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Effect of both potassium phosphate and zinc nanocomposites prepared via gamma radiation on growth and productivity of potato under new

reclaimed soils.

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Abstract

This experiment was carried out during the two successive seasons of 2019 and 2020, to evaluate the effect of PVP and PVA as stabilizers and capping agents to control the size of the potassium mono hydrogen phosphate (potassium phosphate) and zinc oxide nanoparticles produced by gamma irradiation. HRTEM measurement reveals the formation of potassium mono hydrogen phosphate and zinc oxide nanoparticles within the polymeric networks of PVP and PVA, with mean sizes of 6.3 nm and 33 nm, respectively. Fourier transform infrared (FT-IR) spectroscopy revealed the structure formation of PVP/ potassium mono hydrogen phosphate nanoparticles and PVA/ zinc oxide nanoparticles. The formation of potassium mono hydrogen phosphate and zinc oxide nanoparticles is proved by UV–vis spectroscopy measurements, which reveal distinctive absorption peaks. The agriculture study during the two successive seasons of 2019 and 2020, under El Nuberia Region, Beheira Governorate show

that potato plants cv. Spunta sprayed with 8 ml / l of potassium phosphate and 9 ml / l of zinc oxide nano composite gave the tallest plant, highest fresh and dry plant haulm and number of stems per plant. As for potato yield, both previous concentrations scored the highest number of tubers per plant, average tuber weight and total yield per feddan, as well as chemical constituents of tubers such as specific gravity, dry matter percentage, starch, phosphorus and potassium percentage as well as zinc concentration.

Key words: potassium phosphate, zinc oxide, nano composite, gamma irradiation, potato..

Introduction

Potato is one of the most important vegetable crops in worldwide, it ranks the fourth important crop in the world after rice, wheat and maize. Potato has a special feature that it produces in short period more edible energy than grain crops and cereals, which give it the chance to be one of the most important and fundamental non-grain food widely [1]. Potato is not only an important fresh vegetable crop but also has an important role in agriculture manufacturing such as frozen potato, chips, dried potato products and starch production [2]. The nutritional value of potato is about 77% water, 16.3% starch, 0.9% sugar, 4.4 % protein, potassium, magnesium and iron [3].

The high production of potato depends on many factors like cultivar characteristics and quality,

the richness of soil with essential minerals, weather and agriculture practices as well as fertilization [4].

The appropriate fertilization program led to high tubers yield in quantity and quality, the synthesis and the translocation of plentiful quantity of carbohydrates in potato tubers depends on sufficient feeding with essential elements. Nitrogen, phosphorus and potassium are three macro essential elements which are necessary for high potato tuber yield and determining crop quantity and quality [5].

Phosphorus is one of the most critical essential macro elements for profitable potato production, yet many soils lack enough phosphorus to maximize potato yields. Potato has a high_phosphorus needs and is typically thought to be poor at absorbing phosphorus from the soil [6]. Protein synthesis, nucleic acid structure, cell division, and the

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composition of energy molecules such as ATP and ADP are all controlled by phosphorus [7]. Respiration and photosynthesis [8], structural component of phospholipids, nucleic acids, coenzymes, and phosphor proteins, and plays a crucial role in phytic acid storage in seeds [9, 10].

Potassium is an important nutrient for potato productivity, especially when it comes to achieving a high yield while maintaining excellent quality. It plays a variety of important roles in plant growth, including marinating cell growth and turgor pressure [11], translocation of synthesized carbohydrates from leaves to storage organs [12], leaf expansibility [13], and enhancing carbon dioxide penetration via leaf mesophyll [14]. Potassium plays a critical role in potato cultivation since the crop requires a lot of potassium for plant development and starch synthesis, and the optimum yield of marketable potato tubers is dependent on a lot of potassium fertilizer [15].

Bishwoyog and Swarnima [16] discovered that 30 tonnes of potato tubers require 250 kg of potassium per hectare of soil. It was also shown that the potassium concentration in potato tubers is higher than that of other macro elements, reaching nearly 1.7 percent of dry matter [17]. On the other hand, the importance of potassium for potato quality is focused on its role in increasing the content of starch, protein, and decreasing sugars content in tubers, lower sugars content, such as glucose + fructose, is an important quality factor for processed potato, because the highest content of sugars causes potato darkness during frying [18]. Potassium also improves potato storage and shelf life by lowering the severity of black spot damage on tubers [19].

