Preparation and characterization of nano organic soil conditioners and it's effected on sandy soil properties and wheat productivity

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Abstract: Development of technologies that improve food productivity without any adverse impact on the ecosystem is the need of hour. In this context, development of controlled delivery systems for slow and sustained release of agrochemicals or soil conditioners crucial. So, the major advantages of chitosan include its ability to function as a protective reservoir for the active ingredients, protecting the ingredients from the surrounding environment while they are in the chitosan domain, and then controlling their release, in the sandy soil systems'. Also, productivity and study chitosan nanoparticle either alone or in composite with humic acids as soil conditioners were taken in consideration. Production of the chitosan nanoparticle (CS NPs) and chitosan-humic acids nanocomposite (CS-HA nanocomposite) were carried out and using X-ray diffractometer (XRD), Dynamic Light Scattering (DLS) Analysis and transmission electron microscope (TEM) for characterization. Obtained results concluded that the X-ray diffract gram of CS NPs and CS-HA nanocomposite shows a broad peak at around 2=28° where the structure of nanochitosan after crosslinking with tripolyphosphate it shows a decrease in crystallinity of chitosan while CS-HA NPs shows the less intense peak and less crystalline entity. Nanoparticles prepared by gelation method showed a mean size of 20.5 and 37.3 nm as well as mean positive charge of 42 and 22.5 mV for CS NPs and CS-HA nanocomposite respectively, when analyzed by Malvern zeta–sizer. Also, TEM micrograph of the CS NPs and CS-HA nanocomposite showed that the CS nanoparticles have nearly spherical shape, smooth surface and size range of about 17 nm and the cross-linking between chitosan and humic acids was about 36 nm. To study these materials as soil conditioners, a field experiment was carried out during the two successive winter seasons of 2016/2017 and 2017/2018 at the experimental station of the Agriculture Research Center in Ismailia region (Ismailia Governorate), Egypt cultivated with wheat (*Triticum aestivum* L., cv Giza 168). The treatments were arranged in a split plot design with three replicates. The main plot included five treatments, control (recommended NPK), humic acids (HA), chitosan (CS)), chitosan nanoparticles (CS NPs) and chitosan- humic nanocomposite (CS-HA nanocomposte) while the sub-plot areas included their concentrations (C_1, C_2 and C_3) according to type of soil conditioners. In general, results show that mean values of the soil treated with CTS-HA nanocomposite at concentration C_3 was enhanced their total porosity (TP) and moisture content which represented in field capacity (FC), wilting point (WP) and available water (AW). An opposite trend was obtained with soil bulk density where it decreased with increased treatment concentrations in all treatments applied as compared to control. Furthermore, the applied of nano organic soil conditioners were decreased soil reaction (pH) as compared to control and such decreased was proportional to treatment concentrations. On the other hand, both electrical conductivity (EC) and organic matter (OM) were increased significantly with all treatments and concentrations applied as compared to control. The maximum increased was obtained with CS-HA nanocomposite as compared to other normal forms of organic soil conditioners. The same trend was observed with available N and P content in soil. In addition, results revealed that all mean values of wheat growth parameters (biological yield, grain, straw and 1000 grain) were generally increased significantly in all treatments applied as compared to control. The magnitude increases in yield production was observed with chitosan-humic nanocomposite more than unique application of chitosan and humic acid. Such increase reach to (38.1% and 37.9%) for yield, (52.8% and 78.7%) for grain, (20 % and 26.7%) for straw and (62.9% and 59.1%) for 1000 grain in two successive seasons, respectively. Also, mean values of growth parameters were increased by increasing application rates. Finally, from above mention results we can be concluded that the usage of nano organic soil conditioners were more effective than other normal forms which led to improved soil physical and chemical properties along with wheat productivity.

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Key wards: Characterization; XRD; DLS; TEM, organic soil conditioners, chitosan, humic acids, nanocomposite, sandy soil, wheat plant.

1. Introduction

Egypt covers about one million square kilometers. However, arable land is only about 3.5 million ha, while the majority of the land area is classified as deserts, comprising mainly sandy soils. Sandy soils in deserts of arid regions are characterized by low water-holding capacities, high infiltration rates, high evaporation, low fertility levels, and very low organic-matter content that may induce low water and fertilizer use efficiency (**Al-Omran et al., 2004**).

Accordingly, strict management practices are necessary for reclamation of these sandy soils in Egypt. Moreover, it is necessary to find environmentally friendly technique and a cost-effective to improve fertility of sandy soils. As known organic matter providing many benefits to agricultural production is ancient knowledge, but yet little is known about it. Use of organic matter improves soil physical, chemical and biological properties, and has technical advantages.

Humic acids is the major complex organic substances derived from organic matter decomposition, that is the most significant constituents of organic matter in both soils and municipal waste compost, and have a relevant role in the cycling of many elements in the environment and in soil ecological functions (**Senesi et al., 1996**). Humic acids may play a major role in enhancement the plant growth under different soil condition by increasing plant height, leaf number/plant, plant fresh and dry weight, protein and mineral percent (N, P and K) of some plants such as cowpea (**El Hefny, 2010**), potato (**Rizk et al., 2013**).

The Chitosan originally formulated from the glucose circle, however, it contains a group of free amino, carbon atom num2 (called glucose amino) and it classified belongs to the carbohydrate family which contains un ramified chains formula. In addition, chitosan is a natural biopolymer derived from deactylation of chitin and containing a lot of nitrogen molecules that enhance germination index, shoot and root dry weight (**Boonlertnirun et al., 2008** and **Guan et al., 2009**); can increase the microbial population by large numbers because it acting as the carbon source for microbes in the soil and accelerating transforms organic nutrient into inorganic nutrients that are easily absorbed by plant roots (**Bolto et al., 2004**). Moreover, chitosan may improve the sandy lands natural qualities by gathering the soil particles. **Gornik el al. (2008**) used the chitosan in forms of hydrogel which helps containing water in the soil for a long time. It also improves the quality of the soil by increasing the coherence between the soil particles.

