.3. Preparation of the fine natural char (NC) powder

The raw NC mass was collected from Kuhbanan (MASL: 31 27 37 N and 56 16 22 E), Kerman province, Iran (August 24, 2017), then 250 g of the raw NC were ground and sieved with a sieve (2 mm dia sized) to remove large particles. Next, the powder was added to excess amounts of deionized water and stirred vigorously for 15 min, and then the mixture was sustained with no agitation. After 30 min, the heavier part which contained silica or other solid inorganic materials settled down in the bottom of the reaction flask. Then, the supernatant containing floating lighter char particles was decanted to separate from precipitates consisting of silica and mud [44]. The upper aqueous part was centrifuged (5000 rpm) to settle down the fine dark grey NC powder after drying at 70 °C. The raw NC and the resultant fine NC powder were analyzed using EDX mapping analyses (Fig. S1 a,b, see Supplementary Information).

2.4. Synthesis of ball-milled natural chars (BMNCs)

Milling experiments were carried out in a planetary ball-mill machine (NARYA-MPM; Amin Asia Co.) with two 250 mL Teflon (PPTF) mill jars, at room temperature. Accordingly, salt-assisted milling technique using stearic acid crystals and Zirconia (YSZ) grinding media of 5 and 10 mm in size was performed. Each milling run conducted at 350 rpm and total working time of 10 h (after subtraction of rest times). Afterwards, the products were collected, washed with deionized water, then centrifuged at 5000 rpm and finally dried in 70 °C overnight. To achieve BMNCs with the smallest particle sizes with narrow size distributions, different preliminary milling conditions were employed and the dried BMNCs were analyzed using DLS technique (Fig. S2 a,b, see Supplementary Information). The final optimized conditions to produce BMNCs were as follows: time intervals of 5 min working and 5 min rest,
5 mm diameter milling balls, stearic acid weight ratio of 1 %, and ball to NC powder mass ratio of 20:1.

2.5. Synthesis of chemically modified NC nanoparticles (NCNPs)

0.5 g of fine NC powder was added to concentrated H₂SO₄ (50 mL), and then 2 g of KMnO₄ was slowly added and the mixture stirred in an ice bath [45]. After 2 h, the temperature of the reaction was raised to 35 °C while the mixture was stirred gently for another 1 h. Afterwards the ice bath was provided again, and deionized water (150 mL) was added to the reaction mixture gradually. After 30 min, H₂O₂ solution (10 mL) was dropped to the reaction vessel. Next, the precipitates were centrifuged and washed with deionized water until neutralization of the supernatant’s pH. Lastly, the precipitates were dried at 70 °C, and the fine beige color powder was collected and analyzed using DLS technique (Fig. S1 c, see Supplementary Information).

2.6. Synthesis of starch-based superabsorbent hydrogel (nano)composites

For the preparation of NCNPs/Hydrogel nanocomposite sample, the previously reported studies were utilized with some modifications [46]. Starch (10 g) was mixed with 100 mL deionized water in 500 mL 4-necked flask equipped with a mechanical stirrer, condenser, and thermometer. NCNPs (1 g) was separately suspended in 100 mL deionized water (ultrasonic bath 15 min), and then added to the starch suspension. The mixture was stirred for 30 min, next acrylamide (5 g) and acrylic acid (38 mL, 60 % neutralized solution with KOH) were added to the reaction flask. This step continued by addition of cross-linker (0.5 g of MBA) and initiator (1 g of APS) and the mixture was continuously stirred until a homogenous mixture was prepared. In the following, the reaction temperature was raised up to 70 °C, and the mixture was constantly stirred until the gel production. The resultant gel was coagulated through the addition of methanol, washed several times with methanol and dried in a vacuum oven at 60 °C. For the sake of comparison, the pristine hydrogel without any filler (Hydrogel), as well as hydrogel composites with NC and BMNC fillers named NC/Hydrogel and BMNC/Hydrogel, respectively, were synthesized using the same procedure.

