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ORIGINAL PAPER

Enhancing Soil Organic Carbon Content and Water Retention Using Polyvinyl Alcohol Cross-linked with Chitosan and Pectin

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Abstract

Soil organic carbon is considered a candidate without a substitute to be an important indicator of soil degradation by monitoring its amount and changes over time. Organic compounds such as chitosan (CS) and pectin (PC) can increase organic matter content in soils and provide a carbon source for microbes. Organic nanoparticles (NPs) were prepared by polymerization of CS and PC with polyvinyl alcohol (PVA), loaded with NPK nutrients, and evaluated by transmission electron microscope as well as zeta-potential (ZP). This study aims to test the effect of organic NPs on soil organic carbon (SOC) content, available water capacity (AWC), and growth of wheat plant. Thus, a pot experiment was conducted using clay soil. The treatments were NPK at two levels, viz., 50 and 85% of the recommended doses in combination with CS/PVA and PC/PVA as nano-carrier materials, as well as control treatment (85% NPK). Results showed that the loading of organic NPs with NPK nutrients obviously increases the solution stability and the positive as well as negative charges for CS/PVA (50.30 mV) and PC/PVA (− 17.80 mV), respectively. Furthermore, the using of NPK nano-fertilizers was significant for all the studied properties. Likewise, the addition of CS/PVA loaded with NPK decreased soil ZP at a range of − 13.00 to − 16.90 mV. Besides, it shows better carbon-cycling activity by increasing SOC at a range of 9.71 to 11.68 g kg^{-1}. The PC/PVA loaded with 50%NPK not only increases AWC with a rate of 18.23% but also sustains water-release synchronization to meet wheat plant demands.

Keywords Chitosan nanoparticles · Pectin nanoparticles · Soil organic carbon · Available water capacity · Zeta potential

1 Introduction

Achieving and sustaining food security is a global challenge that requires agricultural practices to be modified and may be revolutionized so as to effectively combat the negative pressure of increasing population, changing climate, and the loss of arable land (Abdel-Aziz et al. 2016). Although the soil system is a non-renewable resource, it is the most vital, interactive, and dynamic. These properties render the change in one property will affect other soil properties as well (Obalum et al. 2017). Thus, conservation of its quality, with these limited resources, is essential to support and sustain ecosystem services. There are several reasons for soil degradation, which leads to a decline in its quality (Lal 2009) and consequently negatively impacts agricultural production (Lamb et al. 2005). The degradation of soil can also dampen economic growth when agriculture is the main engine for economic development (Scherr 2001) such as in Egypt. Moreover, it was reportedly reported that it affected 33% of the Earth's land surface globally, which increased more than twofold to reach about 75% in recent decades (IPBES 2018).

Biological degradation is one of the most critical forms of soil degradation which reflects the depletion of the soil organic carbon (SOC) pools and the reduction in soil carbon sink capacity (Lal 2015). According to its influence on the soil's physical, chemical, and biological properties particularly its effects on aggregation, availability of plant nutrients and erosion control (Nciizah and Wakindiki 2015). The SOC always impacts various soil processes and properties as well as engages in multiple reactions in soil (Obalum et al. 2017). That is why soil organic carbon (SOC) is considered a candidate without a substitute to be an important indicator for the biological degradation of soil through monitoring its potential amount side by side with its

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changes over time. The organic nanoparticles (NPs) have a dynamic property and can change their shape and size with time through self-assembly or fusion among them. Also, it can load molecules either by conjugation in the core or on the surface or by physical encapsulation which renders them attractive systems for the delivery of molecules (Romero and Moya 2012). These organic NPs not only store a large quantity of moisture inside their molecular system but also provide a slow release of adsorbed water and nutrients to the soil (Yazdani-Pedram 2000), consequently increasing soil water holding capacity (Jamnongkan and Kaewpirom 2010; Tamura et al. 2006). These hydrophilic polymers contain functional groups such as OH and COOH which are known as hydrogels (Sugahara and Ohta 2001).

The research presents a suggestion to use nanotechnology to synthesize some organic NPs, such as nanochitosan (NCS) and nanopectin (NPC). Also, the paper studies the ability of these nanopolymers to provide the soil with organic carbon that is needed for the various processes in it. Organic compounds, e.g., polysaccharides, have been widely utilized for the production of natural nanoparticles (NPs) as a novel source for increasing the SOC stock in the soil in addition to their biodegradability and hydrophilic characteristics (de Moura et al. 2008). Chitosan is a polysaccharide polymer that is a deacetylated derivative of chitin. It is also considered the second most abundant bio-polymer after cellulose (Calabi-Floody et al. 2018). It is a natural cationic binary hetero-polysaccharide structurally composed of β(1–4) linked 2-acetamide-2-deoxygen-β-D-glucopyranose and 2-amino-2-deoxygen -β-D-glucopyranose units (Yu et al. 2019). Also, it has a majority of the glucopyranose residues in the deacetylated form (Calabi-Floody et al. 2018) and has a high N content of 6–9% (Yen and Mau 2007) and quantities of calcium mineral (Boßelmann et al. 2007).

Another compound is pectin, which is considered a natural anionic polysaccharide consisting of a large quantity of poly-D-galacturonic acid bonded via α-1,4-glycosidic linkage (Burapapadh et al. 2016). It can be utilized as a colloidal stabilizer, a gelling agent (Van Buren 1991), and a high adhesiveness (Cho et al. 2019). Furthermore, it is biocompatible and exhibits very low toxicity, which can be used in agriculture in a safe way.

The available water-holding capacity is the most ordinarily used parameter for quantifying the quantity of soil water that the soil can store and is readily available to plants. SOC and AWC are consequences of the soil development process. Furthermore, AWC could be considered a function of the soil organic matter (SOM) content (Dharumarajan et al. 2013; Yu et al. 2021), where the AWC affects and is affected by SOM changes owing to management practices and climate change (He et al. 2021). On the other side, high proportions of micro-aggregates (<250 μm) of clay soil rendered these soils prone to erosion and drought stress in summer drought periods due to the reduced ability to store plant-available water. Therefore, integrated management of heavy clay soil and understanding the mechanism of soil aggregate breakdown/development is necessary to facilitate soil physical–chemical processes under organic nanoparticles (NPs) application (Minasny and McBratney 2018).

Few studies have been conducted to detect the potential of using organic NPs prepared by chitosan and pectin materials as a source of soil organic carbon (Xu and Mou 2018). Also, these studies failed to consider the impacts of feedback from carbon stock (produced by applying alternative organic materials such as organic NPs) on soil water retention. Also, to understand their interaction with clay minerals charge and electrical double layer (EDL) such as ZP (Melo et al. 2021). Furthermore, recent studies suffer from a lack of information about the suitable concentration of loaded nutrients on nano-carrier materials, which causes changes in the zeta potential and stability of nanopolymers. Also, their effects on soil aggregation and water retention after adding them to the soil. Understanding the potential impact of changing soil organic carbon on plant water availability becomes essential for making informed decisions and managing soil. This study measures how variations in soil organic carbon affect AWC and plant water use. Our research focuses on three main questions: how much NPs affect the SOC content? How much water retention and aggregates formation depends on soil organic content? And what is the impact on plant water use if soil organic content changes?