Recently, nano-technology deals with small particles with the dimension of 1-100 nm. Nano particles with extremely high reactivity and deliverability can be applied as amendments to improve soil quality. These particles have high surface mass ratio and are capable of improving the agricultural inputs. (**Santhosh Kumar, 2012**). Moreover, chitosan nanoparticles (nano chitosan) are one of the engineered nano materials and are natural materials with excellent physicochemical properties; further, they are environmentally friendly as well as bioactive (**Agnihotri et al., 2004**). Such unique properties of the chitosan biopolymer can be enhanced by using it in the form of nanoparticles, as in this form, it can introduce different biological activities with altered physicochemical properties like surface area, size, cationic nature, etc. (**Chandra et al., 2017**). In addition, chitosan nanoparticles were currently used to carry ions of fertilizers to be applied to plants. Foliar application of chitosan nanoparticles showed improvements of growth and yield of wheat plants especially at lower concentration 10% (**Abdel-Aziz et al., 2016**). Chitosan nanoparticles are easily absorbed by the epidermis of leaves translocated to stems which facilitated the uptake of active molecules and enhanced growth and productivity of several crop plants (**Malerba and Cerana, 2016**).

On the other hand, **Ramadan and El Mesairy (2015)** found that the interaction between humic acid and chitosan levels, generally, increased Okra plants growth when received the highest humic acid and chitosan levels (200 ppm).

The aim of the present study is preparation and characterization of nano organic soil conditioners (nano chitosan and chitosan humic nanocomposite. As well as, compared between organic and nano organic soil conditioners with different levels on some properties of sandy soil and wheat plant productivity.

2. Materials and Methods

Egypt is looking towards nanotechnology as a means of boosting agricultural productivity. Recently, nanotechnology research and development could help natural resources such as water, nutrients, chemicals and soil conditioners when used efficiently in agriculture.

Chemical used in this study

Chitosan (CS) with molecular weight 50,000-190,000 Da, degree of deacetylation 75-85% and viscosity: 20-300 cP, glacial acetic acid, sodium tripolyphosphate (TPP), humic acid (HA) and N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide (EDC). All the chemicals used in this study were used without further purification which were purchased from Sigma-Aldrich, USA chemical company.

Preparation of nano materials:

1- Chitosan nanoparticles (CS NPs)

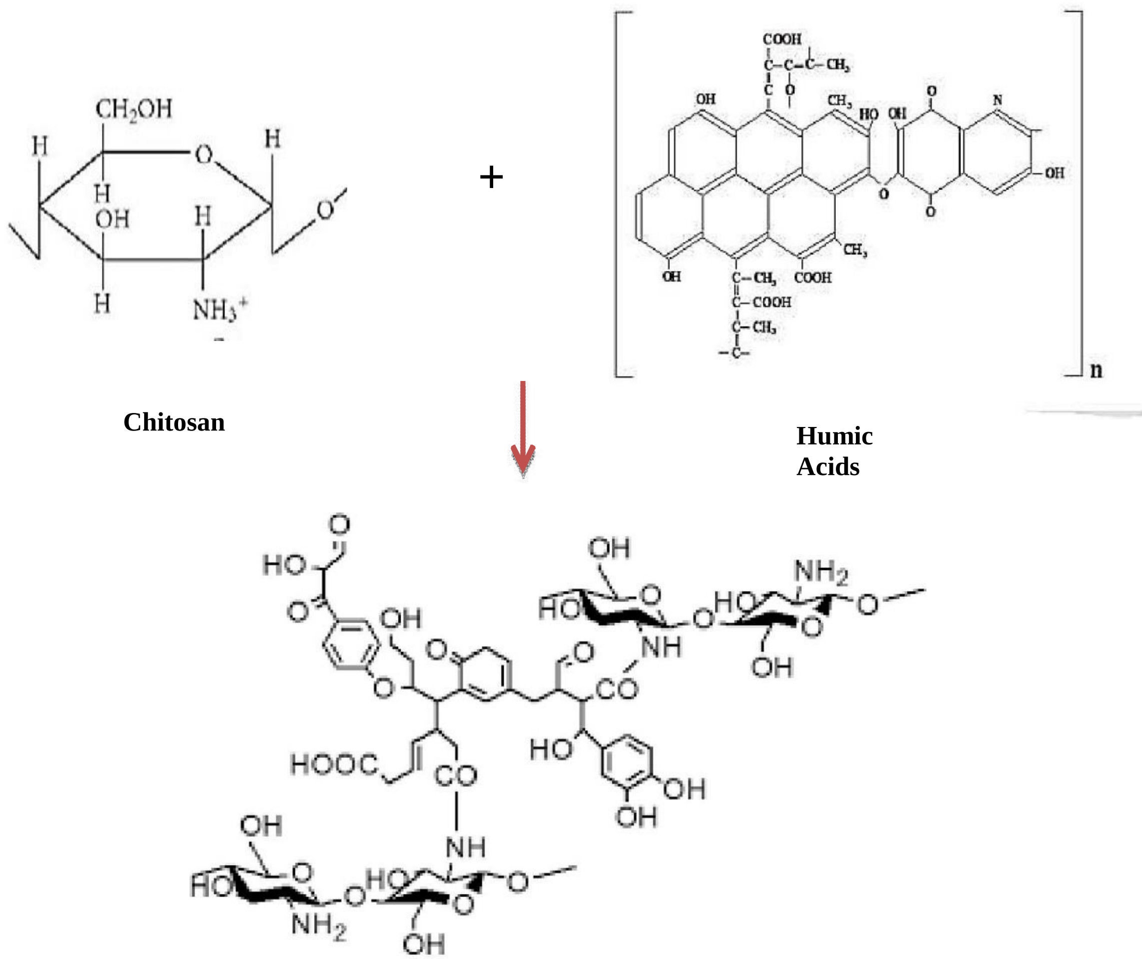
Chitosan nanoparticles (CS NPs) were prepared by ionic gelation method according to **Calvo et al.**

(1997) and **Hu et al. (2002)**. The method utilizes the electrostatic interaction between the amine group of chitosan and a negatively charged group of polyanion such as TPP (tripolyphosphate). Briefly, CS aqueous solution (0.2% w/v) was prepared by dissolving CS in acetic acid solution (1% v/v) at room temperature. Subsequently, TPP solution (0.06% w/v) was added drop wise to CS solution under vigorous stirring for 30 min. The resulting chitosan particle suspension was centrifuged at 12000g for 30 min. The pellet re-suspended in deionized water. The chitosan nanoparticles suspension was then freeze-dried before further use or analysis.