2.7. Efficiency evaluation of synthesized hydrogel (nano)composites

2.7.1. Water absorbency

The as-synthesized samples were weighed and immersed in deionized water until equilibrium swelling, at room temperature. Afterwards, the swollen samples were filtered to remove the excess water and then weighed. The equilibrium water absorbency (Qeq, g g⁻¹) was estimated by Eq. (1) [47].

\[
Q_{eq} = \frac{W_i - W_f}{W_i} \times 100
\]

where \( W_f \) and \( W_i \) are the weight of samples before and after swelling in water, respectively. The Qeq values of samples in the NaCl, KCl, MgCl₂, and FeCl₃ saline solutions with two different concentrations (i.e. 0.01 and 0.001 M) were analyzed. In addition, water absorbencies were examined in a range of pH values (i.e. 3.0–10.0) at ambient temperature for all the as-synthesized samples. The water absorbency values in deionized water at different time intervals (i.e. 5–60 min) were calculated using the above equation. To determine the gel fraction (GF) of the samples, they were weighed and allowed to swell in deionized water, and then the gels were dried at 70 °C. The weights of the dry samples before (\( W_i \)) and after (\( W_f \)) swelling was used to calculate the gel fraction by Eq (2) [47].

\[
Q_{eq} = \left( \frac{W_f}{W_i} \right) \times 100
\]

For all the above experiments, 20 mg of each as-synthesized sample was weighed and then utilized.

2.7.2. Effect of thermal pre-treatment on the swelling behavior of as-prepared hydrogels

In order to evaluate the effect of thermal pre-treatment on water absorbencies of hydrogel (nano)composites, the swelling of samples was measured after their incubation at elevated temperatures. In this sense, accurately weighed a portion of each sample (20 mg) was firstly wrapped in alumina foils and then were put in the oven for 30 min at different temperatures ranging from 60 °C to 120 °C. After thermal pre-treatments, \( Q_{eq} \) of samples were calculated using Eq. (1).

2.7.3. Absorbency under load

The bottom of a hollow plastic cylinder (internal diameter and height of 2.9 and 5.0 cm, respectively) was sealed with a nylon fabric. A certain amount of prepared sample (20 mg) was evenly spread on the fabric surface at the bottom of the cylinder. The whole system was then weighed and put in one beaker. Three different weights (50, 75 and 100 g) which could slip simply in a cylinder was placed on top of the sample, and then deionized water was poured slowly into the beaker. The sample was allowed to soak for 1 h, and the \( Q_{eq} \) values were determined based on Eq. (1).

2.7.4. Water-holding capacity and water retention of soil

Samples were well mixed with dry soil (1 w%, 0.4 g of each sample in 40 g soil) and placed into a PVC tube with a diameter of 4.5 cm and sealed with nylon fabric. Deionized water was gently added to soil tubes to see the seepage from their bottom. The soil tubes were weighed before the addition of water (coded \( W_i \)) and when water seepage was stopped from the bottom of the tube (coded \( W_f \)). The water-holding capacity (WHC %) of the soil was determined from Eq. (3) as follows [48]:

\[
WHC\% = \frac{(W_i - W_f)}{W_i} \times 100
\]

For testing the soil water retention, similar to above mentioned WHC measurements, the PVC tube containing soil and superabsorbent (nano)composites (1 w%) were prepared and drenched with deionized water and then remained under ambient temperature. The tube weights were recorded daily to calculate the water retention (WR%) of soil with each sample through Eq. (4) [48]:

\[
WR\% = \frac{W_f - W_i}{W_i} \times 100
\]

Where the \( W_i \) is the weights of the soaked soil tubes recorded at daily and \( W_f \) is the masses of tubes containing dry soil and hydrogel sample blends.

3. Results and discussion

3.1. Characterization of as-prepared (nano)fillers

SEM images of produced NC, BMNC and NCNPs samples at 50, 100 and 200 KX magnifications are displayed in Fig. 1. The SEM images of NC indicated micrometric stacked smooth hunks with various shapes that their edges were sunk together in a way that a particular separated particle could be hardly seen in the images (Fig. 1a). In the BMNC images, the dense polygonal shape particles were observed, which mostly aggregated to each other and made larger particles with several hundred-nanometer sizes (Fig. 1b). In contrast, the SEM images of NCNPs portrayed close-packed tiny spherical nanoparticles which appeared as bright dots, particularly at higher magnifications (Fig. 1c). These results showed that although the grinding process has been able to decrease the size of particles successfully; however, particle sizes were still large in comparison to particles produced by the chemical oxidation, and the broaden size distribution was also achieved.
Moreover, TEM images of NCNPs sample also affirmed the oxidation reaction could effectively produce uniform and tiny nanoparticles which were agglomerated (Fig. 1d).