First, we synthesize the NPs loaded with NPK with both concentrations of 50 and 85%. Then, we directly evaluate the effect of NP additions on SOC content, clay zeta potential, and aggregate formation after 40 days of wheat plant growth. Also, determining the degree to which organic carbon content affects soil water retention by identifying a correlation between measured AWC and SOC concentration and its threshold. Finally, determining the suitable concentration of NPK loading on NPs for the wheat plant grown in a heavy clay soil.

2 Materials and Methods

2.1 Materials

Polyvinyl alcohol (PVA) with a polymerization degree of 1700–1800 and 98–99 degrees of hydrolysis, chitosan (MW 71.3 kDa, deacetylation degree 94%), pectin (esterification degree 60–62%), potassium di-hydrogen phosphate (KH_2PO_4), and ammonium chloride (NH_4Cl) were purchased from Merck, Germany. All reagents were of analytical grade. Double-distilled water was utilized as the aqueous phase in all preparations. The composition of both chitosan and pectin are shown in Table 1.

Table 1 Chemical composition of chitosan and pectin compounds

Character		Chitosan (CS)	Pectin (PC)	Method/equipment
Moisture content	% (w/w)	6.4702 ± 0.28	5.4477 ± 0.15	Dry combustion using the Thermo Scientific Flash 2000 elemental analyzer
Carbon (C)		39.2327 ± 0.54	35.6748 ± 0.87	
Nitrogen (N)		7.2709 ± 0.21	1.2304 ± 0.13	
Barium (Ba)		0.0013 ± 0.0002	0.0008 ± 0.0001	Inductivity coupled plasma (Thermo Scientific™iCAP™ 7000 Plus Series ICP-OES)
Calcium (Ca)		0.5917 ± 0.01	0.2585 ± 0.001	
Magnesium (Mg)		0.2701 ± 0.001	0.0375 ± 0.0001	
Sodium (Na)		0.0704 ± 0.001	1.8676 ± 0.17	
Potassium (K)	mg kg^{-1}	ND	714.25 ± 2.76	
Copper (Cu)		28.31 ± 0.76	23.10 ± 0.54	
Iron (Fe)		312.73 ± 2.65	166.87 ± 1.38	
Manganese (Mn)		11.44 ± 0.32	4.71 ± 0.65	
Zinc (Zn)		57.72 ± 1.02	52.26 ± 0.95	
Nickel (Ni)		16.02 ± 0.11	4.49 ± 0.25	
Chromium (Cr)		29.08 ± 0.31	24.17 ± 0.43	
Cadmium (Cd)		1.29 ± 0.32	0.47 ± 0.01	
Lead (Pb)		ND	ND	

ND means not detected (below the detection limit); mean values ± SD, $n = 3$

2.2 Preparation of CS and PC/PVA Nanoparticles

The CS and PC/PVA nanoparticles were prepared using the procedure de Moura et al. (2008), with the detailed description as follows: 1.0 g of PVA was dissolved in 100 mL of double-distilled water and stirred for 12 h at 70 °C until the PVA was completely dissolved. The prepared PVA solution was used for the synthesis of CS and PC/PVA nanoparticles. The CS (1.0 g) was dissolved in acetic acid aqueous solution at 2% (v/v) for 12 h at 1000 rpm at a temperature of 70 °C under a magnetic stirring device. The PC (1.0 g) was dissolved in 100 mL of water under magnetic stirring for 10 h at 70 °C. The CS and PC/PVA nanoparticles were produced by the polymerization of PVA in CS and PC solutions under magnetic stirring for 12 h at 70 °C.

2.3 Loading of NPK Fertilizer in CS and PC/PVA Nanoparticles

In this study, NH_4Cl was used as sources of nitrogen (N) and KH_2PO_4 were used as sources of phosphorus (P) and potassium (K). The loading of NPK fertilizers in CS and PC/PVA nanoparticles was produced by dissolving different amounts of NPK into nanoparticle solutions under magnetic stirring for 4 h at 25 °C. The incorporation of NPK into the nanoparticles gives those concentrations: (i) 85% from recommended doses (RD): 136 ppm N (0.519 g NH_4Cl), 75 ppm P and 100 ppm K (0.348 g KH_2PO_4). (ii) 50% NPK were 80 ppm N (0.251 g NH_4Cl), 45 ppm P and 60 ppm of K (0.209 g KH_2PO_4) with an average recovery ranged between (98.231–101.87%).

2.4 Characterization of CS and PC/PVA Nanoparticles with NPK Fertilizers

The morphology, size, and stability of the synthesized CS and PC/PVA nanoparticle suspensions with N, P, and K were evaluated by transmission electron microscope (TEM) analysis using (JEOL- JEM-2100, Japan). CS and PC/PVA nanoparticles with NPK fertilizers were sonicated to prevent the agglomeration of the nanoparticles on the copper grid. Thin film of the sonicated nanoparticles was prepared on a carbon-coated copper grid; then, it was dried under a mercury lamp for 5 min for TEM. The scale bar of measurements was 100 nm with a magnification range of 40,000 ×. The nanoparticle sizes were determined directly from the figure using the Image-Pro plus v4.5 software. Malvern Zeta sizes Nano ZS90 (Malvern Instruments Ltd., UK) was used to measure ZP of CS and PC/PVA nanoparticles with NPK fertilizers at 25 °C. In short, ZP cells were washed with ethanol and double-distilled water followed by nanoparticle samples.

2.5 The Pot Experiment

A pot experiment was conducted under outdoor conditions at the Agriculture Research Station of Mansoura Univ., Dakahlia Governorate, Egypt. Each pot was filled with 250 g clay soil. The nano-NPK fertilizers were applied to soil. The initial soil physical and chemical analyses of the studied soil particles less than 2 mm yielded the following results as shown in Table 2.