2- Chitosan-humic (CS-HA) nanocomposite

Chitosan-humic (CS-HA) nanocomposite was prepared according to **Akinremi et al. (2016)** with some modifications. The method utilizes the Humic acids was used for intramolecular cross-linking of the chitosan linear chains to increase the active sites on the chitosan biopolymer.

Briefly, CS (0.5% w/v) was dissolved in Humic acids solution and stirred with a magnetic stirrer for 2 h at room temperature. Subsequently, EDC solution was added dropwise to CS-HA solution under vigorous stirring for 24 h. The cross-linked CS-HA was obtained by freeze drying. The preparation and structure of chitosan-humic nanocomposite are shown in Fig.1.



CS-HA nanocomposite

Fig.1: Structure of chitosan-humic nanocomposite (Cs-HA nanocmposite)

Characterization of nanomaterials

1- X-Ray diffraction (XRD) pattern and Dynamic Light Scattering (DLS) analysis

The crystalline and phase structure of the synthesized CS-HA was studied by an X-ray diffractometer (XRD, X'Pert Pro, Pan Alytical, Netherlands). The size (Z-average mean) and zeta potential of the nanoparticles were analyzed by photon correlation spectroscopy and laser Doppler anemometry, respectively, in triplicate using a Zeta sizer 3000HS (Malvern Instruments, UK).

2- Transmission Electron Microscopy (TEM)

The morphology and size were determined by the transmission electron microscopy ((TEM, Tecnai G20, FEI, Netherlands). For TEM analysis, a drop of the solution was placed on the carbon coated copper grids and dried by allowing water to evaporate at room temperature. Electron micrographs were obtained using GEOL GEM-1010 transmission electron microscope at 70 kV.

All the preparation and characterization processes were conducted at Nanotechnology and Advanced Materials Central Lab (NAMCL), Agricultural Research Center, Egypt.

Field experiment design and statistical analysis

To investigate the effect of organic and nano organic soil conditioners on the sandy soil properties and its effect of wheat productivity. A field experiment was carried out during the two successive seasons of 2016/2017 and 2017/2018 cultivated with wheat (*Triticum aestivum* L., cv Giza 168) at the experimental station of the Agriculture Research Center in Ismailia region (Ismailia Governorate), Egypt.

The treatments were arranged in a split plot design with three replicates. The main plot included five treatments while the sub main-plot areas included three concentrations (C_1, C_2 and C_3) of different treatments according to type of soil conditioners. Some physical and chemical properties of the experimental soil are presented in Table (1).

Table (1): Some physical and chemical properties of investigated soil

Soil property	Value	Soil property	Value
Particle size distribution %		**Soil physical properties:-**	
Coarse sand	49.5	BD (g/ cm^3)	1.82
Fine sand	40.5	Total porosity %	33.2
Silt	4.00	WHC %	21.2
Clay	6.00	WP %	3.00
Texture class	Sandy	FC %	10.23
		AW %	7.23
Soil chemical properties:-		**Available macronutrients (mg kg^{-1})**	
pH (1:2.5 soil: water suspension)	7.90	N	52.0
EC (dSm^{-1}) in soil past extract	0.93	P	3.60
OM %	0.38	K	54.8

Fertilizers application

The quantity of nitrogen fertilizer was divided into four equal doses. The source of mineral-N fertilizer was ammonium nitrate (33.5% N) which added with rate of 360 kg fed^{-1}. In addition, superphosphate (15. % P_2O_5) fertilizer was added before cultivation at a rate of 200 kg fed^{-1}. The amount of potassium fertilizer was applied at rate of 50 kg fed^{-1} as potassium sulphate (48% K_2O) in one dose after 30 days from sowing. The normal agricultural practices were carried out during the growing season as recommended.

Treatments and doses:

1- Control (recommended NPK).
2- Humic acids (HA): humic acids in a solid form as potassium humate (65%).
3- Chitosan (CS).
4- Nanochitosan (CS NPs).
5- Chitosan-Humic acid nanocomposite (CS-HA nanocomposite).

Normal forms of both humic acid and chitosan were applied at three concentrations (0.1%, 0.3% and 0.5 %) while the nano material treatments were prepared in lab and applied in field at three concentrations (0.05%, 0.1% and 0.2%). All treatments applied three times with 15 day interval from sowing.

Soil hydro-physical properties

Soil bulk density and total soil porosity were determined according to **Richards (1954).** Soil moisture equilibrium values were determined according to the methods described by **Richards and Weaver (1944) and Richards (1947).** Wilting point was determined according to **Stakman and Vanderhast (1962),** while field capacity was determined as described by **Richards (1954).**

Soil chemical properties:

Soil samples were taken at surface layer (0-20 cm) after wheat crop harvested air-dried, and passed through 2 mm sieve for analysis according to **Cottenie et al. (1982)** as follow**:**

1- Electrical conductivity (EC) dSm^{-1} in soil water extract at ratio (1:5).
2- pH in soil water suspension at ratio (1:2.5).
3- Organic matter (OM) and available N, P and K.

Wheat productivity

Wheat plant samples were taken at harvested stage after 100 days from planting in one square meter to determine yield (straw and grains) by weight. Plant samples were oven dried at 70 ^{0}C for 48 hr, up to constant dry.

Statistical analysis:

All obtained results in each growing season were exposed to statistical analysis to compare the means through L. S. D. test at level of significant (0.05) as described by **Gomez and Gomez (1984).**

3. Results and Discussion

I - Characterization of nano materials:

1- X-Ray diffraction (XRD) pattern of chitosan nanoparticles (CS NPs) and chitosan-humic (CS-HA) nanocomposite

X-Ray powder diffraction patterns of CS NPs, and CS-HA nanocomposite were shown in Fig. 2(A and B), respectively. No peak was found in the diffractgrams. Chitosan nanoparticles (Fig.2A) was comprised of a dense network structure of interpenetrating polymer chains cross-linked to each other by TPP counter ions while humic acids was used for intramolecular cross-linking of the chitosan which characteristic of an amorphous form as shown in (Fig. 2B).