In order to determine the prime functionalities and surface morphology of as prepared NC, BMNC, and NCNPs samples, FT-IR spectroscopy and AFM microscopy were utilized, and their results were described in details in Supplementary Information (Fig. S3 and S4). Moreover, elemental mapping images of BMNC and NCNPs demonstrated that carbon, oxygen and nitrogen elements were presented in both as-prepared samples (Fig. 2 a,b). The EDX mapping exhibited much higher oxygen content (green dots) in NCNPs sample, which could be attributed to the chemical oxidation of char surface during reaction with a very strong oxidant. In addition, carbon atoms (yellow dots) in NCNPs were spread quite uniformly throughout the sample structure, while in the case of BMNC, their distribution in some part of the sample were denser and rather heterogeneous. This suggested that the operating conditions in a mechanochemical ball-milling process could result in the homogeneous distribution of the microstructure of the product [49]. The elemental MAP also revealed that rather small amounts of nitrogen (red dots) were presented evenly throughout both sample matrices. Moreover, size distribution histograms of samples were prepared from measuring about 100 particles through SEM images.
of BMNC and NCNPs samples (Fig. 2 c,d). The average particle sizes based on SEM images histograms were to be 157.9 ± 34.3 nm and 14.8 ± 3.0 nm for BMNC and NCNPs samples, respectively, which agreed well with the particle sizes estimated from AFM images. Besides, the Boehm titration results were consistent with FT-IR and elemental mapping findings and showed that the total acidic groups of the samples followed the following descending order of NCNPs > BMNC > NC (Table S1, see Supplementary Information).

3.2. Characterization of as-prepared hydrogel (nano)composites

SEM images of (nano)composite samples evidently displayed that size of (nano)fillers had a prominent effect on the microstructure of resulting product. Specifically, SEM images of NCNPs/Hydrogel nano-composite in three different magnifications showed a random distribution of tiny NCNPs particles in the matrix of hydrogel (Fig. 3a). In higher magnifications, lots of white NCNPs particles (< 20 nm in diameter) could be seen which presented the dense and even dispersity of nanoparticles in the curly and crumpled polymeric backbone. Such uniform distribution of NCNPs in the polymer structure without the addition of any surfactant, ligand or stabilizing agent would confirm the key role of functional groups in the formation of stabilizing interactions between NCNPs and polymer matrix. It could be observed that a number of BMNC particles (size at micrometric ranges) were integrated into BMNC/Hydrogel composite structures (Fig. 3b). The dispersion of BMNCs was not uniform, and in some parts of the sample they were aggregated to each other and made clusters. Similarly, SEM images of NC/Hydrogel composite showed some clustered micro particles with non-uniform distribution in the polymer matrix (Fig. 3c). Moreover, in comparison with the BMNC/Hydrogel sample, the sizes of fillers were larger, and so the SEM images were taken in lower magnifications. These results displayed that the spatial distribution of (nano)fillers in the hydrogel structure was controlled by particle sizes (entropic effects) along with their functionalities (enthalpic effects). Larger particles with micron size ranges could not incorporate well in the hydrogel because they expelled from the polymer architecture. In other words, with increasing the particle radius and accordingly decreasing the conformational entropy of polymer, the larger particles were not evenly distributed in the polymer backbone [50]. This results could be supported by the fact that the orientation of the reacting molecules according to their polarity could provide favored/disfavored interactions between the functionalities of the grafting moieties/fillers with the backbone of the natural polymer which would finally lead to determination of the degree of substitution or the quality of filler’s distribution in the hydrogel matrix [47].

From another viewpoint, enthalpic interactions between the polymer chains functionalities and active sites on the surface of (nano)filler can be utilized to achieve homogenous loading of (nano)filler in the polymer. SEM results altogether proved that in the case of NCNPs, the combination of enthalpic and entropic interactions led to the
uniform distribution of nanoparticles in the host hydrogel backbone which could be resulted in the higher performance of final nano-composite product. Besides, to investigate the thermal stability of as-prepared neat hydrogel and its nanocomposite, the TGA analyses were performed where the results were described in details in Supplementary Information (Fig. S5).