The experimental design was completely randomized (CRD), with three replicates. It consists of two nano-carrier materials (CS and PC/PVA) and two NPK rates (50 and 85% of

Table 2 Physical and chemical properties of the studied soil

Soil attribute	Unite	Value	Assessment	Method/equipment	Reference
pH†	-	7.99 ± 0.21	Alkaline	pH-meter (Jenway 3505 pH/mV/Temperature Meter	Jackson (1967)
Electrical conductivity (EC)††	dS m^{-1}	1.04 ± 0.14	Non-saline	EC-meter (Jenco 3173)	
Organic carbon (OM)	%	0.82 ± 0.03	Low	Dry combustion using the Thermo Scientific Flash 2000 elemental analyze	ISO 10694 (1995)
Calcium carbonate ($CaCO_3$)	%	1.15 ± 0.12	Non-calcareous	Calcimeter method	Piper (1966)
Bulk density (ρ_b)	Mg m^{-3}	1.15 ± 0.05	-	Cylinder method	Piper (1966)
Field capacity (FC)	%	37.6 ± 0.81	-	Pressure chamber apparatus	Klute (1986)
Zeta potential (ζ)	mV	− 20.2 ± 0.32	-	Malvern Zeta Sizes Nano ZS90	
Particle size distribution			Clay texture	Pipette method	Piper (1966)
Sand	%	27.27 ± 0.78			
Silt	%	32.50 ± 1.04			
Clay	%	49.23 ± 1.28			

† Measured in soil paste, †† Measured in saturation extract at 25 °C; mean values ± SD, $n = 3$

recommended doses), as well as an 85% control treatment with conventional fertilizers $(NH_4)_2SO_4$, $Ca(H_2PO_4)_2$, and K_2SO_4. Wheat plant (*Triticum aestivum*, var., Giza 168) was sown on November 16, 2019, for 40 days, with basic fertilization of 180, 15, and 90 kg h^{-1} N, P, and K, respectively, by using five seeds per pot. The nano-fertilizers were synthesized according to the nutrient requirements of wheat plant. The synthesized CS and PC/PVA nanoparticles loaded with N were applied by diluting 0.8 mL of each nanosolution with 70 mL of fresh water to maintain the soil water content at FC. Nano-PK was added after 20 days of planting. The added volume of NPK nanofertilizer (1.6 mL) was calculated to contain 50% and 85% of the recommended doses with the mentioned concentrations by using two solutions, N separately and PK together. Consequently, the rate of application will be 0.8 mL pot^{-1} for each solution. For this period of plant growth, the wheat plant needs only 20% of the N amount according to the agricultural system of wheat plants in Egypt. The moisture content of the studied soil was maintained at field capacity (FC) with a moisture level of 37.6% throughout the experiment. Total organic carbon in synthesis nano-fertilizers was 10.25 and 11.45 g kg^{-1} for CS/PVA and PC/PVA, respectively.

2.6 Soil Analytical Methods

The collected soil samples were prepared according to ISO 11464 (2006). The soil organic carbon (SOC, g kg^{-1}) was measured according to ISO 10694 (1995).

The available water capacity (AWC%, w/w) is generally calculated from the difference between field capacity (FC) and permanent wilting point (PWP) at a soil depth of 15 cm.

$$\mathbf{AWC = FC - PWP} \tag{1}$$

The pressure chamber apparatus was used to determine the soil water retention content at FC (− 33 kPa) and PWP (− 1500 kPa) according to Klute (1986). The soil aggregates were examined by mean weight diameter (MWD) which calculated according to Kemper and Rosenau (1986):

$$\mathbf{MWD} = \sum_{i=1}^{n} X_i W_i \tag{2}$$

where X_i is the mean diameter of any size range of aggregates separated by sieving (mm) and W_i is the weight of the aggregates in that size range (g).

2.7 Quality Control and Assurance

All chemicals used in the equipment calibration were purchased from Merck KGaA, Germany. Average recovery was adjusted between 99.05 and 101.68%. The accuracy of SOC was verified by calibrating the equipment with a certified reference material (Aspartic acid, $C_4H_7NO_4$). The pH-electrode was calibrated by two Merck standard buffer solutions at 20 °C: KH_2PO_4/Na_2HPO_4 (pH 7) and $H_3BO_3/KCl/NaOH$ (pH 10), both of them directly traceable to primary SRM from NIST/PTB, and the EC-electrode was internally calibrated by standard solution (HANNA, HI 7031, 1413 µS cm^{-1}) at 25 °C. The accuracy of inductivity coupled plasma (ICP-OES) was verified by the calibration curves of standard solution (ICP multi-elements standard solution IV, Merck, 1000 mg l^{-1}). The precision of the analytical methods was obtained by repeating the samples thrice (repeatability test) and expressed as the standard deviation (SD). Furthermore, all the research analyses were subjected to a laboratory control sample (LCS) for validation and checked by the quality control charts.

2.8 Statistical Analyses

Experimental data were analyzed as a one-way analysis. The analyses of variance ANOVA and standard deviation values were calculated using the CoStat software package (Version 6.30, CoHort, USA, 2004). The Duncan test was used to compare the treatments at a 95% significance level ($p < 0.05$). Pearson correlations and nonlinear regression between AWC and SOC were established at the $p < 0.05$ probability level.

3 Results

PVA has excellent processing properties and physicochemical stability. In the synthesis of CS and PC nanoparticles, it was observed that adding CS or PC solutions to PVA changed the final solutions from a clear to a turbid suspension. This transformation considers an indicator of the formation of CS and PC nanoparticles with PVA.

3.1 Characterization of CS and PC/PVA Nanoparticles

Micrograph recorded from a drop-coated film of CS and PC/PVA nanoparticles loaded with NPK fertilizers (at a rate of 50%) was characterized by TEM as mentioned in (Fig. 1). TEM analysis showed a quite spherical shape with a homogeneous morphology with the ordinary size distribution. The mean diameter of CS/PVA nanoparticles ranged from 7 to 10 ± 0.5 nm and from 6 to 11 ± 0.5 nm for PC/PVA nanoparticles loaded with N (Fig. 1 A and B). On the other hand, after loading with P and K, the CS/PVA nanoparticle diameter was approximately 9 ± 0.5 nm and the PC/PVA nanoparticle size ranged from 12.12 to 27.39 ± 1.0 nm (Fig. 1 C and D).

The amorphous nature of CS and PC/PVA nanoparticles loaded with NPK fertilizers (at a rate of 50%) is also proved by the selected area electron diffraction pattern (EDP), as shown in Fig. 2. The CS and PC/PVA nanoparticles containing NPK fertilizers are crystalline, as can be seen from the selected area EDP recorded from one of the nanoparticles in the aggregates. The brightest ring