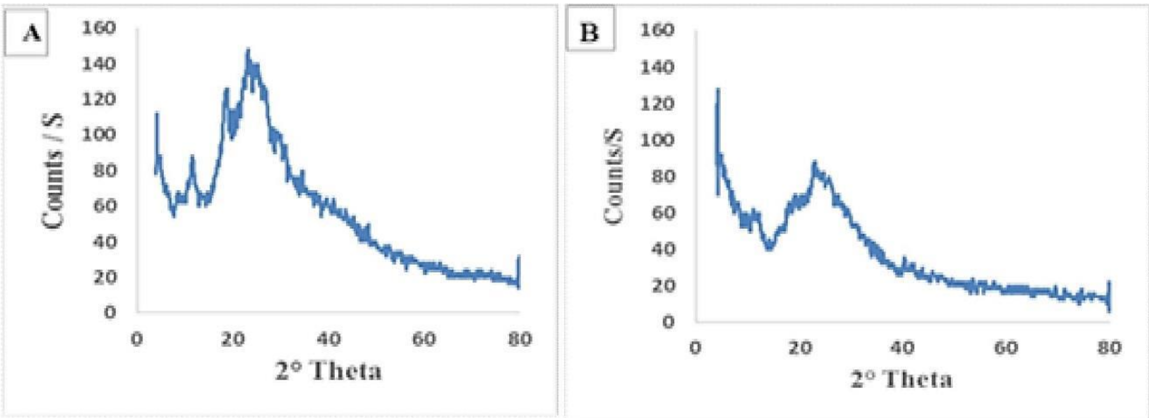


Fig. 2. X-ray powder diffraction patterns of chitosan nanoparticles (A) and chitosan- humic nanocomposite (B).

The above X-ray diffraction pattern of nanochitosan obtained using ionic gelation technique is shown in Fig. 2A. The X-ray diffractogram of nano chitosan shows a broad peak at around 2=28°. The broadening of the peaks is due to the deformation of the crystalline regions by the increased packing of chitosan chains by ionic crosslinking (**Martinez-Camacho et al., 2010)**]. The structure of nanochitosan after crosslinking with tripolyphosphate it shows a decrease in crystallinity of chitosan. This could be attributed due to the deformation of the hydrogen bond in original chitosan by the substitution of hydroxyl and amino groups (**Raut and Khairkar, 2014**), which efficiently destroyed the regularity of the packing of the original chitosan chains resulting in the formation of amorphous nano chitosan.

Moreover, the X- ray diffractogram of CS-HA nanocomposite (Fig. 2B) shows compacted peaks at various 2θ values such 28^o. Due to the dispersion of the polymer matrix in the CS-HA nanocomposite, certain changes in the degree of crystallinity have been occurred. The less intense peak and less crystalline entity (broad nature-more amorphous) obtained in CS-HA nanocomposite might be due to the destruction of the packing of the polymers by the strong interaction which occurred between the nanochitosan and humic acids (**Elmotasem, 2008)**. On comparing the XRD details of CS-HA nanocomposite with nanochitosan, it was observed that the prepared CS-HA nanocomposite has amorphous nature suitable for a variety of applications.

2- Dynamic Light Scattering (DLS) Analysis

DLS was used to measure hydrodynamic diameter in the nanometer range. The size of CS NPs and CS-HA nanocomposite were 20.45 nm and 37.34 nm (Fig.3A & C) while zeta potential 42and 22.5 Mv (Fig.3B & D), respectively.

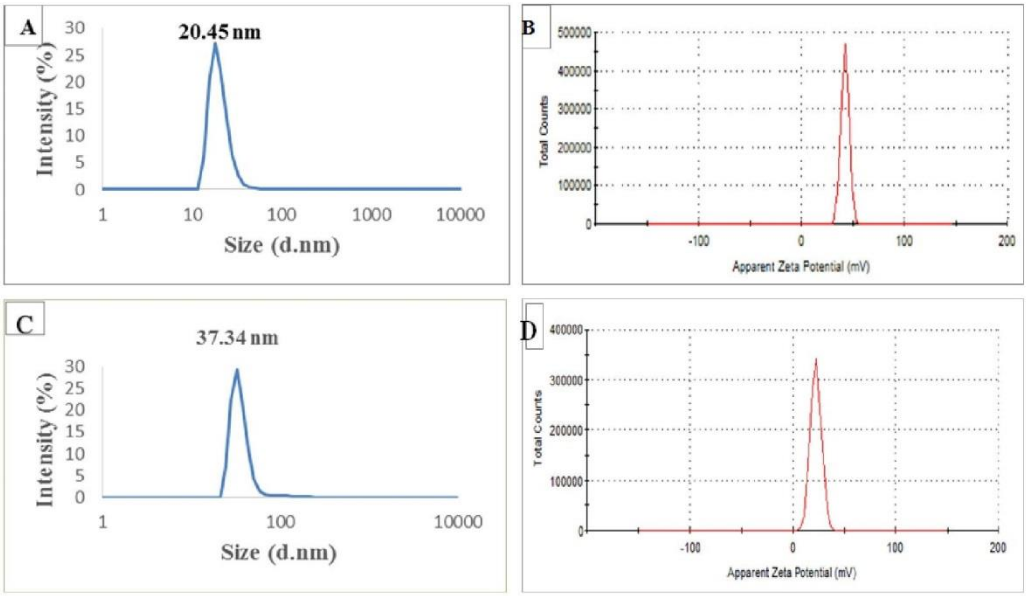


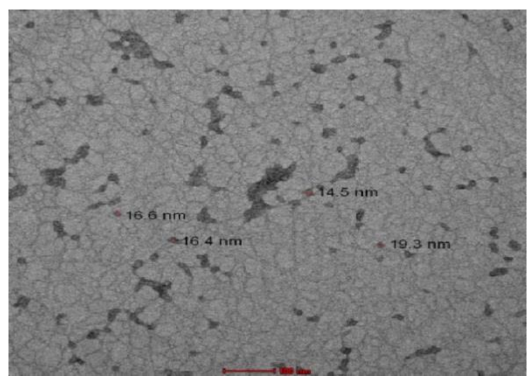
Fig. 3. DLS analysis of CS NPs, and CS-HA nanocomposite particle size (CS NPs (A), CS-HA nanocomposite (C), and Zeta potential CS NPs (B), CS-HA nanocomposite (D)

Obtained results revealed that zeta potential of nanochitosan (42mV) was higher than that of CS-HA nanocomposite (22.5 mV). The important of zeta potential represented in stability of nanoparticles in aqueous media, therefore nanochitosan and CS-HA nanocomposite with higher zeta potential showed high stability in aqueous solution in present study **(Brunel et al., 2013**). Furthermore, the decline in zeta potential in CS-HA nanocomposite indicated the strong linkage between nano particles and humic acids.

