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Research Article

Magnetic Nanoparticles-Grafted-Poly (Acrylic Acid) as a Super-Hydrogel Composite: Preparation, Characterization and Application in Agriculture

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Abstract

Background and Objective: Owing to swelling properties and easy fabrication, hydrogels are employed intensively in agricultural applications. Nano-particles were used in agriculture due to their high surface area and reactivity in soil. This study aims to improve the adsorption capacity of soil from nutrients and enhance water holding capacity using hydrogel grafted with magnetic nanoparticles. **Materials and Methods:** Herein, hydrogel composite of acrylic acid or sodium acrylate co-polymer cross-linked with magnetic nanoparticle (HG-MNP) were synthesized and characterized by FTIR, TGA, BET and TEM techniques as compared with the hydrogel (HG). A pot experiment was conducted to evaluate the effects of HG and HG-MNP on crop productivity, quality and water-use efficiency of eggplant under different irrigation and mineral fertigation doses. **Results:** The results indicated that the incorporation of magnetic nanoparticles (MNP) into the hydrogel matrix can significantly improve both the thermal stability and the swelling ratio of the hydrogel samples. The results of the pot experiment conducted on eggplant treated with the modified HG showed a significant increase in the studied morphological characteristics including plant high, stem diameter, number of branches, leaves, fruits, chlorophyll concentrations and crop yield compared to the control. This was attributed to the higher swelling ratio of HG-MNP and the higher adsorption ratios of nutrients than HG, which ensured an adequate supply of water and nutrients throughout the growth period of the crop. **Conclusion:** These results indicated that the integration of HG-MNP is beneficial for agricultural applications, especially under water stress.

Key words: Poly acrylic acid, hydrogel, swelling ratio, water holding capacity, magnetic nanoparticles, eggplants, sandy soil

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Hydrogels had been studied, since their first report in the 1960s, by several researchers dealing with synthesize, characteristics and applications[1]. The great interest is recognized in the fact that hydrogels can be synthetic from different polymers (synthetic, natural or both)[2,3] as well as their broad applications in several fields e.g., biomedical and agriculture applications. Besides, hydrogels can present different features depending on external stimuli (pH, temperature, ionic strength)[4]. Hydrogels are well-defined as physically or chemically cross-linked three-dimensional polymer networks that swell in water or biological fluids without dissolving or losing their shapes[5]. Hydrogels can absorb an amount of liquid greater than 100 times its own dry weight[6,7]. Most of the traditional super absorbent hydrogels are prepared from petroleum-based polymers, which decrease their range of applicability and raise environmental concerns (degradability, toxicity, etc.)[8].

Currently, the combination of natural polymers in the super-hydrogel absorbents has been used to increase their applicability, bio-compatibility and biodegradability. Furthermore, the preparation of hydrogel composites, by incorporating another class of materials including different fillers (e.g., ashes, cellulose nano whiskers, clays, carbon nanotubes, inorganic particles, magnetite, etc.), can increase or provide new characteristics to the innovative material[9,10]. Nanomaterials were reported by different scientists that have impressive applications in agriculture fertigation due to physical and chemical characteristics[11,12]. Iron magnetic nanoparticles (MNPs) were applied in catalysis, biomedicine, water treatments and other different fields[13,14]. MNPs were applied in agriculture and succeeded to improve seed germination of Peanut and increased shoot and root growth[15,16].

Metal-based nanoparticles (NPs) in the environment tend to aggregate into larger clusters and thus they lose their size-related nano-scale properties[17]. Moreover, in the soil matrix, NPs aggregation can be quickly fixed into soil solids and significantly lose their reactivity[17].

NPs with minimized aggregation tendency can typically travel long distances and therefore, have a high impact on the surrounding environment. Therefore aggregation process governs metal-based NPs mobility, reactivity and the associated risks in the agriculture system.

The current study aims to minimize the aggregation and maximize the reactivity of magnetic nanoparticles (MNPs) by grafting them into the hydrogel (HG). In addition, establish a pot experiment using sandy soil to apply the synthesized material (HG-MNPs) for reducing the amount of water and nutrients demanded by eggplant compared with solely HG.

MATERIALS AND METHODS

Preparation of MNP: The magnetic nanoparticles were prepared by the co-precipitation method described by Jeon *et al.*[18]. Briefly, dissolving a molar ratio of Fe $(Cl)_3$ and $FeSO_4$ using ultrasonic waves. The NaOH (6.5 M) was dropped wisely into the previous solution under stirring to precipitate magnetic nanoparticles (Fe_3O_4) with an average diameter of 10 nm. The black precipitates were collected by the magnetic field and heated in the muffle at 300°C to produce γFe_2O_3 nanoparticles (MNPs). The obtained MNPs were ground and kept in a desiccator for hydrogel immobilization.