3.3. Water absorbency properties of as-prepared hydrogel (nano)composites

The swelling behavior of samples in different pHs were illustrated in (Fig. 4a), where all samples swelled very little at acidic medium (pH < 3), but the water absorbencies were continuously enhanced with increasing the pH, at neutral solutions, reached its maximum, and then were almost fixed in basic pHs (up to 10). This could be attributed to the protonation of most carboxylic functionalities in the hydrogel at acidic pHs. At pH < 4.5, there is no COO¯ group, and this caused restriction of electrostatic repulsions between carboxylate groups and diminishing the swelling capacity of hydrogel [51–53]. Moreover, the significant superiority of NCNPs/Hydrogel nanocomposite over commercial hydrogel and other reinforced samples, in all various pHs, could be seen clearly in Fig. 4a. This approved the homogeneous dispersion of NCNPs, which would act as physical cross-linkers in the matrix of the hydrogel. Linking of the flexible and soft polymeric chains by NCNPs nanoparticles resulted in a strengthened hybrid polymer with modified performance even better than commercially available samples. Unlike NCNPs/Hydrogel sample, both NC/ and BMNC/Hydrogel composites showed weak performances, and their water absorbencies were similar or slightly lower than the neat hydrogel sample. These results suggested that the coexistence of the physical and covalent cross-linkage was highly depended on the properties of the fillers (i.e., morphology, surface chemistry and functionalities) which directly affect the homogeneity and distribution quality of fillers in the hydrogel matrix. On the
other word, the presence of oxygen-containing groups on the surface of small particles of NCNPs made it capable of forming H-bonding interactions with the functional groups of hydrogel and physically cross-linked the copolymer chains. This effect has been reported before for synthesis of hydrogel nanocomposites reinforced with graphene oxide nanosheets or cellulose nanocrystals [20,23,54]. In these cases, similar to the present study, the researchers have firstly oxidized the surface of nano-fillers to improve the physical cross-linkage between them and hydrogel matrix [20,23,54].

Moreover, based on the gel fraction results, the pristine hydrogel showed the least gelation, and its gel fraction was found to be 53.8 %. Addition of (nano)fillers improved the gel fraction of the samples, and the measured GFs were 61.9, 63.4 and 74.1 % for NC/Hydrogel, BMNC/Hydrogel and NCNPs/Hydrogel, respectively. The commercial hydrogel showed 81.5 % gel fraction. Since the gel fraction could reflect the intra- and inter-molecular chemical stabilization of hydrogels, so the GF results confirmed that among all as-synthesized samples, NCNPs/Hydrogel nanocomposite had the highest chemical stability [47].

In addition, for evaluation of the effect of (nano)fillers on thermal characteristics of as-prepared hydrogel (nano)composites, the swelling behaviors of samples after thermal pretreatments were investigated (Fig. 4b). The results showed that unlike commercial sample, the water absorbencies of all synthesized hydrogels were decreased after keeping for 30 min at temperatures above 60 °C, specifically, in the case of neat hydrogel. For example, water absorbency of the neat hydrogel was decreased from 190.8–135.8 and finally 99.1 g/g, after thermal pretreatment at 80, 100 and 120 °C, respectively (a decrement of 91.7 g/g). In contrast, the water absorbency of NCNPs/Hydrogel sample, under similar conditions was decreased from 366.3–345.9 and then 337.8 g/g — a decrement of 28.5 g/g. These results confirmed that the presence of NCNPs in the polymer matrix could reduce its thermal degradation resulted from the decomposition of the cross-linked hydrogel. Such degradations at higher temperatures were mainly caused by the formation of free radicals at the chain ends/weak bonds, which could result in inter-chain reaction and consequent radical transfer to nearby chains. The increased thermal stability of hydrogel (nano)composites compared to pristine hydrogel could be attributed to the fact that the mobility of the polymer chains was restricted in the (nano)composite hydrogel sample. In fact, homogenous dispersion of NCNPs made strong interfacial interactions among nanoparticle surfaces and hydrogel which caused suppression of chain transfer reaction trough reduced chain mobility, and as a result, lower polymer decomposition process occurred at higher temperatures.

Water absorbency under load (AUL) is another important characteristic of hydrogels which could portray their stability/strength [55,56]. Interestingly, the AUL values of all synthesized samples are higher than commercial hydrogel, which were correlated to their higher gel strength (Fig. 4c). NCNPs/Hydrogel showed the highest AUL amounts, and under all loading weights, the values were almost similar. It could be deduced that the presence of NCNPs nanoparticles in the polymer matrix resulted in porous gel mass and improved liquid distribution in the absorbent network during the swelling process, which finally made more strength hydrogel [55]. Since increasing the cross-linking degree of polymer is proven as a typical reason for enhancing the polymer gel strength [55], the physical crosslinking of NCNPs in the polymer matrix could be probably responsible for such strength of the swelled hydrogel. As could be seen in Fig. 4c, despite the nearly similar AUL amounts for all synthesized hydrogels at loading weights of 50 g, with increasing the weights the gel stabilities were decreased, particularly in the case of the neat hydrogel. The AUL amount for BMNC/Hydrogel and NC/Hydrogel samples slightly decreased with increasing the loading weights from 50 g to 75 g, but with increasing the weight up to 100 g, the former sample showed more gel stability. Among three reinforced hydrogels, the NC/Hydrogel composite displayed the lowest AUL value in loading weight of 100 g, and its gel strength dropped apparently from 113.9–93.5 g/g when the loading weight increased from 75 g to 100 g. Considering the above observations into account, the gel strength of samples displayed the following descending order of NCNPs/Hydrogel > BMNC/Hydrogel > NC/Hydrogel > Hydrogel > commercial hydrogel. Besides, the effects of salt solutions (i.e., NaCl, KCl, CaCl₂, MgCl₂ and FeCl₃) on the swelling behavior of samples along with their recyclability/reusability were described in details in