Both phosphorus and potassium are lost at a rate of 80 percent to 90 percent and 50 percent to 90 percent, respectively, by soil addition, resulting in a significant loss of resources. By 2050, worldwide macronutrient consumption (nitrogen, phosphorus, and potassium) will have increased from 175.5 million tonnes to 263 million tonnes. In addition, high phosphorus consumption resulted in element transportation into groundwater, destroying the aquatic ecosystem and affecting human health. As a result, the use of macronutrient nano fertilizer is critical as a safe method for plants to meet their mineral needs while reducing transportation costs and increasing yield when compared to traditional fertilizers [20].

Zinc is an essential micro element for plant growth. It is involved in a variety of crucial processes in plants, including enzyme activation (RNA polymerase and superoxide dismutase), plant cell propagation and differentiation, and chloroplast enlargement. Although it plays an important function in plant development, its high amount can be harmful to plants [21]. The amount of Zn required for proper plant growth in soil solution is estimated to be around 0.05 mg 1^{-1} , with higher levels causing phytotoxicity [22]. Despite the fact that there are numerous sources of zinc nanoparticles (such as ZnS, ZnSe, or quantum dots CdSe / ZnS), zinc oxide nanoparticles are still one of the most effective forms of zinc for plants that scientists have been studying in the last two years [21].

Radiation emitted by electromagnetic waves or photons, such as gamma rays and X-rays, or particle-like radiation, such as electron beam radiation, is referred to ionizing radiation. Such particles, also known as photons, are known to have enough energy to break or induce chemical bonds, as well as to produce electrically charged particles when they interact with atoms or molecules that aren't their source. Ionizing radiation has been promoted as a valuable method for the production and synthesis of metal nanoparticles, with applications ranging from medical device sterilization to polymer crosslinking. In concept, using radiation to synthesize metal nanoparticles involves solvent radiolysis, as opposed to using a chemical reductant, in which a solvent molecule is ionized and excited, resulting in a variety of reactive species that trigger nanoparticle formation [23].

As radiation is used to develop new and optimized ways of gold nanoparticle synthesis, many advantages can be seen when compared to other approaches or traditional technologies, such as superior yields of monosized and highly monodispersed metallic clusters. Other advantages and potential of radiolytic synthesis include conducting studies under mild temperature and pressure settings, without the need of chemical reducing agents, and with good reproducibility [24].

Another advantageous feature of this method is its adaptability in terms of radiation sources, since it may be carried out using gamma, e-beam, X-rays, or even UV light without compromising the end product or necessitating formulation changes, aside from modifying the radiation source.

The ability to combine sterilization with nanoparticle production in a single operation is a unique benefit that ionizing radiation may provide [25].

Passivating chemicals can also reduce the polydispersity of nanoparticles by chemically stabilizing the nanocrystals, i.e., ligands bearing thiol groups; and by varying the amount of capping agents, such as polymers or small molecules bearing surfaceactive functional groups, i.e., polyvinylpyrrolidone (PVP). However, polymers like PVP and polyvinylalcohol (PVA) are the most used stabilizers in radiolytic synthesis. Polyvinylpyrrolidone binds to metal nanoparticles through the functional groups C=O and N, which have lone pairs of electrons that aid in the covalent stabilization of nanomaterials at their surfaces, while the long polymer chain exerts a steric hindrance that prevents interaction with other nanoparticles, preventing aggregation.

On the other side, the suppression of metal hydroxide clusters in PVA chains hinders nanoparticle aggregation. PVP (polyvinylpyrrolidone) is a soluble polymer in water.

Because of its good solubility, excellent affinity for polymers various and resins. nontoxicity. biodegradability, and compatibility, it has been used in medicine, pharmaceuticals, cosmetics, foods, printing inks, textiles, and many other fields [26]. This chemical has been approved by the US Food and Drug Administration (FDA) for a variety of applications. Inactive Ingredients in drugs approved by the FDA Office of Generic Drugs, Division of Labeling and Program Support, FDA/Center for Drug Evaluation and Research Quarterly database updates are performed. Data is up to date as of January 6, 2010. Database last updated on January 13, 2010 - for a list of permitted goods. It's also usually thought to be safe.