Fabrication of HG and HG-MNP: The hydrogel was produced at a factory in Agricultural Research Center (ARC), Giza, Egypt. In a cooperation project between ARC and NIPPON SHOKUBAI Co. Ltd., HG was manufactured using ACRYHOPE (acrylic acid or sodium acrylate copolymer cross-linked) and silt. Briefly, acryhope was dried and mixed with silt with a ratio of 1:5, then the mixture was wet mixed and transferred into pellets using the pelletizing tool. These pellets were oven dried at 70-90°C, cut into smaller pellets, sieved and kept for later use. The synthesized polymer was defined as hydrogel (HG). The same process was followed for synthesizing HG-MNP but with the addition of a specific amount of MNPs into the dry mixture of the acryhope and the silt.

Characterization of the synthesized hydrogel: The surface morphology of the dried HG was investigated by an SEM (Jeol, JSM-6360LA, Japan) at low magnification. The powder of HG was fixed onto the specimen holder and was covered by gold-coated layers by the sputtering method. The SEM images were taken at a magnification of 1000× using a 10 kV accelerating voltage.

Functional groups initiated onto HG and HG-MNPs surfaces were tested using Fourier Transform Infrared Spectroscopy (FTIR) and data were generated from the diffused reflectance style by employing Bruker Vertex 80 joined with Ram-FT module (RAM II) spectrometer. Thermo-Gravimetric Analysis (TGA) of HG and HG-MNPs samples was performed by TA equipment (SDTQ600) from ambient temperature to 1000°C at a speed of 10°C/min at nitrogen atmosphere with a gas flow of 20 mL/min.

The specific surface area, total pore volume and pore size distribution of the HG and HG-MNPs samples were analyzed by a surface area analyzer (Model Quantachrome TouchWin™

Table 1: Initial chemical and physical characteristics of used soil

Parameters	Unit	Concentration
Sand	%	97.2
Silt	%	2.0
Clay	%	0.8
Texture		Sandy
Bulk density	(gm cm^{-3})	1.4
EC (1:5)	(dS m^{-1})	3.81
pH (1:2.5)		7.8
Total $CaCO_3$	%	2.6

version 1.21). Samples were firstly evacuated and degassed at 200°C for 2 hrs before the analysis. The surface areas of the studied materials were detected by the multi-point Brunauer-Emmett-Teller (BET) method. Pores size and pore volume were calculated by Barrett-Joyner-Halenda (BJH) method.

Pot experiment: A pot experiment was executed to investigate the effect of HG and HG-MNPs on the growth and the yield of eggplant (*Solanum melongena*) grown in sandy soil at the Dokki site in El-Giza governorate, Egypt, which is sited at 30°03'N latitude, 31°20'E longitude during the winter season of 2020 and 2021. Pots (0.2 m^2) were filled with sandy soil and washed with irrigation water three times to eliminate different salts. The chemical and physical characteristics of soil were shown in Table 1. A split plot design was employed in this experiment as follows: Main pots were designated with irrigation treatments 100% (R_1) and 75% (R_2) from evapotranspiration (ET0), while in sub-main pots different hydrogel treatments were applied, including the control (H_1), HG (H_2), HG-MNPs (H_3). Finally, in sub-sub main pots, different doses of mineral fertigation were applied, including 100% (F_1) and 75% (F_2) from the recommended mineral fertilizer dose of eggplants. The hydrogel dose was fixed at 5 g kg^{-1} of soil[19]. Each treatment was replicated three times. The hydrogel dose was added to the selected pots and was topped with 3 cm of soil. The recommended doses of mineral fertilizers were added in four batches, the first batch was mixed with hydrogel before seedling. The other three doses were added after 1 month, 2 months and at the flowering stage, respectively.