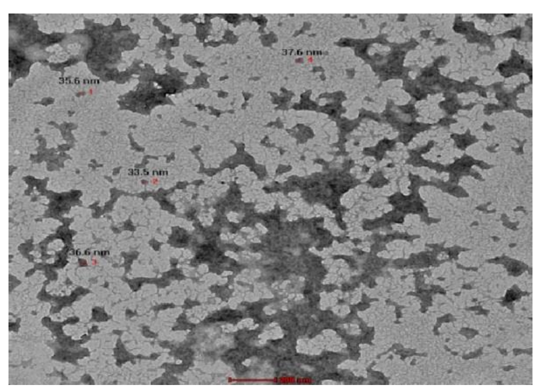
Also, though the DLS data show a small increase in size of the nanocomposite when conjugated to the humic acid, this increase may be due to the increase in the polymer size by the addition of the humic to the chitosan backbone. The nanocomposite was having most of the positively charged -NH_2 groups are free, and hence lead to a high positive zeta potential. When chitosan is conjugated with the humic acids, many of the terminals free -NH_2 react to form amide bonds between chitosan and COO^- of humic acids. This lowers the cationic charges by the absence of free -NH_2 groups, and hence lowers the zeta potential. Improved methods of preparation might improve the stability of these chitosan humic nanoparticles in solution. These results similar to data obtained with **Melamangalam et al. (2012)** when prepared chitosan peptide nano particles.

3- HR-TEM analysis result

Transmission electron microscope (TEM) gave us information on the particle shape and the determination of particle size. A typical TEM micrograph of the CS NPs and CS-HMA nanocomposite was shown in Fig. 4. The CS nanoparticles have nearly spherical shape, smooth surface and size range of about 17 nm and the cross-linking between chitosan and humic acids was about 36 nm.



(A)



(B)

Fig. 4. HR-TEM image of CS NPs (A), and CS-HA nanocomposite (B).

Soil physical properties:

1- Bulk density and total porosity:

Bulk density has relationship with other properties of the soil such as porosity and moisture content. Obtained results in Table (2) noted that there were reveres fit between organic soil conditioners with different concentrations and soil bulk density, whereas it's decreased with all treatments applied as compared to control treatment. Also, by increasing rate of application generally decreased soil bulk density; the C_3 is highly positive effect more than other concentrations. Such decreased by organic amendments refers to increasing pore spaces which led to increasing soil aeration and improve water content in soil **Barzegar et al. (2002 and Zeleke et al. (2004**). **Wael and Blumenstein (2015)** found that the treated sandy soil with 0.4% from nanocomposite was decreased bulk density from 1.51 to 1.21 g cm^3. Such decreased may be due to hydrogel particles within the soil matrix absorb water and become larger in size. The soil volume increases and hence the ratio of the dry mass of the soil to its volume decreases because the soil particles are displaced and rearranged around the swollen particles of the hydrogel. (**Liu et al., 2007; Bai et al., 2010**)

Moreover, the use of humic acids in soil as an organic source improved the physical condition of soil by improving the aggregate stability of soil and reducing the compactness of soil which result in decrease in bulk density and increase in porosity of soil and finally improved the water infiltration (**Zeleke et al., 2004).**

On the other hand, an opposite trend was observed with total porosity in sandy soil treated with organic and nano organic soil conditioners. Average values of total porosity at two seasons were increased either with humic and chitosan in normal form or in nano form as compared to control treatment. Furthermore, mean values of total porosity were increased with increased soil conditioners concentration. The highest values were obtained with CS-HA nanocomposite at C_3. Such increment may be due to the increase in the pore space between coarse sand particles reoriented around the swollen hydrogel particles. Easier displacement of larger sand particles by swollen hydrogel may create new pores (**Bai et al., 2010**).

Table (2): Bulk density, total porosity and soil moisture constants in the investigated soil after wheat crop harvested

Treatments	Conc.	Average of two seasons				
		BD (g cm^3)	T.P %	Soil moisture content %		
				FC	WP	AW
Control		**1.68**	**36.6**	**11.8**	**1.65**	**10.1**
HA	**C1**	**1.59**	**40.0**	**13.0**	**3.67**	**9.34**
	C2	**1.59**	**40.0**	**15.4**	**5.50**	**8.50**
	C3	**1.54**	**41.9**	**23.5**	**7.92**	**15.6**
CS	**C1**	**1.67**	**37.0**	**12.7**	**3.96**	**8.69**
	C2	**1.60**	**39.6**	**18.2**	**5.62**	**8.98**
	C3	**1.56**	**41.1**	**20.2**	**7.70**	**12.5**
CS NPs	**C1**	**1.59**	**40.0**	**13.4**	**4.33**	**9.11**
	C2	**1.59**	**40.0**	**14.0**	**6.27**	**9.13**
	C3	**1.54**	**41.9**	**24.6**	**9.06**	**15.6**
CS-HA nanocomposite	**C1**	**1.59**	**40.0**	**13.8**	**4.74**	**9.05**
	C2	**1.56**	**41.1**	**14.6**	**10.2**	**8.05**
	C3	**1.54**	**41.9**	**28.6**	**11.3**	**17.2**
Mean of soil conditioners	**HA**	**1.68**	**36.6**	**17.3**	**5.70**	**11.1**
	CS	**1.59**	**40.0**	**17.0**	**5.76**	**10.1**
	CS NPs	**1.59**	**40.0**	**17.3**	**6.55**	**11.3**
	CS-HA nanocomposite	**1.54**	**41.9**	**19.0**	**8.74**	**11.4**
Mean of conc.	**C1**	**1.67**	**37.0**	**13.2**	**4.17**	**9.05**
	C2	**1.60**	**39.6**	**15.5**	**6.89**	**8.66**
	C3	**1.56**	**41.1**	**24.2**	**9.00**	**15.2**

BD= Bulk density T.P= Total porosity F.C = Field Capacity. A.W = Available Water. W.P = Wilting Point.

The hydrogel particles are also taken as "miniature water reservoir" in the soil and water will be detached from these reservoirs upon the root mandate through osmotic pressure difference (**Azzam et al., 1980**). Due to the respectable volume reduction of the hydrogel as water is released to the plant, hydrogel creates at intervals the soil, free pore volume providing further space for air and water infiltration, storage and root growth. (**Milani et al., 2017**).