Thus, the aim of this study was to evaluate the influence of gamma irradiation on preparing potassium mono hydrogen phosphate (potassium phosphate) and zinc oxide nano composites and study their foliar application effect on growth and productivity of potato under new reclaimed soil.

2. Materials and Methods

2.1. Chemical study

Orthophosphoric acid (85%) H₃PO₄ (M.W.98) and Potassium hydrogen carbonate obtained from Alpha Chemika. Poly (vinyl pyrrolidone) (PVP); average molecular weight of 30000 was purchased from Universal Fine Chemicals PVT. LTD. Polyvinyl alcohol (PVA) with molecular weight 1, 15,000, (-C₂H₄O)n by Loba Chemie, India. Acetic acid glacial; M.W. 60.05, with assay (acidimetric) min 99.5% purchased from Loba Chemie. Zinc sulfate, Ethanol and Glycerine USP 99.5% obtained from El Gomhouria Co., Egypt.

Preparation of potassium mono hydrogen phosphate (potassium phosphate) nanocomposites

20% (v/v) of phosphoric acid was added to an equivalent amount of bi-distelled water. Also, 1% of Polyvinylpyrrolidone (PVP) was added via continuous stirring at 70°C. After dissolving PVP, an equivalent amount of Glycerin (glycerol) was added. Finally, after fully mixing of the components, 10% (w/w) of potassium hydrogen carbonate was added to the solution with continued stirring. The resulted solution was exposed to gamma radiation dose at 4 kGy (Indian cell - ⁶⁰Co) separately with dose rate of 1.16 kGy/h., at NCRRT, Cairo, Egypt [27, 28].

Preparation of PVA/ zinc oxide nanocomposites

14% (v/v) of acetic acid was added to an equivalent amount of bi-distelled water. Also, 1% of

Polyvinyl Alcohol (PVA) was added via continuous stirring at 70°C. After dissolving of PVA, an equivalent amount of Ethanol was added. Finally, after fully mixing of the components, 10% (w/w) of zinc sulfate was added to solution with the continued stirring. The resulted solution was exposed to gamma radiation dose at 4 kGy (Indian cell - 60 Co) separately with dose rate of 1.16 kGy/h., at NCRRT, Cairo, Egypt [27, 28].

Characterizations

High Resolution Transmission electron microscopy (HRTEM)

High Resolution Transmission Electron Microscopy (HRTEM) measurements were performed with (JEOL, JEM 2100, Japan) operating at 200 kV. HRTEM was used to find out the distribution and size of zinc nanoparticles.

UV-Vis absorption spectra

The UV-Vis absorption spectra were taken by double beam spectrophotometer provided with computer data acquisition Type JASCO 670UV-Vis/NIR.

FT-IR spectroscopy

FTIR was carried out by using FT-IR 6300, Jasco, Japan in the range 400–4000 cm⁻¹.

2.2. Agricultural study

This experiment was performed at the Agricultural Production and Research Station, National Research Centre, El Nubaria Province, El Behira Governorate, Egypt during the two successive seasons of 2019 and 2020 to evaluate the effect of four foliar applications of both nano potassium mono hydrogen phosphate (potassium phosphate) (control, 2, 4 and 8 ml/l) and nano zinc oxide (control, 3, 6 and 9ml /l) on growth and productivity of potato cv. Spunta. The potato seed tubers were imported from Holland and were planted on the 14th of January in both seasons. Potato seed tubers were planted at distance 25 cm between plants and 75 cm between rows. Physical and chemical analysis of soil is presented in Table (1).

The foliar application was carried out at 31 days after sowing then 15 and 30 days after the first foliar application treatment. The experiment was laid out in a split plot design where Nano potassium phosphate composites treatments were arranged in the main plots and zinc oxide nano composites were randomly distributed in the sub-plots. The experiment was consisted of 16 treatments with three replicates. The plot area was 9.6 m² consisted of four inner rows of 3 m in length and 80 cm in width and drip irrigation system was used for irrigation. As for fertilization, 30m³ organic manure per feddan as well as 75 units /feddan of Calcium super-phosphate (15 % P2O5) were added during soil preparation for agriculture. Nitrogen fertilizer was added in the form of ammonium sulphate (20.6 N /fed) at 150 units/ fed. as two equal portions (30 and 45 day old) and Potassium sulphate (48 % K2O) was applied at a rate of 96 units per feddan at two times first dose was added during preparation the soil for planting the second dose at the beginning of the formation of the tubers. Cultural practices, disease and pest control management were followed according to the recommendations of the Egyptian Ministry of Agriculture.