Soil and plant analysis: The chemical properties of the soils were measured before the seedling harvest process (Table 1). Soil samples from two points at a depth of 0-10 cm were collected from each section randomly excluding the edges and after removing the fallen leaves on the soil surface. After the sampling, the two samples of each section were mixed and prepared for soil analysis. The soil, organic manure and plant samples were analyzed as follows. The soil samples were air-dried at room temperature to study soils' chemical and physical properties as shown in Table 1. The soil texture was analyzed at a constant temperature of 30°C by using the hydrometer method and the organic matter content was detected by the Tyurin method. To measure soil pH, 10 g of soil was stirred with distilled water at a ratio of 1:5 and the pH was measured with a pH meter. P and K concentrations were measured according to Cottenie *et al.*[20] after sample digestion using hydrochloric and nitric acid, while N contents in these samples were determined after digestion by another acidic mixture according to the method described by Jones[21].

Plant samples were collected for nutrient analysis at the physiological age (55 days from seedling) for qualitative and quantitative analysis. To determine P and K soil samples were digested using hydrochloric and nitric acid[20], while for N determination another mixture of acid was used for digestion as described by Jones[21]. Nutrients accumulated in fruits were determined after digestion using a mixture of sulfuric and perchloric acid (5:1). The P was determined in the solution digested using inductively coupled plasma (ICP- JY ULTIMA).

RESULTS AND DISCUSSION

Characterization of the synthesized hydrogel

Morphological analysis: The changes in the morphology of HG caused by the addition of MNPs were investigated by SEM images Fig. 1a-d. It was noticed that the HG grafted with MNPs has a spongy and porous structure compared to the bulky and solid structure of the HG sample. Furthermore, the higher magnification of the MNP-GH sample (Fig. 1d) shows spherical-like particles hydrogel which could be a result of the strong bonds formed between MNPs and the functional groups on the polymer surface (as confirmed by FTIR analysis) which had led to adhesion of the polymer molecules onto the MNPs nanoparticles. This kind is of porous rough surface desirable for enhancing water diffusion into the HG polymeric network, which can favour the water uptake of the superabsorbent hydrogels composites.

Brunauer-emmett-teller (BET) surface area analysis: Hydrogel is a water-absorbing polymer used to increase water holding capacity, increase water use efficiency, reduce soil erosion and nutrient losses and absorb the nutrients to gradually release them[22]. Therefore, the surface area and pore size volume of hydrogel were measured and illustrated in Table 2.

These results revealed that the combination of MNPs with HG resulted in 2.4 and 2.7 times the higher surface area and pore volume compared to HG, respectively. This reflects the role of MNPs in turning the bulk HG into a spongy/porous

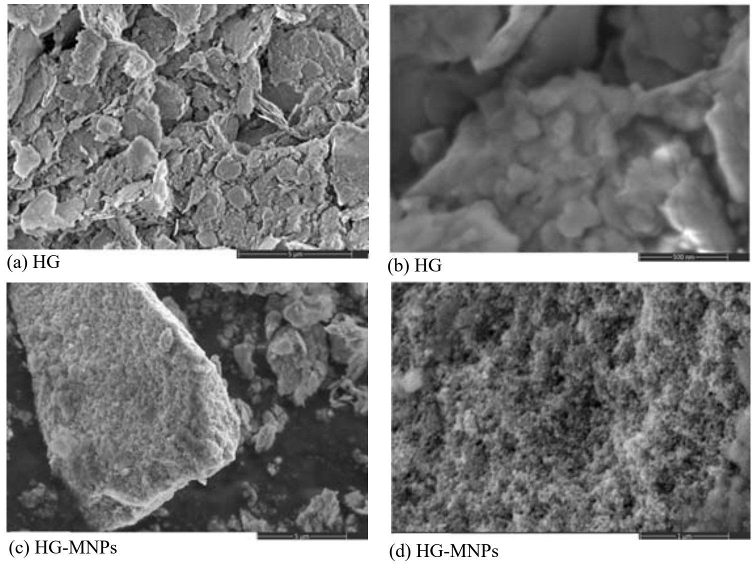

Fig. 1(a-d): SEM images of (a, b) HG and (c, d) HG-MNPs, respectively

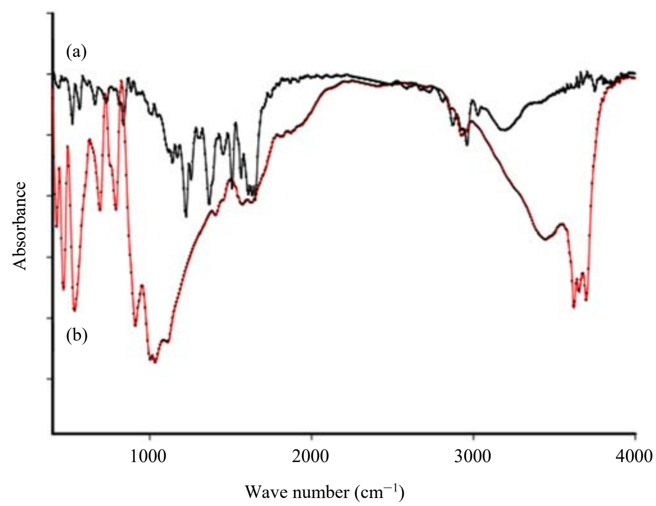

Fig. 2: FTIR spectra of (a) HG and (b) HG-MNP composite

Table 2: Data of surface area (BET), average pore radius (APS) and total pore volume (TPV) of HG and HG-MNPs samples