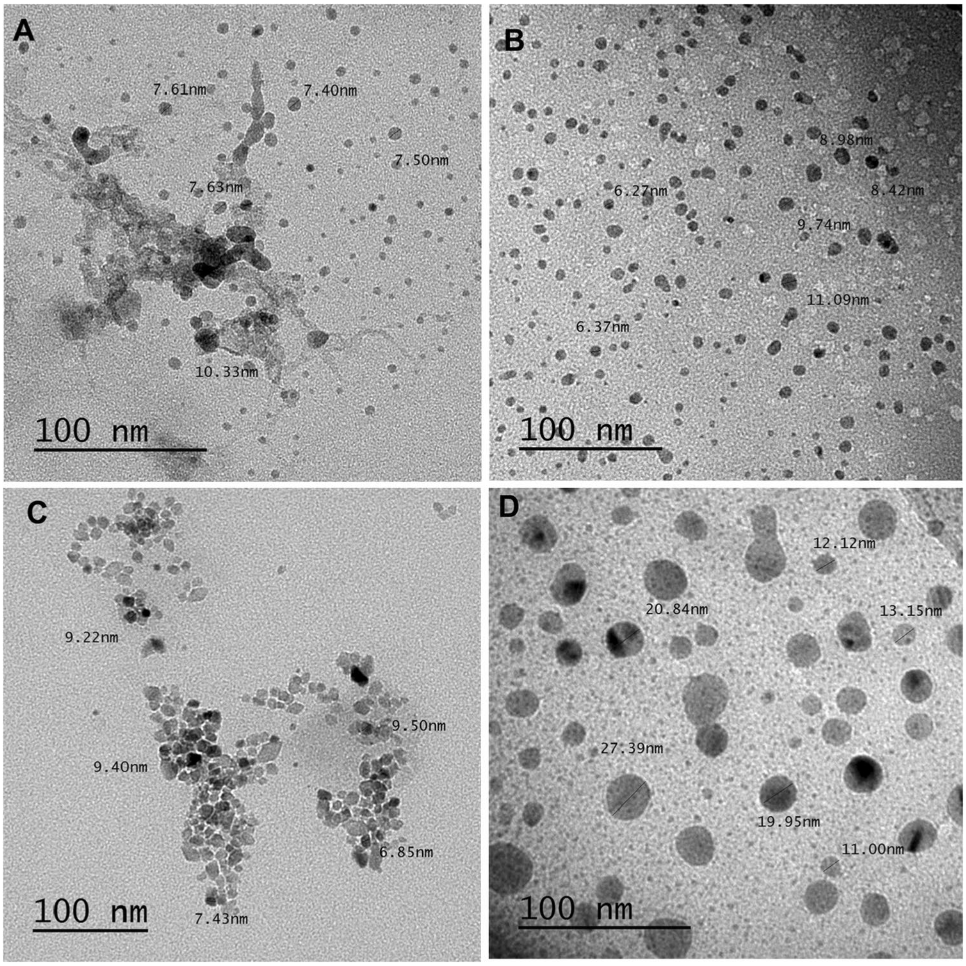


Fig. 1 TEM image obtained for CS/PVA (**A**), PC/PVA (**B**) loaded with nitrogen (N) and CS/PVA (**C**), and PC/PVA (**D**) loaded with phosphorus (P) and potassium (K)

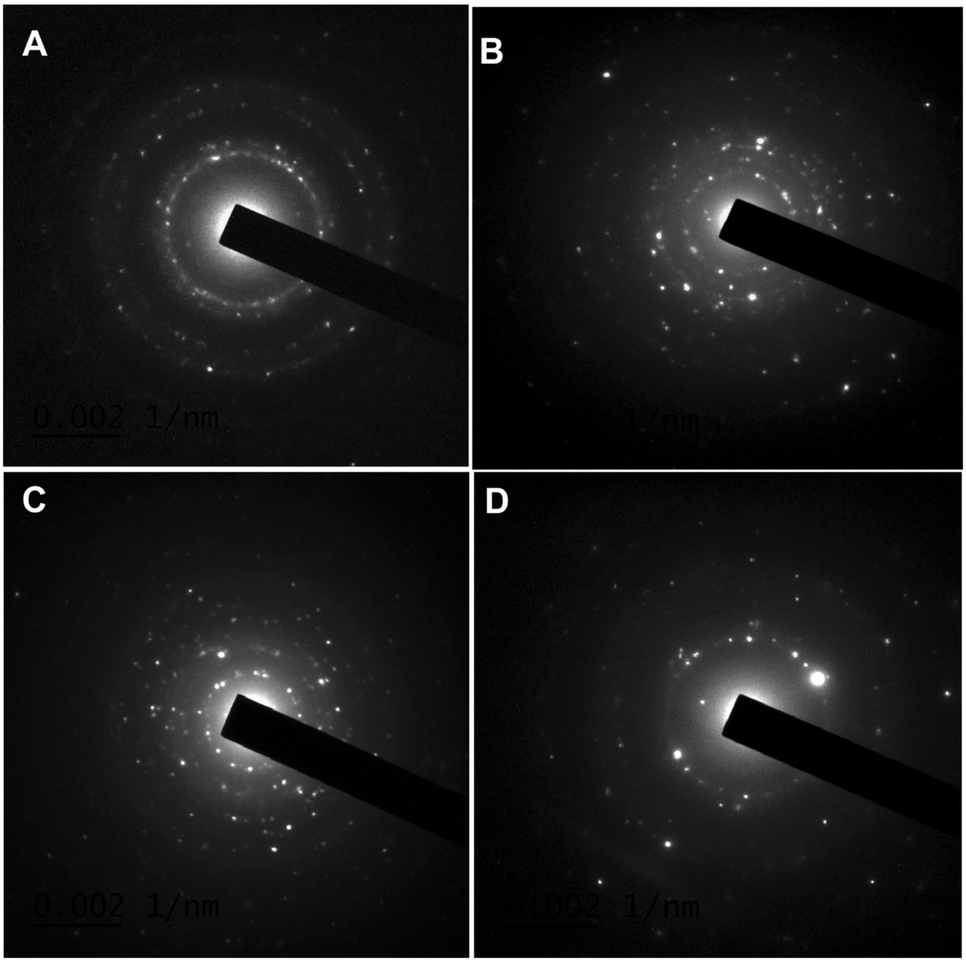


Fig. 2 Selected area electron diffraction pattern obtained for CS/PVA (**A**), PC/PVA (**B**) loaded with nitrogen (N) and CS/PVA (**C**), and PC/PVA (**D**) loaded with phosphorus (P) and potassium (K)

may strongly correspond to (111) reflection of hexagonal NPK, and the rings of lower brightness probably allot to (200), (220), and (311) (Ahmed and Sharma 2012).

Zeta potential (ζ) as a function of the soil reaction (pH) for the CS and PC/PVA nanoparticles and it could be seen that the positive values (7.95 ± 1.23) and (50.3 ± 4.05) of the ZP for CS/PVA loaded with N and PK (50%), respectively. In contrast, the negative ZP values (– 3.94 ± 0.67) and (– 17.8 ± 4.16) are observed in the case of PC/PVA incorporated with N and PK (50%), respectively (Fig. 3).

Data in Fig. 4 illustrate the alkalinity and salinity of different treatments after dilution with 500 ml tap water. The salinity of CS-PC/PVA nanoparticles loaded with NPK decreased significantly ($p < 0.05$) with diluting by irrigation water compared to the treatment of conventional fertilizers (85%NPK), while these nano-solutions showed a very slight effect on alkalinity. The nanoparticles loaded with 85% NPK have a reversible effect on pH value which is increased with dilution by irrigation water.