Fig. 5. (a) Swelling behavior of synthesized and commercial hydrogels as a function of time in distilled water (b) plots of Ln (Qt/Qm) versus Ln (t), (c) Pseudo-second order, and (d) Pseudo-First order models of swelling kinetics.
Supplementary Information (Fig. S6 and Fig. S7, respectively).

Altogether, all the above typical experiments which are common tools for evaluating superabsorbent hydrogel efficiencies approved that NCNPs could efficiently incorporated in the matrix of polymer and boosted its characteristics remarkably.

3.4. Swelling kinetics of as-prepared hydrogel (nano)composites

In addition, the effect of incorporation of (nano)fillers on their swelling kinetics and diffusion behavior were investigated (Fig. 5). All as-synthesized and commercial samples showed similar swelling kinetics which water absorbency sharply increased at the initial of the swelling process, and then the slower rates of swelling were observed until reaching to the equilibrium (Fig. 5a). However, the water absorbency for the NCNPs/Hydrogel was always the highest amount, and the required equilibrium swelling times were about 20 – 30 min for all samples.

To evaluate the effect of (nano)fillers on water diffusion behavior of hydrogel (nano)composites, the pseudo-hydrogel (nano)composites complied with Fickian di, respectively. The calculated BMNC/Hydrogel, NC/Hydrogel, commercial hydrogel, and NCNPs/Hydrogel, respectively (Fig. 6b). During 14 days, despite the control group which had almost lost all its moisture, the soil samples with NCNPs/Hydrogel, commercial hydrogel, NC/Hydrogel, BMNC/Hydrogel, and neat hydrogel still preserved 23.1, 19.9, 14.4, 10.4, and 7.15 % of water, respectively. The reason is that the hydrogel (nano) composites could absorb huge amounts of water and gradually release it out during the time. These results confirmed the efficiency of synthesized samples, especially NCNPs/Hydrogel in absorption large amounts of water and retaining of it in the soil which could grow up its application in agricultural fields. NCNPs/Hydrogel could act as a water reservoir to supply moisture for plants within a long time.

Finally, water sorption performances of the as-synthesized super-absorbent hydrogels were compared and contrasted with other re-inforced starch-based hydrogels reported in the literature (Table 2). Ebru Al et al. have been reported the synthesis of starch-g-acrylic acid/Na-montmorillonite (Na-MMT) superabsorbent nanocomposite hydrogels [39]. Their results displayed that Na-MMT content affected the swelling behavior of hydrogels. While the amount of Qe for pristine hydrogel was found to be about 700 g/g, it was increased up to 900 g/g when the Na-MMT/monomers ratio reached 1 % [39]. Synthesis of starch-graft-poly(acrylamide)/attapulgite superabsorbent composite have been reported by Liu et al. [40]. The water absorbency of composite with an attapulgite content of 10 % was 1317 g/g in deionized water, and the pristine hydrogel showed Qe of 545 g/g, at same conditions [40]. Conversely, the addition of magnetic Fe3O4@SiO2 nanoparticles (0.5 g) in the matrix of starch-graft-poly(acrylic acid) hydrogels resulted in a decrement of water absorbency of hydrogel (from 610.2–408.2 g/g) [41]. Hosseinzadeh et al. studied the effects of graphene oxide/hydroxyapatite (HAP) on the synthesis of starch-graft-poly (acrylamide) composites and showed that the addition of HAP resulted in a decrease in water uptake of polymer [18]. Generally, one may conclude that the absorption characteristics of superabsorbent hydrogels largely depends on many synthetic parameters which type and concentration of fillers is one of them. Therefore, based on the polymer backbone and grafting monomers, the fillers could be designed, modified and incorporated in the matrix of hydrogels with the aim of improving the properties of base polymers.