Samples	Surface area ($m^2 g^{-1}$)	Average pore radius (nm)	Total pore volume ($cc g^{-1}$)
HG	7.62	7.29	0.0278
HG-MNPs	18.65	8.02	0.075

structure as confirmed by the SEM images. The higher surface area not only improves HG swelling ratio but also increases the accumulation of nutrients within the HG matrix.

FTIR spectra analysis: To identify the existence of MNP on HG, FTIR analysis was executed to define functional groups functionalized onto synthesized materials.

The FTIR spectra of HG and HG-MNP were shown in Fig. 2a-b. The bands assigned to the main vibrational modes of SiO_2 and Si-O-Si bonds at 1100, 800 and 471 cm^{-1} are observed in both spectrums. These bands are attributed to asymmetric and symmetric stretching and angular deformation[23,24]. The broad bands at 3448 and 1627 cm^{-1} are assigned to hydroxyl groups. The band with low intensity at 617 cm^{-1} in the FTIR spectra of HG was a characteristic of crystalline cristobalite[25,26]. These bands were formed due to the existence of silt in the HG formation. Absorption peaks at 2924 and 2854 cm^{-1} region refer to the aliphatic C-H stretching[27]. Furthermore, the bands at 1458, 1396 and 1342 cm^{-1} indicated the existence of poly (acrylic acid) chains[23,24]. These spectra showed the appearance of the bands at 1111, 794 and 424 cm^{-1}, assigned to SiO_2 and Si-O-Si bonds[23,24]. The same pattern appeared in the MNP-HG spectrum (Fig. 2b). However, more bands appeared at 1404 and 1570 cm^{-1}, which were referred to as the symmetric and asymmetric carboxylate groups (COO-) and the intense peaks observed between 540 and 470 cm^{-1} were attributed to the stretching vibration mode associated to the metal-oxygen Fe-O bonds in the crystalline lattice of MNP. These results confirmed the chemical bonds formed between HG and MNPs in the composite.

Thermogravimetric analysis (TGA): The TGA and DTGA of both HG and HG-MNP were shown in Fig. 3. Both hydrogel samples exhibit two stages of the decomposition process as shown in Fig. 3a-b. The HG sample (Fig. 3a) showed an initial weight loss of 10.29% in the range of 37-146.7°C (~96.22°C), followed by 38.13% weight loss at 322.37°C and ends at 567.35°C (~473.27°C). The final residual left was 63.638% at 800°C. While less weighting loss happened with HG-MNP at higher temperature rates (Fig. 3b). Since, the initial weight loss of 3.6% happened in the range of 26.45-167.6°C (~68.16°C), followed by 13.8% weight loss started at 376°C and ended at 615.7°C (~508.5°C). The final residual left was about 79.2% at 800°C. The first stage between temperatures of 50 and 110°C accompanied by a minor weight loss is related to the water evaporation of samples[28]. Continuing the largest weight loss at higher temperatures rate can be attributed to the formation of anhydride by the association of the two neighbouring carboxylic groups on the polymer chains and elimination of water molecule, breakage of copolymer chains and destruction of the cross-linked network structure[29]. These results implied that HG-MNPs have greater thermal stability and higher moisture preserving capability compared with the HG sample (Fig. 3c). The HG-MNP sample demonstrated a lower weight loss within the temperature range of 30-615°C compared to the HG sample.

Swelling ratio analysis: The swelling ratio was measured according to Pan *et al.*[30]. Briefly, a dry synthesized hydrogel (1 g) was soaked in 500 mL of deionized water at room temperature for 4 hrs until reaching the swelling equilibrium. The swollen samples were then filtered through a 100-mesh screen and separated from the unabsorbed water. The water swelling ratio (W, g g^{-1}) of the synthesized hydrogel was calculated as follows:

$$W = \frac{(W_s - W_d)}{W_d}$$

where, W_s and W_d are the weights of the swollen and dry hydrogel (g), respectively.