3.2 Plant Biomass

The additions of organic NPs significantly increased the fresh and dry biomass (Table 3). Maximum fresh and dry biomass of wheat plant were 26.97 and 5.23 g pot^{-1}, respectively, which were produced by using CS/PVA loaded with 50% NPK. These results were very close to the control (85% NPK).

3.3 Zeta Potential and Soil Organic Carbon (SOC)

The zeta potential of treated soil with organic NPs varied from – 16.90 to – 31.07 mV, according to the nanomaterial type and loaded NPK concentration. The soil application of CS/PVA showed low ZP at a range of – 14.95 mV. In contrast application of PC/PVA showed high ZP at a range of – 26.62 mV (Table 3).

The organic NPs loaded with NPK had a very significant effect ($p < 0.05$) on raising the SOC in the studied soil (Table 3).

Fig. 3 Zeta potential obtained for CS/PVA (**A**) and PC/PVA (**B**) loaded with 50% phosphorus (P) and potassium (K)

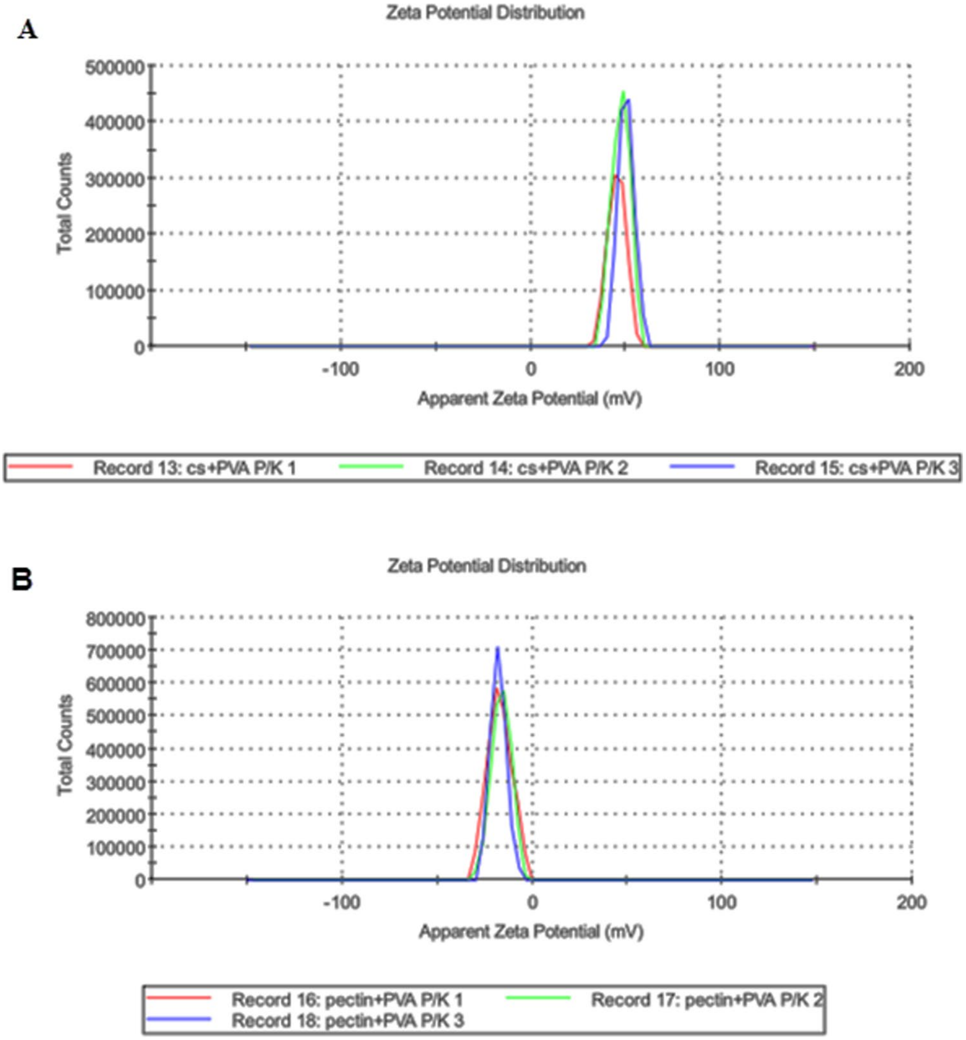


Fig. 4 Salinity and alkalinity of nanoparticles after loading and diluting for irrigation

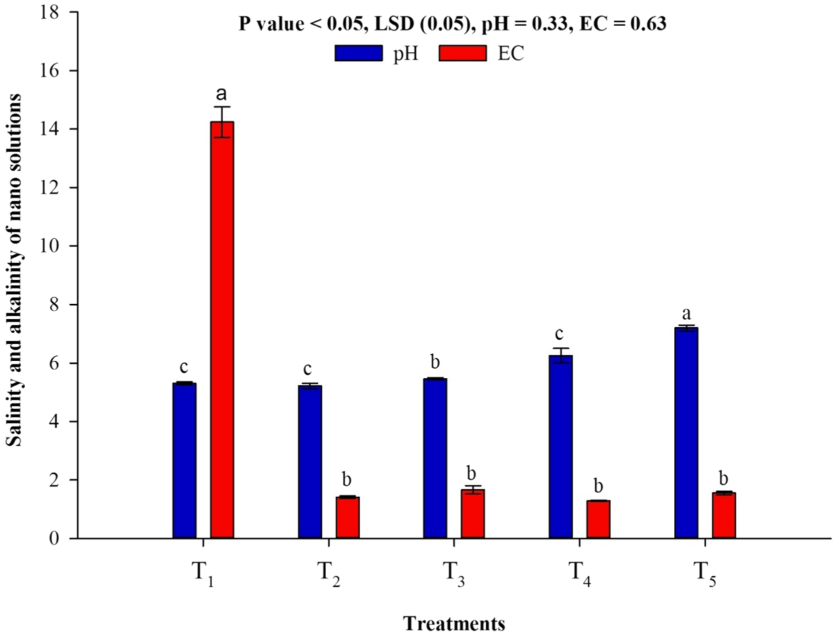


Table 3 Plant biomass, zeta potential, and soil organic carbon as affected by nano-fertilizers applications