2- Soil moisture content:

Concerning the effect of organic and nano organic soil conditioners on soil moisture content represented as field capacity (FC), wilting point (WP) and available water (AW). Results in Table (2) clear that application of different forms of organic material either in normal form or in nano form were increased mean values of all parameters of soil moisture content were positive effect as compared to control treatment (recommended NPK). Such increases ranged from 11.8 to 28.6 for FC, 1.65 to 11.3 for WP and 10.1 to 37.7 for AW. In addition, soil moisture content was proportional to application rates of soil conditioners, i.e. increasing concentration of organic and nano organic soil conditioner resulted in increasing soil moisture content.

Moreover, the interaction effect between soil conditioner and their concentrations obtained results showed that CS-HA nanocomposite is superior treatment at third concentration (C_3) in enhancement of soil moisture content and delay wilting point of plant due to the ability of chitosan as polymer in reserve large amount of water near root zoon of plant and became available to absorb by plant for long time. **Abobatta (2018)** explain that when the hydrogel is mixed with the soil, it forms an associate amorphous gelatin–like mass on hydration and is adept of absorption and desorption for an extended time, thus acts as a slow unharness supply of water within the soil. Also, **Johnson (1984)** reported that added hydrogel to the soil increased the plant circumference; this may be due to increasing the amount of available water in the root zone, which inferring longer irrigation intervals.

In this concerned, **Wael and Blumenstein (2015)** mentioned that the addition of nanocomposite polymers was increased the moisture content at field capacity of sandy soil. As well as, increased field capacity by 28, 60, 92 and 130% with 0.1, 0.2, 0.3 and 0.4% of nano composite, respectively, compared with untreated soil. Also, nanocomposite increased significantly water holding capacity (from 45.65-66.11% (v/v)), field capacity (from 22.45-33.11% (v/v)) and wilting point (from 11.51- 13.91% (v/v)) for 0.1 and 0.4% application rates of nanocomposite, respectively. Also, the amount of available soil water (AW) increased significantly and linearly in soil with the addition of nanocomposite compared with untreated soils. The synthesized nanocomposite enhanced the moisture retention of sandy soil and plant available water significantly, thereby slowing down the rate of moisture loss, due to which a delay of 20-25 days in wilting point was observed. Such a delay in wilting point reduces the water requirement of plants.

YE et al. (2017) reported that humic acids mainly composed of carbon, when carbon is added up in soil it improves the soil aggregate stability by binding the aggregates resulting in improvement of micro and macro pore of the soil. Macro pore of soil enhances the aeration as well as increase root penetration into the soil, while micro pores enhances the water holding capacity and increase the water contents of soil. While, **Yu et al. (2012)** suggested that the differences in water release between soil–super absorbance (SAP) polymer mixtures and the soil only systems could be related to the balance between two affecting op- posing mechanisms. The presence of water containing soil particles that are surrounded by the SAP grains may reduce the hydraulic gradient difference between soil particles and the swollen SAP. This, in turn, results in slower water evaporation rate from each component in the soil–SAP mixtures compared with a system containing soil particles alone. Also, **Arancibia et al. (2014**) concluded that the nano chitosan showed high water absorbance which reveals the property of higher hygroscopicity nature.

Shahid et al. (2012) reported that the application of superabsorbent hydrogel/ potassium humate nanocomposite was increased soil available water and delay wilting point by 6-9 days.

Soil chemical properties:

1-Soil reaction (pH)

Changes in soil reaction are responsible for nutrients availability in soil and easily to change according to type and amount of soil conditioners applied. So, data in Table (3) cleared the effective of pH with different forms of organic and nano organic soil conditioners and its application rates.

As compared to control mean values of soil pH after wheat harvested were slightly decreased in all treatments applied either in normal form or in nano form at two successive seasons. As well as, CS-HA nanocomposite was the superior treatment to decreased soil pH followed by humic acids, chitosan and nano chitosan. Such decreases in pH values may refer to the acidity and functional group of applied material.

Table (3). Effect of humic, chitosan, nanochitosan and chitosan - humic nanocomposite on chemical properties of sandy soil at two successive seasons

Treatments	Conc.	1st season			2nd season		
		pH (1:2.5) suspension	EC dSm-1 (1:5extract)	OM %	pH (1:2.5) suspension	EC dSm-1 (1:5extract)	OM %
Control		8.37	0.121	0.38	8.38	0.116	0.35
HA	C1	8.38	0.150	0.71	8.38	0.154	0.50
	C2	8.34	0.163	0.70	8.25	0.166	0.68
	C3	8.05	0.200	0.72	8.15	0.217	0.71
CS	C1	8.29	0.161	0.48	8.35	0.155	0.46
	C2	8.24	0.172	0.51	8.29	0.166	0.52
	C3	8.04	0.174	0.74	8.25	0.173	0.64
CS NPs	C1	8.33	0.175	0.48	8.30	0.185	0.41
	C2	8.29	0.185	0.50	8.24	0.219	0.56
	C3	8.24	0.233	0.62	8.15	0.221	0.60
CS-HA nano composite	C1	8.27	0.186	0.54	8.34	0.332	0.62
	C2	8.24	0.238	0.60	8.21	0.214	0.72
	C3	8.03	0.252	0.84	8.21	0.293	1.03
Mean of soil conditioners	HA	8.25	0.171	0.71	8.20	0.179	0.63
	CS	8.28	0.169	0.58	8.30	0.165	0.54
	CS NPs	8.31	0.198	0.53	8.19	0.208	0.52
	CS-HAnano composite	8.14	0.225	0.66	8.21	0.280	0.79
Mean of conc.	C1	8.32	0.168	0.55	8.34	0.207	0.50
	C2	8.28	0.190	0.58	8.25	0.191	0.62
	C3	8.09	0.215	0.73	8.19	0.226	0.75
LSD at 0.05%:							
A (Conditioner)		0.154	0.03	0.155	0.134	0.05	0.08
B (Conc.)		0.131	0.027	0.10	0.128	0.04	0.116
A*B		0.261	0.053	0.192	0.256	0.08	0.232

Moreover, the effect of applied different concentrations rates data in Table (3) show that the soil pH values were decreased gradually by increasing rate of application, whereas the highly positive effect C_3 on soil pH decreasing at two successive seasons.