Each sample was tested in triplicate. The results revealed that the HG-MNP sample has a higher swelling ratio of 65.43 g g^{-1} than that of the HG ratio of 45.54 g g^{-1}. These results can be attributed to the higher surface area and pore volume of HG-MNP compared to the HG. Similar results were reported by Dong *et al.*[31] as magnetic nanoparticles increased the mesoporosity of HG and ultimately increased its swelling ratio.

Effects of hydrogel application on plant growth and crop yield

Growth proprieties: The application of hydrogel leads to enhancement in water use efficiency by preventing water leaching and therefore decreasing the irrigation frequency[19]. The incorporation of MNP in HG increased HG-specific areas. This higher surface area can enhance the availability of nutrients in soil and nutrient uptake by plants, which was beneficial for plant morphology[32]. A pot experiment was conducted to study the effects of HG and HG-MNP on the morphological properties of eggplant under the stress of 75% from ET0 and 75% of the recommended N.P.K. doses. Figure 4a-f represented the plant highest (a), No. of branches (b), No. of fruits (c), Stem diameter (d), No. of leaves (e) and conc. of chlorophyll (f) of eggplant treated with HG and HG-MNP. The results revealed that plants treated with HG showed a significant increase in the number of the studied morphological properties (Fig. 4). In general, sandy soil has low water holding capacity and applying HG increased its water holding capacity due to its water swelling feature. These results were in agreement with those obtained by Ekebafe *et al.*[33], who reported that the hydrogels can be most beneficial when applied to sandy soil maximizing the crop yield despite climatic conditions. Consequently, the irrigation rate with 75% of ET0 showed insignificant effects on different morphological characteristics of the grown plant compared to 100% of ET0. The modified hydrogel (HG-MNP) showed a significant increase in different morphological parameters (e.g., stem diameter, No. of branches, No. of leaves and chlorophyll content) at both irrigation rates. This was attributed to the higher surface area and pore volume of HG-MNP that sustained the availability of water and nutrients for plants. Rui *et al.*[32] reported that MNPs increased root length, plant height, biomass and SPAD values of peanut plants. The MNP promoted the growth of peanuts by regulating phytohormone contents and antioxidant enzyme activity.