Moreover, as could be seen in Table 2, these starch-based super-absorbent hydrogels have wide applications in a variety of fields including agriculture, drug delivery, water treatment and tissue engineering. One of the most important applications of starch-based superabsorbents is the development of efficient carriers for plant nutrients making slow-release fertilizers (SRF) [13,52,62-66]. Such SRF formulations could provide appropriate bioavailable nutrients and water at the same time, throughout the plant growth periods [67]. In this regards, the addition of NCNPs as low-cost, available and renewable nanofillers in the matrix of starch-based hydrogels could result in the reduction of their production costs and expansion of their utilization in the agriculture/horticulture.

4. Conclusions

In summary, fabrication of a novel, cost-effective and efficient starch-based hydrogel nanocomposite reinforced with chemically

Table 1

Parameters of P-F-O and P-S-O kinetic models, and diffusion kinetics of swelling of synthesized and commercial hydrogels.

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<th></th>
<th>qe (g/g)</th>
<th>k1 (min⁻¹)</th>
<th>R²</th>
<th>qe (g/g)</th>
<th>k0 (g g⁻¹ min⁻¹)</th>
<th>R²</th>
<th>n</th>
<th>k</th>
<th>R²</th>
</tr>
</thead>
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<tr>
<td>Hydrogel</td>
<td>149.86</td>
<td>0.2266</td>
<td>0.9864</td>
<td>208.33</td>
<td>0.0068</td>
<td>0.9997</td>
<td>0.1028</td>
<td>0.7257</td>
<td>0.9956</td>
</tr>
<tr>
<td>NCNPs/Hydrogel</td>
<td>177.75</td>
<td>0.1477</td>
<td>0.9741</td>
<td>400.00</td>
<td>0.0024</td>
<td>0.9996</td>
<td>0.0831</td>
<td>0.7433</td>
<td>0.9611</td>
</tr>
<tr>
<td>BMNC/Hydrogel</td>
<td>81.34</td>
<td>0.1107</td>
<td>0.9707</td>
<td>192.30</td>
<td>0.0034</td>
<td>0.9985</td>
<td>0.1995</td>
<td>0.5232</td>
<td>0.9825</td>
</tr>
<tr>
<td>NC/Hydrogel</td>
<td>88.54</td>
<td>0.0986</td>
<td>0.9971</td>
<td>175.43</td>
<td>0.0023</td>
<td>0.9989</td>
<td>0.2716</td>
<td>0.4224</td>
<td>0.9712</td>
</tr>
<tr>
<td>Com. Hydrogel</td>
<td>55.58</td>
<td>0.1456</td>
<td>0.9339</td>
<td>322.58</td>
<td>0.0060</td>
<td>0.9999</td>
<td>0.0872</td>
<td>0.7711</td>
<td>0.9875</td>
</tr>
</tbody>
</table>
modified natural char nanoparticles (NCNPs) were presented. The study was begun with the preparation and characterization of pristine natural char (NC) and its two different modified structures through mechanical ball-milling method (BMNC) and chemical oxidation and then followed by evaluating the performance of the as-prepared natural-based nano/micro particles in the synthesis of starch-based hydrogels. The results showed that methods of modification of pristine NC had a pronounced effect on the swelling behavior, water absorbency, water retention ability, and thermal stability of reinforced starch-based hydrogels. Finally, NCNPs was selected as the best filler candidate of choice to produce high-performance NCNPs/Hydrogel where nanoparticles (average sizes of 14.8 nm) were homogeneously distributed in the matrix of hydrogel stabilizing interactions (i.e. hydrogen bonds and electrostatic interactions) between NCNPs and polymer. In fact, NCNPs acted as not only nano-filler but also physical cross-linker, which could result in enhanced water absorbency, water retention and boosted thermal properties of NCNPs/Hydrogel nanocomposite. The highest amount of water-holding and water-retention capacity of NCNPs/Hydrogel nanocomposite beside its natural-based character would expand its potential applications as an eco-friendly and economical agricultural hydrogel.

Author contribution

Dr. Motamedi: Synthesis of nano-micro particles, synthesis of hydrogel samples, designing the experiments, and writing of the manuscript and preparing its revise version.

Dr. Motesharezedeh: Preparation of raw NC powder, assisting in design of experiments, reading and editing the manuscript and its revise version.

Dr. Shirinfekr: Assisting in test of hydrogel performance in the soil, reading and editing the manuscript.

Dr. Samar: Assisting in test of hydrogel performance in the soil, reading and editing the manuscript.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

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References