Table (1): Physical and chemical analysis of the experimental soil of El Nobaria Region, Behira Governorate during 2019 and 2020 seasons.

		Particle si	al properties ize distribut	ion						
			ze distribut							
		Clay %								
73		Citay 70	Sand% Clay % Silt %							
	.15	6.1		20.75						
		Chemi	cal analysis							
pН	1:2.5	EC dSm ⁻¹	CaCC) ₃ %	CEC C mole Kg ⁻¹	O.M %				
7.	7.63 0.98		3.22		4.95	0.04				
7.30 1.09		1.09	2.76 4.32		0.02					
Macronutrients (%)				Micronutrients (ppm)						
Ν	Р	K	Fe	Zn	Mn	Cu				
2.10	0.53	1.19	231	145	322	76				
2.11	0.69	1.68	324	172	286	41				
	7. 7. M 2.10	7.30 Macronutz N P 2.10 0.53	pH 1:2.5 EC dSm ⁻¹ 7.63 0.98 7.30 1.09 Macronutrients (%) N P K 2.10 0.53 1.19	pH 1:2.5 EC dSm ⁻¹ CaCC 7.63 0.98 3.2 7.30 1.09 2.7 Macronutrients (%) K Fe 2.10 0.53 1.19 231	7.63 0.98 3.22 7.30 1.09 2.76 Macronutrients (%) Min N P K Fe Zn 2.10 0.53 1.19 231 145	$\begin{array}{c c c c c c c c c c c c c c c c c c c $				

Vegetative characters:

A random sample of ten plants was taken from each plot at 75 days after planting for the determinations of vegetative growth, i.e., plant height, fresh and dry weight of plant haulm and number of stems per plant.

Tuber yield and its components:

Each experimental plot was harvested at 120 days after planting and average tuber weight, number of tubers per plant and total yield per feddan were recorded.

Chemical constituents of tubers:

A random sample of 30 tubers was selected from each experimental unit then washed, dried and cut into small pieces, which were mixed and grounded for the determination of starch in tubers according to A.O.A.C. [29]. Tuber specific gravity was calculated from samples weights measured in air and water. Total carbohydrates were determined as glucose after acid hydrolysis and spectro photomericully determined using phenol acid regent according to Dubbois et al. [30], Dry matter percentage of tuber was estimated according to the following formula: Plant dry matter% = (dry weight of tuber / fresh weight of tuber) x 100, phosphorus percentage in tubers was determined according to John [31], potassium percentage was determined according to Brown and Lillel[32] and zinc was determined as described by Chapman and Pratt [33].

Statistical analysis: All data were subjected to statistical analysis using MSTATC Computer Program [34]. The Duncan's New Multiple Range test at 5% level of probability was used to test the significance of differences among mean values of treatments [35].

Results and discussion

Nanostructure analysis is required to uncover the properties of nanostructured materials while examining materials at the nanoscale scale. This goal will not be met unless effective characterization instruments are used. Over the years, the transmission electron microscope (TEM) has grown into a very complex device with applications in a wide range of scientific disciplines. TEM has evolved into an invaluable tool for studying the properties of nanostructured materials and altering their behaviour due to its unprecedented capacity to offer structural and chemical information throughout a range of length scales down to the level of atomic dimensions. TEM is used to characterize the size, grain size, size distribution, and homogeneity of nanoparticles, lattice type, crystal structure, dispersion, chemical and physical properties of phases such as number, morphology, and structure of phases at the nanoscale.

Fig.1(a and b) shows a typical transmission electron microscope image of potassium mono hydrogen phosphate nanoparticles embedded in PVP network matrix fabricated by gamma irradiation. From the HRTEM images, it was observed that potassium phosphate mono hydrogen has different morphological features such as rhombus, cubic and qausispheical. In Fig. 1 (c and d), the nanoparticles showed a homogeneous size distribution. Also, the size of nanoparticles is in the range between (5.9 - 7)nm. This range of size confirm the role of PVP in stabilizing potassium mono hydrogen phosphate nanoparticles [36].

Fig 2 (a, b) shows the SAED pattern. The Electron diffraction pattern shows characteristic bright

spots, which is associated with the crystalline nature of potassium mono hydrogen phosphate nanoparticles. SAED pattern reveals single crystal structure for the prepared nanoparticles which confirm the highly ordering of the nanoparticles [37].