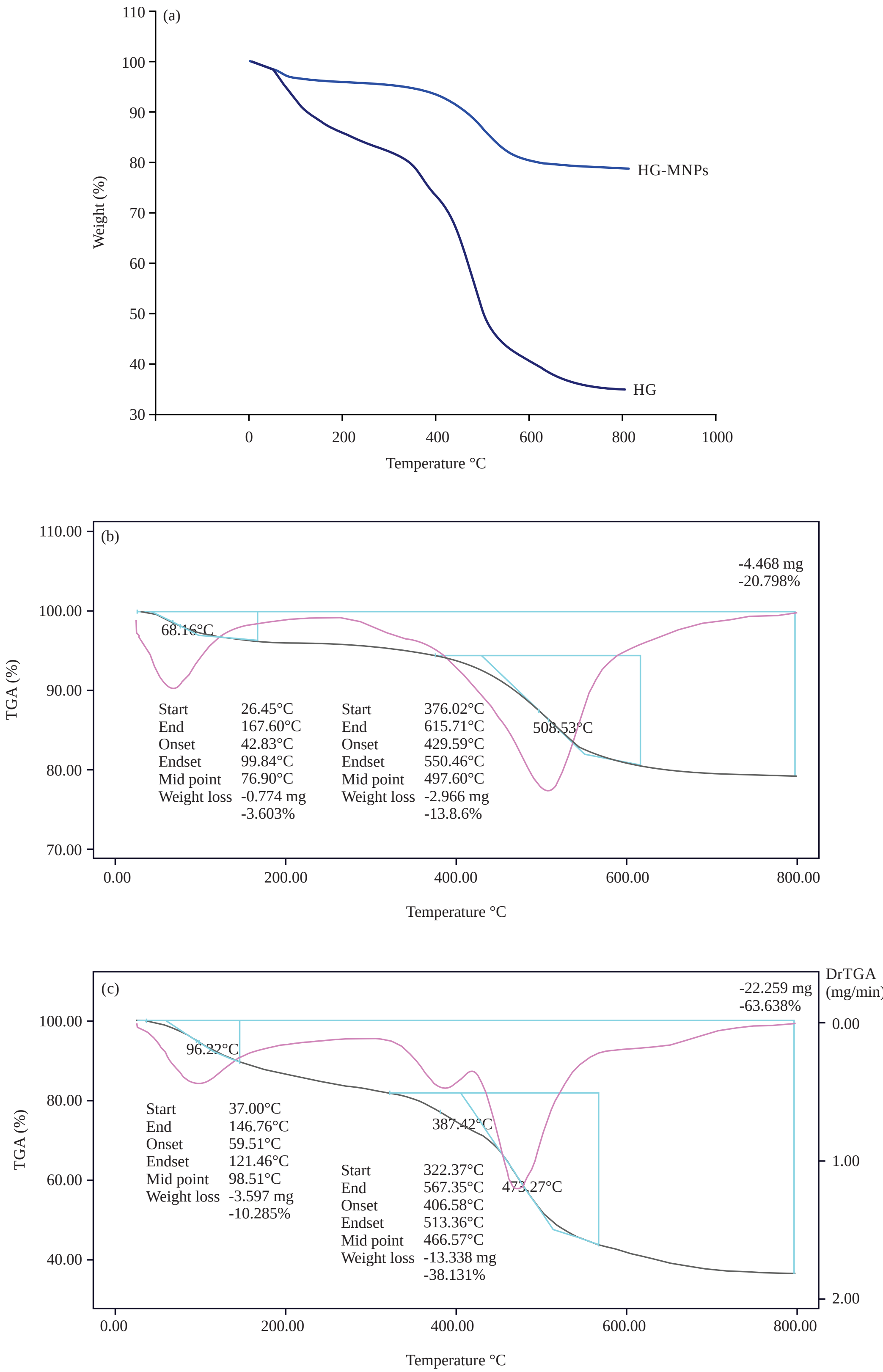

Fig. 3(a-c): (a) TGA comparison of both materials synthesized, (b) TGA % and DTGA (mg/min) for HG-MNP and (c) HG
x-axis: Temperature °C