In addition, data in Table (3) observed the interaction between conditioners form and application rates, the addition of CS-HA nanocomposite as composite led to highly decreased in soil pH more than other treatments applied in two seasons.

These results are in agreement with **Sarwar et al (2008)** who observed a decrease in soil pH after the use of organic materials. The production of organic acids (amino acid, glycine, cystein and humic acids) during mineralization (amminization and ammonification) of organic materials by heterotrophs and nitrification of NH4 produced by autotrophs would have caused this decrease in soil pH.

2- Electrical conductivity:

Concerning data in Table (3) showed the soil salinity under effect of applied organic and nano organic soil conditioners with different application rates. Obtained results revealed that the mean values of EC were increased significantly in all applied treatments as compared to control. The nono forms were generally more effective than normal form; CS-HA nanocomposite was superior treatment in enhancing the liberated ions in soil followed by CS NPs, HA and CS, respectively. Moreover, by increasing rate of application EC values were increased.

Nada et al. (2015) who reported that the discharge of soil inorganic salts thereby increasing EC of the soil was enhanced by decrease pH of the soil. Similar effect on the pH and EC of soils due to the chemical structure of the superabsorbent polymer and soil characteristics have previously been appraised by **Liu et al. (2007)** and **Bai et al. (2010)** while studying the characteristics of chitosan-graft-poly (acrylic acid)/sodium humate superabsorbent. **Akinremi et al. (2016)** reported that the amine groups of chitosan reacted with the carboxylic groups of humic acid electrostatically, this is because carboxylic groups of humic acids release protons (H^+) and convert to COO− anions, whereas amine groups of chitosan as a base can accept protons and convert to cations. Hence, crosslinking between humic acids and chitosan can be considered to occur chemically. So, it was expected that the electrical conductivity may increase due to increasing ion mobility in soil.

3- Organic matter

According to obtained results in Table (3) data demonstrated that the applied of organic soil conditioners with different forms either in normal form or in nano form were significantly increased mean values of OM content in sandy soil compared to control treatment at two successive seasons. The highest increase was observed with CS-HA nanoomposite treatment (0.66% and 0.79%) for first and second season respectively.

Meanwhile, mean values of soil organic matter content was proportional to treatments rate, i.e. by increasing applied concentration the soil organic matter was increased. The mentioned results in Table (3) showed the interaction effect of organic and nano organic soil conditioners with their different concentration on OM content in sandy soil. The maximum increased was obtained with high concentration (C_3) in the present of CS-HA nano composite and reach to (0.84% and 1.03%) for two seasons, respectively. Also, data indicated that the soil conditioners in nano form are superior in their effect more than normal form. Such increased may be due to increasing specific surface of nano material which led to improving their action. However, **Issak and Sultana (2017)** included that the application of chitosan powder in the seedbed soil tends to increment of organic carbon content. The organic carbon content was increased with increasing the level of chitosan. Also, the application of humic acids improved soil organic carbon status as it is majorly composed of organic carbon. Humic acids increases the soil organic matter as it consists of 50-90 % organic matter (**Kulikova et al., 2005**). Moreover it prevents loss of carbon due to refractory nature of its chemical structure which makes it resistant against microbial attack. **Melero et al. (2007)** added that amendments from organic source were generally increased the total organic carbon in soil**.**

4-Available macronutrients content:

Sandy soil is known for its low fertility and always needed to supply more amount of fertilizer; so can be compensate its losses by applied organic soil conditioners either in normal form or in nano form.

Generally, the mentioned results in Table (4) revealed that the mean values of available N and P content in soil were enhanced with applied different organic soil conditioners form as compared to control (recommended NPK) in two seasons. An opposite trend was observed with available K content in sandy soil under the same condition. The highly positive effect was noted with CS-HA nanocomposite more than CS, CS NPs and HA in descending order, respectively.

Table (4). Effect of humic, chitosan, nanochitosan and chitosan - humic nanocomposite on available NPK content (ppm) in sandy soil at two successive seasons

		1st season			2nd season		
Treatments	**Conc.**	**N**	**P**	**K**	**N**	**P**	**K**
Control		**98**	**13.1**	**154**	**97**	**13.2**	**154**
HA	**C1**	**105**	**14.4**	**135**	**141**	**14.6**	**127**
	C2	**113**	**15.9**	**137**	**161**	**19.9**	**130**
	C3	**131**	**19.4**	**138**	**176**	**22.8**	**140**
CS	**C1**	**114**	**17.7**	**133**	**128**	**17.1**	**124**
	C2	**148**	**24.1**	**132**	**146**	**17.5**	**137**
	C3	**152**	**24.1**	**133**	**179**	**25.9**	**136**
CS NPs	**C1**	**102**	**15.8**	**123**	**115**	**23.8**	**128**
	C2	**122**	**21.7**	**124**	**156**	**19.2**	**118**
	C3	**155**	**24.6**	**133**	**168**	**23.3**	**122**
CS-HA nanocomposite	**C1**	**114**	**21.5**	**124**	**175**	**26.0**	**127**
	C2	**160**	**25.3**	**130**	**191**	**20.2**	**128**
	C3	**176**	**25.8**	**138**	**198**	**31.3**	**133**
Mean of soil conditioners	**HA**	**116**	**16.9**	**136**	**152**	**18.6**	**130**
	CS	**138**	**22.0**	**133**	**151**	**20.2**	**132**
	CS NPs	**126**	**20.7**	**127**	**146**	**22.1**	**123**
	CS-HA nanocomposite	**150**	**24.2**	**131**	**188**	**25.8**	**129**
Mean of conc.	**C1**	**109**	**17.4**	**129**	**140**	**20.4**	**127**
	C2	**136**	**21.8**	**131**	**164**	**19.2**	**128**
	C3	**154**	**23.5**	**136**	**180**	**25.8**	**133**
LSD at 0.05%:							
A (Conditioner)		**25.2**	**5.47**	**4.48**	**25.3**	**3.38**	**10.8**
B (Conc.)		**16.7**	**4.24**	**8.93**	**23.2**	**3.21**	**8.49**
A*B		**33.4**	**8.48**	**17.9**	**46.4**	**6.43**	**17.0**