Treatments	Fresh weight (g pot^{-1})	Dry weight (g pot^{-1})	Zeta potential (mV)	Soil pH (before)	Soil pH (after)	SOC (g kg^{-1})
(T_1) 85% NPK (control)	$26.85^{a} \pm 1.65$	$4.45^{ab} \pm 0.25$	$-20.33^{c} \pm 0.38$	8.62	8.65	$5.39^{d} \pm 0.03$
(T_2) CS + 50% NPK	$26.97^{a} \pm 1.67$	$5.23^{a} \pm 0.33$	$-16.90^{b} \pm 0.30$	8.40	8.45	$10.73^{bc} \pm 0.01$
(T_3) CS + 85% NPK	$22.07^{b} \pm 1.20$	$3.80^{bc} \pm 0.71$	$-13.00^{a} \pm 0.30$	8.54	8.56	$10.39^{c} \pm 0.01$
(T_4) PC + 50% NPK	$23.47^{b} \pm 0.83$	$4.05^{abc} \pm 0.21$	$-22.17^{d} \pm 0.06$	8.81	8.86	$11.68^{a} \pm 0.03$
(T_5) PC + 85% NPK	$20.80^{b} \pm 0.94$	$3.09^{c} \pm 0.11$	$-31.07^{e} \pm 0.85$	8.94	8.98	$11.26^{ab} \pm 0.02$
LSD ($p < 0.05$)	3.36*	ns	0.83**	-	-	0.54**

Mean values followed by dissimilar letters were significantly different at $p < 0.05$ according to the Duncan test and LSD least significant difference test; mean ± SD, $n = 3$

CS chitosan, *PC* pectin, *SOC* soil organic carbon, *ns* non-significant

*$P < 0.05$, **$P < 0.01$

The PC/PVA recorded the highest value of SOC by 116.4 and 108.5% for 50 and 85% NPK levels, respectively. Table 3 illustrates that the SOC in all the studied soil increased in the order of PC/PVA (11.47) > CS/PVA (10.56) > control (5.40) g kg^{-1}.

3.4 Soil Aggregates and Available Water Capacity (AWC)

Data in Table 4 shows the aggregate size distribution of the studied soil which ranged from more than 1000 to less than 53 µm. Generally, the PC/PVA (85%NPK) treatment recorded the highest macro-aggregates < 1000 µm, while CS/PVA (50%NPK) treatment was the highest one in a range of 1000–500 µm, while the micro-aggregates less than 250 µm prevailed at the control treatment with conventional fertilizers.

The macro-aggregates of more than (> 250 µm) were dominated at all the treatments under the studied soil except the control. Furthermore, organic NPs have improved macro-aggregate (> 250 µm) percentage. The soil macro-aggregate by a size (> 250 µm) incremented for all organic NPs treatments, while micro-aggregates by a size (< 250 µm) incremented for the control treatment (Table 4). The treatments which received organic NPs were similar in the formation of macro-aggregates. It was noticed that a relative increase compared to the control treatment (T_1). The recorded values were 57.44, 57.10, 56.01, and 54.99% for T_3, T_2, T_4, and T_5 respectively. As well as PC/PVA (85% NPK) recorded the highest mean weight diameter (MWD) of 0.696 mm followed by PC/PVA (50% NPK) of 0.671 mm.

Furthermore, data in Fig. 5 illustrated the effect of the nanoparticles application on the amount of water retention (per cent mass) at field capacity (FC) and wilting point (WP) of the experimented soil. The organic NP additives caused an increase in soil water retention at FC (− 33 kPa), WP (− 1500 kPa), and AWC. The treatments of CS and PC/PVA loaded with 85% NPK recorded the highest values for FC and WP. However, the increase of AWC was observed at the treatments received a low rate of NPK (50%), such as T_2 (18.64%) and T_4 (18.23%) as compared with the un-amended treatment (T_1—17.09%).

As expected, there is a positive correlation (0.998) between the SOC and AWC (Fig. 6; $r^2 = 0.999$). SOC incremented (in the range of 5.39–9.71 g kg^{-1}) as AWC incremented obviously (when the value of AWC is more than 17.57%). SOC incremented (in the range of

Table 4 Aggregate size distribution with concentration over two types of organic nanoparticles

Treatments	Size distribution of aggregates (%)						MWD (mm)
	> 1000 µm	1000–500 µm	500–250 µm	250–106 µm	106–53 µm	< 53 µm	
(T_1) 85% NPK (control)	$17.90^{d} \pm 0.71$	$21.17^{c} \pm 1.31$	$17.61^{a} \pm 1.09$	$30.09^{a} \pm 0.63$	$9.19^{a} \pm 1.54$	$4.03^{a} \pm 0.94$	$0.366^{c} \pm 0.015$
(T_2) CS + 50% NPK	$45.37^{bc} \pm 0.64$	$33.71^{a} \pm 0.41$	$13.20^{b} \pm 0.73$	$5.39^{c} \pm 0.52$	$1.75^{b} \pm 0.10$	$0.76^{b} \pm 0.05$	$0.660^{b} \pm 0.008$
(T_3) CS + 85% NPK	$44.94^{c} \pm 0.17$	$33.60^{a} \pm 0.35$	$14.13^{b} \pm 0.56$	$5.43^{c} \pm 0.13$	$1.15^{b} \pm 0.06$	$0.67^{b} \pm 0.01$	$0.660^{b} \pm 0.003$
(T_4) PC + 50% NPK	$46.70^{b} \pm 0.90$	$32.19^{a} \pm 0.55$	$12.68^{b} \pm 0.05$	$5.75^{c} \pm 0.40$	$1.85^{b} \pm 0.01$	$0.82^{b} \pm 0.01$	$0.667^{b} \pm 0.006$
(T_5) PC + 85% NPK	$50.89^{a} \pm 0.62$	$30.06^{b} \pm 0.48$	$10.12^{c} \pm 0.12$	$6.98^{b} \pm 0.01$	$1.31^{b} \pm 0.18$	$0.65^{b} \pm 0.07$	$0.693^{a} \pm 0.004$
LSD ($p < 0.05$)	1.68**	1.83**	1.64**	1.06**	1.78**	1.09**	0.02**

Mean values followed by dissimilar letters were significantly different at $p < 0.05$ according to the Duncan test and LSD least significant difference test; mean ± SD, $n = 3$