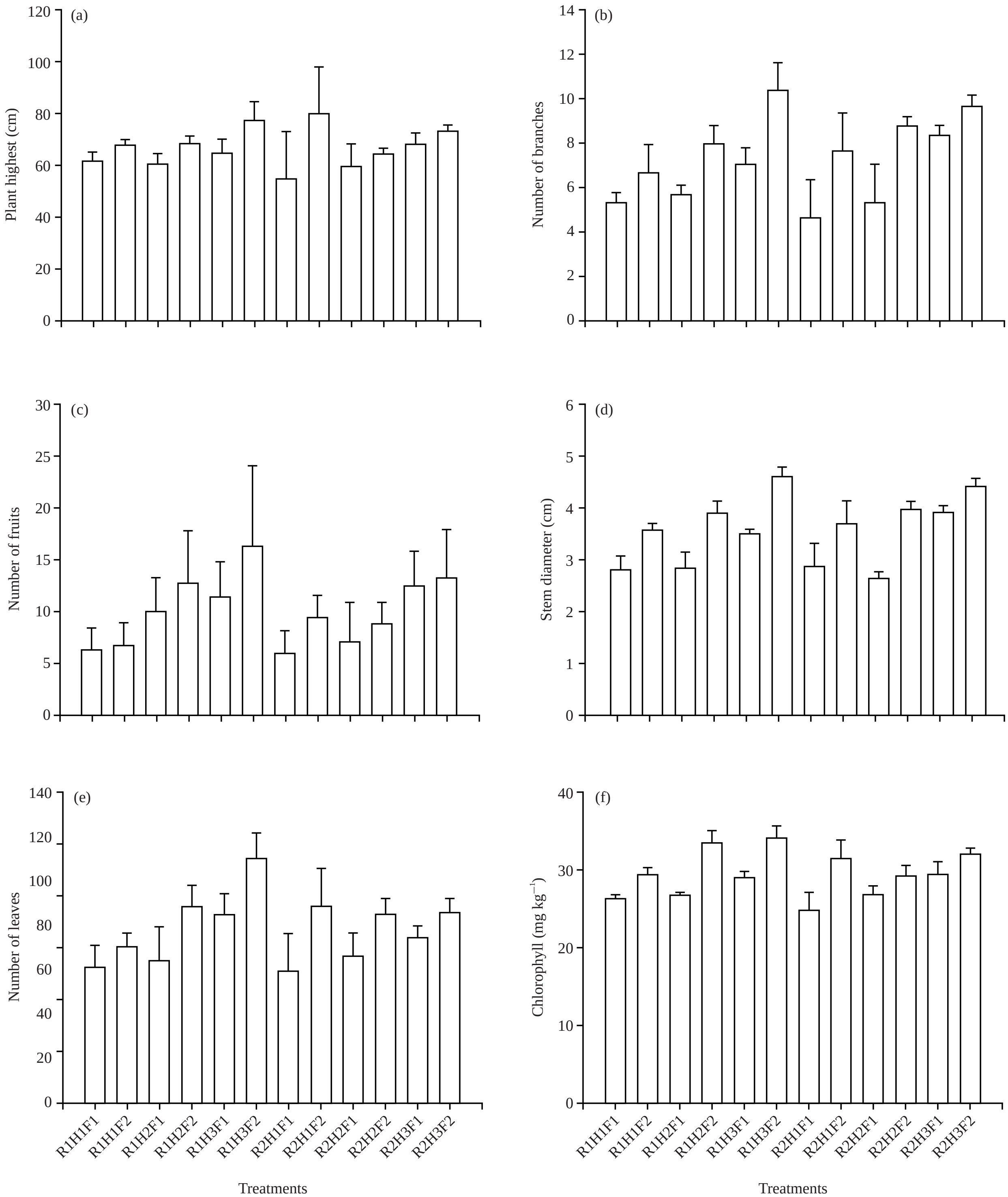

Fig. 4(a-f): Influence of HG and HG-MNP on (a) Plant highest, (b) Number of branches, (c) Number of fruits, (d) Stem diameter, (e) Number of leaves and (f) Concentration of chlorophyll

Yield attributes: Substantial improvement was achieved by the application of the HG-MNP. The yield of eggplant fruits generated from pots treated with non-modified hydrogel (HG), HG-MNP and without HG (control) was shown (Fig. 5). The pots treated with hydrogel (HG) achieved significant improvement in crop yield than control (without HG). These