As compared to rate of application obtained data in Table (4) showed that by increasing organic soil conditioners concentration the availability of N, P and K in soil were increased especially with C_3 followed by C_2 and C_1. Such increases refer to the zwitter ionic character of humic acids allows the interaction of anions with its positively charged groups and cations with its negative charged groups (**Pena et al., 2005**). Along with the use of humic acids to prevent nitrate leaching out into the groundwater (**Liu et al., 2010**). Also, humic substances may be improving soil physical and biological properties, which are reflected generally, on soil fertility status and thus the dynamic changes of N in the upper 30 cm of soil could be influenced, to a great extent **(Gulshan and Singh, 2006)**. Moreover, the addition of humic acids to the soil increases the recovery of Olsen P in soil **(Delgado et al., 2002).**

Plant productivity:

The response of wheat plant to different forms of organic and nano organic soil conditioners are shown in Table (5). Obtained results revealed that all mean values of wheat growth parameters (biological yield, grains, straw and 1000 grain) were generally increased significantly in all treatments applied (HA, CS, CS NPs and CS-HA nanocomposite) as compared to control. The magnitude increases in yield production was observed with chitosan-humic nanocomposite more than unique application of chitosan and humic acids. Such increase reach to (38.1% and 37.9%) for biological yield, (52.8% and 78.7%) for grain, (20 % and 26.7%) for straw and (62.9% and 59.1%) for 1000 grain in two successive seasons respectively. This increase may be due that the chitosan NPs had a positive ionic charge which chemically binds to plant nutrients that showed a negative ionic charge resulting in a slowly released action in plants which closely contributed to yield increase **Behboudi et al. (2018)**. Also, **Malerba and Cerana (2016)** reported that the Chitosan nanoparticles are easily absorbed by the epidermis of leaves translocated to stems which facilitated the uptake of active molecules and enhanced growth and productivity of several crop plants (**Abdel-Aziz et al., 2016**).

Table (5). Effect of humic, chitosan, nanochitosan and chitosan - humic nanocomposite on wheat yield ($kg\ fed^{-1}$) growing in sandy soil at two successive seasons

Treatments	Conc.	1st season Biological Yield	1st season Grain	1st season Straw	1st season 1000 grain	2nd season Biological Yield	2nd season Grain	2nd season Straw	2nd season 1000 Grain
Control		4396	1596	2800	29.7	4371	1655	2716	30.7
HA	C1	4435	1607	2828	31.7	5140	1738	3402	36.0
	C2	5084	1640	3444	38.7	5220	1804	3416	39.0
	C3	5391	1829	3562	42.0	5904	2082	3822	41.3
CS	C1	5742	1668	3948	37.3	5756	2004	3752	42.3
	C2	5909	1961	4074	40.7	6013	2111	3902	44.7
	C3	6565	2113	4452	48.7	6319	2178	4141	48.0
CS NPs	C1	5683	1651	4032	37.3	4808	1812	2996	44.7
	C2	5731	1699	4032	45.7	5346	1986	3360	46.0
	C3	6666	1962	4704	48.7	5768	2100	3668	48.7
CS-HA nano Composite	C1	5772	2034	3738	44.7	6652	2032	4620	44.7
	C2	6612	2412	4200	49.3	7302	2654	4648	50.3
	C3	7511	2615	4897	51.0	8047	2755	5292	51.3
Mean of soil Conditioners	HA	4970	1692	3278	37.4	5422	1875	3547	38.8
	CS	5406	1712	4158	42.2	5627	1964	4932	45.0
	CS NPs	5681	1819	4256	43.9	5891	2066	3341	46.4
	CS-HA nanocomposite	6072	1914	4278	48.3	6029	2098	3853	48.8
Mean of conc.	C1	5408	1740	3668	37.8	5589	1896	3513	41.9
	C2	5834	1928	3906	43.6	5970	2139	3766	45.0
	C3	6533	2130	4404	47.6	6510	2279	4476	47.3
LSD at 0.05%:									
A (Conditioner)		262.1	211.1	185.5	4.956	158.5	145.2	76.3	6.32
B (Conc.)		202.5	143.0	157.3	5.079	165.7	120.9	108.4	4.81
A*B		405.1	286.0	314.5	10.16	331.3	241.7	216.8	9.61

Furthermore, our results showed that chitosan NPs may increase photosynthetic pigments and leaf area by enhancing endogenous levels of cytokinins, which stimulated chlorophyll synthesis and growth or to the greater availability of amino compounds released from chitosan (**Behboudi et al., 2018**).

With respect to the effect of treatment concentrations data in Table (5) show the significantly increased in wheat productivity (biological yield, grain, straw and 1000 grain) by increasing concentration levels in all treatments applied, the superior one is C_3 (3% for organic and 0.2% for nano organic soil conditioners. These results agree with **Ramadan and El Mesairy (2015).** In addition, **El-Tanahy et al. (2012)** added that the cowpea plant growth was increased significantly by increasing chitosan levels from 1% to 5%. In this concerned **Shams and Morsy (2014)** found that increasing the concentration of chitosan nanoparticles increased tomato early and total yields; however, such increases were insignificant. Thus, using chitosan nanoparticles at 0.5% concentration is considered more economically than using it at 1% for obtaining highest early and total yield.

Regarding to the interaction effect of organic and nano organic soil conditioners with those concentrations applied data in Table (5) clear that as compared to control the positive effect of all treatments applied were observed with CS-HA NPs at 0.2% more than unique application of HA, CS, CS NPs. Obtained data agreement with **Ramadan and El Mesairy (2015)** added that the interaction between humic acids and chitosan levels, generally, increased Okra plants were those received the highest humic acids and chitosan levels (200 ppm). From this discussion can be expected that the nano form of chitosan and humic in combination is more effective than normal form.

Conclusion

In the current agricultural system, the extensive use of agrochemicals to boost agricultural production. Nanotechnology is becoming increasingly important for the agricultural sector. Promising results and applications are already being developed in the areas fertilizers and soil conditioners for plant growth. This new approach showed promising in utilizing natural resource such as chitosan and humic acids in the production of organic soil conditioner useful for sandy soil mitigating the drought stress tolerance in the plant. Results indicated that application of high rate of chitosan-humic acids nanocomposite (CS-HA nanocomposite) was more effective than other normal forms which led to improved soil physical (bulk density, total porosity, moisture content and available water) and chemical properties (pH and OM) along with nutrients (N& P) availability. In addition, wheat yield components (straw, grains and weight of 1000 grain) were increased as a resultant of applied high rate of chitosan-humic acid nanocomposite.

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