CS chitosan, *PC* pectin, *MWD* mean weight diameter, *ns* non-significant

*$P < 0.05$, **$P < 0.01$

Fig. 5 Available water capacity as affected by nano-fertilizer applications

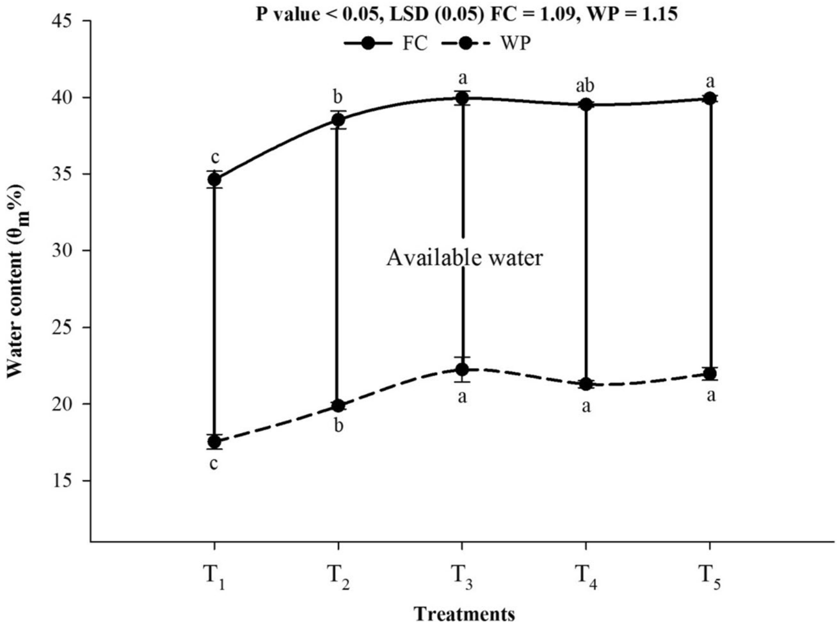
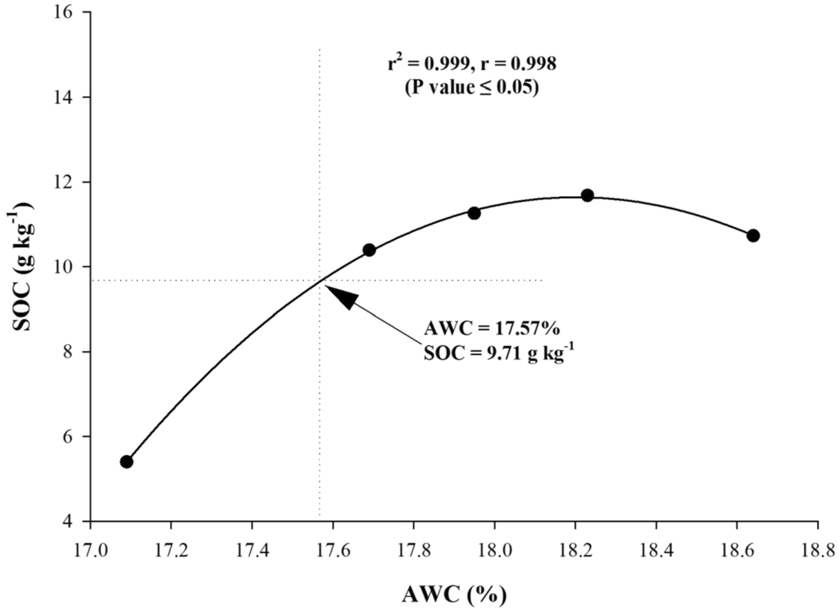


Fig. 6 Soil organic carbon (SOC) and its relation to available water capacity (AWC)



9.71–11.26 g kg^{-1}) as the AWC incremented slightly (when the value of AWC is less than 17.57%), and thus, the threshold for AWC was set as 17.57%. At a depth of 15 cm, the relationship between the SOC and AWC created a convex curve, and inflexion point occurred at 17.57%. Furthermore, the polynomial regression showed that the sensibility of SOC to any changes in AWC decreased as the value of AWC increased. The polynomial regression equation (Fig. 6) is:

$$\mathbf{SOC} = \boldsymbol{F}_0 + \boldsymbol{a}(\mathbf{AWC}) + \boldsymbol{b}(\mathbf{AWC})^2 + \boldsymbol{c}(\mathbf{AWC})^3 \quad (3)$$

where F_0, a, b, and c are fitting parameters.

4 Discussions

The characterization of nanoparticles by TEM, as mentioned in part 3, illustrated the success of the nano fertilizer synthesis at a range of nanoparticles. The mechanism for the formation of the organic NPs occurs through intra- and intermolecular linkages between PVA hydroxyl groups (-OH) and amino (-NH_2) and carboxyl groups (-COOH) of CS and PC, respectively, during the polymerization of PVA (de Vasconcelos et al. 2006; Zhu et al. 2014). The estimation of the zeta potential of nano solutions showed the positive value of

CS/PVA loaded with NPK indicates that the surface of the nanoparticles is positively charged due to the cationic characteristics of CS at pH ranging from (2 to 5.5). It is evident that the system has a certain instability. On the contrary, the negative value of PC/PVA loaded with NPK suggests that the surface of the nanoparticles is negatively charged due to the ionization of the (-COOH) groups of PVA and PC at pH greater than 5.5 (Corradini et al. 2010; Mittal et al. 2014).

Besides, the concentration of loaded NPK on the nanocarrier materials affected the NP charge. The ZP of CS and PC/PVA loaded with 50% PK (50.30 and − 17.80 mV), respectively, were found to be higher than that of CS and PC/PVA loaded with 50% N (7.95 and − 3.94 mV), respectively. This reaction implies that the incorporation of potassium dihydrogen phosphate (KH_2PO_4) renders the organic NPs more electrically stabilized leading to reduce the flocculation tendency in suspension. Shankar et al. (2004) confirm these results, which found that zeta potential (ζ) higher than 30 mV or lesser than − 30 mV is expressive of a stable system. The stability of a colloidal media is a result of the EDL on the surface of the colloidal particles. Adding an electrolyte to a colloidal media inhibited the diffuse EDL and decreases the ZP and the electrostatic repulsion between the clay particles and aggregates of the colloid particles. As a result of the sensitivity of the colloid to the opposite sign of ions, the ions are incorporated into the fixed part of the EDL, reducing the total charge of the clay particle. In the same way, positive ions will make the negatively charged colloidal dispersion less stable (Corradini et al. 2010).

The addition of nanofertilizers has caused significant changes in the soil due to their important properties. Firstly, it affects the charges of clay minerals, especially those with a positive charge such as CS/PVA, which were measured by the zeta potential property. Clay zeta potential influences the soil's internal forces, the electrostatic fields, and aggregate stability. In this study, ZP of heavy clay soil was compared as a result of using two types of nano-carrier in combination with two concentration treatments including (CS + 50%NPK), (CS + 85%NPK), (PC + 50%NPK), and (PC + 85%NPK). The PC/PVA (50%NPK) treatment, which had the highest concentration of SOC (11.68 g kg^{-1}), caused a clay ZP of − 22.17 mV with the ability to form macro aggregates larger than 250 µm with 91.57%. Variations in ZP of clay minerals among NP treatments might be attributed to their different charge before use in soil. However, the silica surface charge of clay minerals is negatively practically in the whole range of studied pH (8.40–8.98); the changing of clay ZP of the studied soil might be related to the following reasons: (1) The presence and concentration of PVA in the organic NP formation have significant influence in the increasing ZP value in acidic part and decreasing in alkaline part (Moayedi et al. 2011); data proved that both PC/PVA and CS/PVA trended to alkaline part (8.40–8.98). (2) The increasing of pH value induces stronger electrostatic repulsion between the negatively charged surface and dissociated acetate groups in PVA macromolecules (Moayedi et al. 2011). (3) CS/PVA nanoparticles have a positive charge and a negative charge for PC/PVA. (4) The application of all organic NPs increases SOC and the amount of macro-aggregates portion (> 250 µm) of studied soil. (5) The adsorption of organic molecules such as organic NPs increases the repulsive forces between clay particles, rendering the suspension dispersed (Nguyen et al. 2013). For these reasons, the CS/PVA decreased the clay ZP consequently increasing the AWC and wheat growth. In contrast, PC/PVA increased the clay ZP.