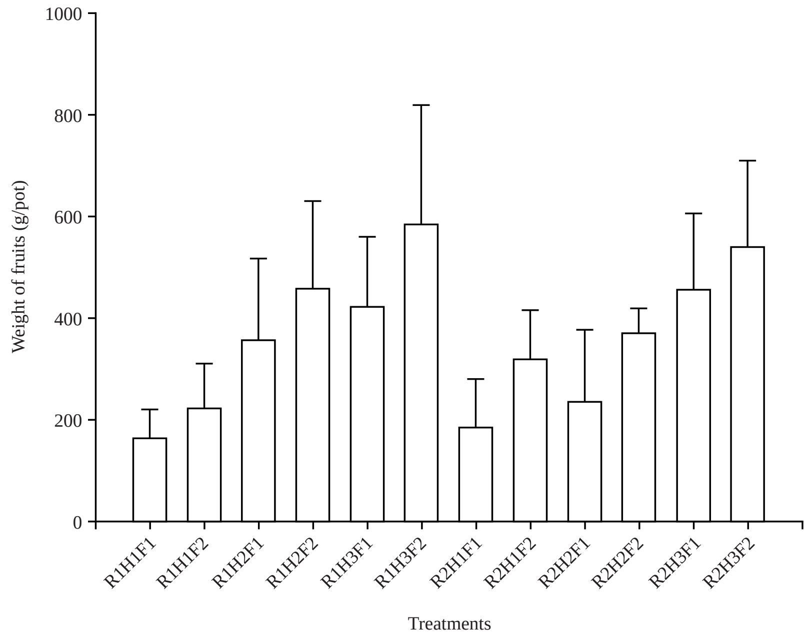

Fig. 5: Influence of synthesized materials on eggplant crop yield

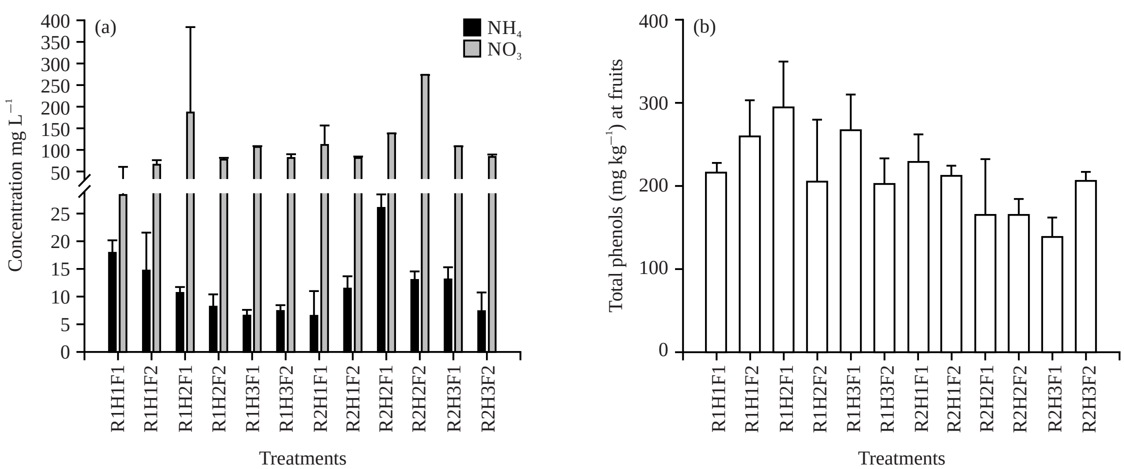

Fig. 6(a-b): Influence of synthesized materials on eggplant fruit content from (a) NH_4 and NO_3 and (b) Total concentration of phenols

results were attributed to the high swelling ratio of HG for water which enhances water use efficiency and water uptake by the plant as mentioned above. However, a remarkable improvement in crop yield was achieved using HG-MNP, which was expected because of its higher surface area and pore volume (Table 2). That enabled a higher holding capacity of water and nutrients and released slowly to plants during the growth period. Also, we noticed that irrigation rates haven't significant impacts on the crop yield, due to the highly swelling ratio of HG and HG-MNPs as mentioned before.

The influence of synthesized materials on eggplant fruit content from NH_4 and NO_3 and the total concentration of phenols was shown in Fig. 6(a-b). Phenolic acids are aromatic secondary metabolites biosynthesized by plants and are ubiquitous throughout the plant kingdom[34]. In recent years, phenolic acids have received considerable attention due to their health beneficial effect on protection against certain forms of cancers and cardiovascular diseases[35]. Eggplant (*Solanum melongena* L.) was ranked among the top 10 vegetables in terms of antioxidant capacity[36]. Eggplants are a rich source of phytochemicals including anthocyanins as well as phenolic acids (mostly hydroxycinnamic conjugates, with chlorogenic acid as the predominant compound[37]. These substances were substrates for the polyphenol oxidase enzyme whose activity leads to the rapid browning of cut or injured tissues. In addition, they contribute to the fruit's organoleptic properties because they generally impart a bitter taste and interfere with other molecules during the cooking process[38]. Therefore, total phenols were measured in eggplant fruits to be an indicator of yield quality. Generally, 100% of the recommended dose of N.P.K and irrigation achieved higher contents of phenolic acids. On the other hand, phenolic contents didn't influence significantly by the application of HG. While concentrations of nitrate were significantly decreased with both HG and HG-MNP treatment. These results were attributed to the slow release of NO_3 using HG and HG-MNP, which make NO_3 metabolism more efficient in plants.

CONCLUSION

Results concluded that incorporation of MNP into the hydrogel matrix can significantly improve the thermal stability and swelling ratio of the hydrogel sample. The results of the pot experiment conducted that eggplant treated with HG showed a significant increase in different morphological effects studied (plant high, stem diameter, number of branches, No. of leaves, No. of fruits and chlorophyll concentrations) and crop yield than control. In addition to, an essential improvement in morphological parameters and crop yield was achieved using HG-MNP rather than solely HG. This was explained by the higher swelling ration of HG-MNP and higher adsorption ratios of nutrients than solely HG, which ensure the plant needs water and nutrients along the length of the period of growth. These results indicated that the integration of HG with nanoparticles was found beneficial for agricultural applications, especially under stress irrigation conditions.

SIGNIFICANCE STATEMENT

Magnetic nanoparticles (MNPs) in the environment can lose their nano-size diameter and nano-scale properties due to aggregation. Moreover, MNPs aggregation might quickly be fixed into soil solids and lose their reactivity. Also, MNPs with minimized aggregation tendency can typically travel long distances and therefore, have a high impact on the surrounding environment. Therefore aggregation process governs MNPs mobility, reactivity and the associated risks in the agriculture system. Based on that we hypothesized the possibility to minimize the aggregation and maximize the reactivity of magnetic nanoparticles (MNPs) by grafting them into the hydrogel. Then, study the efficacy of grafting MNPs on hydrogel characteristics and to which extent can enhance the hydrogel adsorption capacity from water and nutrients during the pot experiment.

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