Furthermore, the chitosan compound contains a proportion of calcium content reaching (0.59 ± 0.01) %; the released Ca^{+2} will be adsorbed on clay surface formed Ca-clays. With more alkaline solution, the $CaCO_3$ has been formed which led to charge reduction on the clay surface, resulting in reduction of ZP and increasing flocculation of the clay particles (Chorom and Rengasamy 1995). On the other hand, the pectin compound has a low proportion of Ca and a high proportion of Na reaching (0.26 ± 0.001) and (1.87 ± 0.17) %, respectively, consequently an excess of negative charges. Despite the addition of PC/PVA particularly at 85% NPK increased the clay ZP according to the mentioned reasons, it was able to form a great proportion of macro-aggregates > 250 µm and high MWD. These results illustrated that the high adhesiveness and gelling properties of nano-pectin overcame the dispersion effect caused by increasing clay ZP.

AWC measures the capability of the soil to retain water and reflects the effects of soil structure, textural, management practices, and its content of SOM (Arya et al. 2008). Some studies have proved that the soil AWC is a function of the SOC content (Dharumarajan et al. 2013; Yu et al. 2021). Consequently, in this study, soil water retention could be increased by the addition of organic NPs. When soil organic carbon increases, so do the corresponding AWC values. Because the soil tends to start with more water, which is retained at FC, the soil water retention in soils with greater organic carbon has higher AWC values. Furthermore, at WP, the soil holds onto more water, rendering a greater quantity of water unavailable to plants (Ankenbauer and Loheide II 2017); also, they found that the increase in AWC was from 17 to 37% (v/v) in a meadow soil for an increase of 15% organic carbon (OC). Also, Jordán et al. (2010) noted an increase in available water capacity by 3.7% (v/v) after the addition of 10 Mg ha^{-1} organic matter for an increase in 4% of OC. By increasing the suction in the direction of FC decreasing, it improves the buffering capacity of soil against water losses and increases saturated hydraulic conductivity and infiltration rate (He et al. 2021). On the other hand, PVA polymer has perfect emulsifying, adhesive properties, and film forming. It has high oxygen, as well as flexibility and tensile strength (Viswanath and Thachil 2008). However, these characteristics are dependent on humidity. Indeed, more water is absorbed when humidity gets higher. PVA is also fully degradable and a rapid dissolver (Gohil and Ray 2009).

Moreover, the organic NP structure affects the capacity of water retention when the water content (θ) is close to the FC to a greater extent compared with that situation when it is close to the WP (Rawls et al. 2003). The reflection point of the relationship curve between AWC and SOC is 17.57%. It was noted an increase in AWC resulted in an increase in SOC when AWC is greater than 17.57%. Furthermore, this positive correlation (r^2) was very strong (0.998). Earlier studies confirmed these results which found a significant relationship between SOC (produced by organic matter) and AWC (Olness and Archer 2005). According to these results, the input of organic material is a function of soil–water dynamics since plant productivity varies with changes in water availability. The output of SOC from soil respiration is higher in unsaturated conditions persistently (Moyano et al. 2013). Aridification can result in losses of SOC, which can range from 50 to 97% of the original organic content, because both the input and output of organic material to soil can be a function of soil–water dynamics. Thus, the importance of studying the relationship between SOC and AWC under NP additions (Ankenbauer and Loheide II 2017).

For wheat plant, the application of the organic NPs increased plant biomass and soil organic carbon as well as available water capacity as compared to the addition of conventional fertilizers. Dry matter (DM) production of wheat plant is a function of fertilizer use. Fertilization caused an increase in photosynthesis and leaf area, which in turn influenced the accumulation of DM. Nanofertilizers showed a great capability to enhance photosynthesis, growth, and productivity of several crop plants such as wheat (Abdel-Aziz et al. 2016). The nutrients loaded on nanoparticles can be released over 40 to 50 days in a slow-release fertilizer rather than the 4 to 10 days by conventional fertilizers (Chen and Wei 2018). In addition to loaded nutrients, the increases in AWC may be attributed to the positive role of SOC in enhancing the formation of aggregates and the NP hydrophilic nature. Also, SOC increases macro-aggregate formation (> 250 µm) and aggregate stability, thereby enhancing infiltration and water retention and modifying pores that support the provision of plant-available water throughout the rhizosphere (Huntington 2020). Moreover, the proposed CS and PC compounds were used in the synthesis of the nano fertilizers as a way to protect wheat plant growth against abiotic conditions, improving soil properties as well as reducing the amount of mineral fertilizers (Williams et al. 2016).

5 Conclusions

In this study, the authors tried to answer the question of how much nano-fertilizers affect the soil organic carbon content. How much water retention and aggregate formation depends on soil organic content. And what is the impact on plant water use if soil organic content changes. The measurements of soil treated with nano-fertilizers revealed that soil water retention, especially the moisture at field capacity, depends significantly on organic carbon. The measured water retention indicates that increased soil organic carbon increases the wheat plant available water capacity. By comparing the traditional treatment with nanoparticles treatments, we observed that plants are impacted by changes in organic carbon and hydrophilic characteristics of nanoparticles. The increase in soil organic carbon affects not only the total amount of water available to plants but also the duration and timing of water stress as well.

The difference in the macro-aggregation (> 250 µm) is an indicator of the significant benefit of organic carbon and the high nanoparticle adhesiveness force. The strong correlation between the formation of macro-aggregates and soil organic carbon indicates that the loss of organic carbon from the soil would decrease the portion of the macro-aggregates as the soil becomes degraded, consequently, lowering the quality of the soil–water relationships. Acknowledgement of the role of organic carbon in providing water for plants throughout the growing season advises that it is imperative to identify restoration strategies that boost plant productivity and increase inputs of organic carbon to the soil. Preserving and promoting organic matter should be a part of management techniques in similar conditions, especially in areas with the least amount of organic matter under arid and semiarid soil such as Egyptian soils.

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Data Availability All data presented or analyzed during this research are included in this published article.

Declarations

Ethics Approval and Consent to Participate All soil and plant sampling procedures and standard methods were performed according to the relevant regulations and guidelines.

Consent for Publication Not applicable.

Competing Interests The authors declare no competing interests.

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