The size distribution range plots of potassium mono hydrogen phosphate nanoparticles were fit using

a Gaussian model with Microcal Origin 5.0 graphing software to determine the widths and centres of the size distributions. The width of the distribution gives an information of how narrow or wide of the size distribution is and the centre of the distribution is the most probable or average size of the nanoparticles (depending on the shape of the distribution).

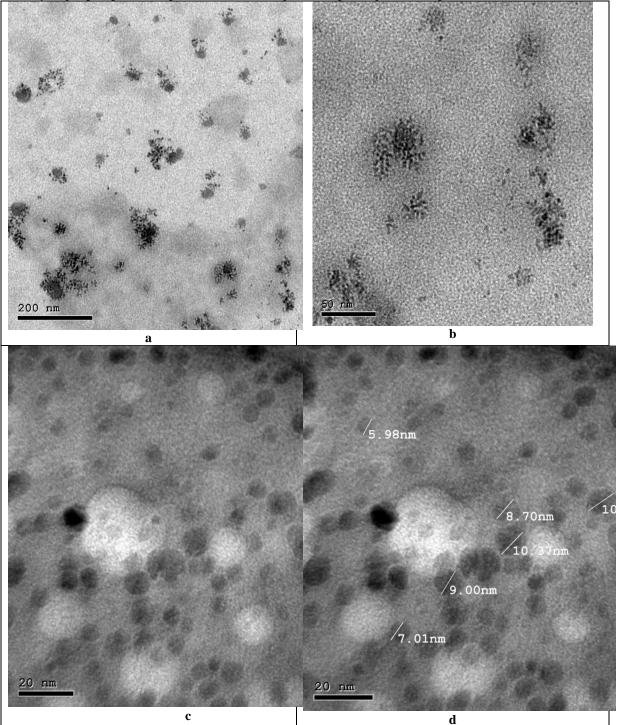
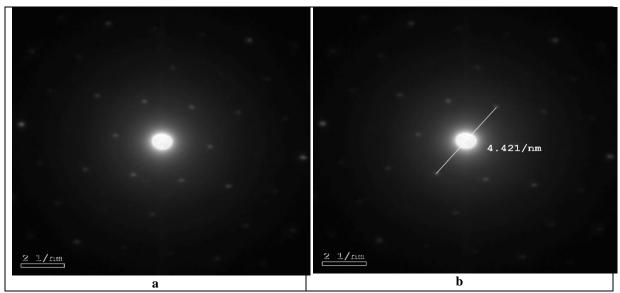
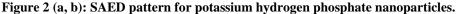


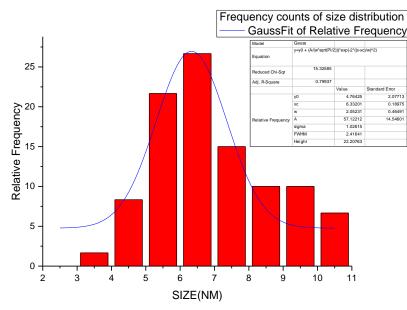
Figure 1: show HRTEM photographs for (a, b, c) PVP/ potassium hydrogen phosphate nanoparticles and (d) Size distribution of potassium hydrogen phosphate nanoparticles.





As a result, the size distribution histogram of nanoparticles is depicted in fig.3. The size of potassium mono hydrogen phosphate nanoparticles was found to be in the range of (3 - 10.9) nm. The average size of potassium mono hydrogen phosphate nanoparticles was discovered to be approximately 6.3

nm. The HRTEM Gaussian fit histogram sizecontrolled potassium nanoparticles increase the successful synthesis and good stabilization of potassium hydrogen phosphate nanoparticles in PVP matrix [36], [38, 39].



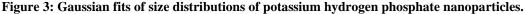


Figure 4 shows HRTEM images of zinc nanoparticles (ZnO), which clearly reveal that the zinc nanoparticles have a wurtzite crystal structure (hexagonal) [40]. The size distribution of zinc nanoparticles over the polymer network is shown in Fig. 4 (b). Zinc nanoparticle size distribution values were found to be in the range of (11-98) nm. The average particle size in the TEM image was 33, which was calculated by averaging the sizes of 30 particles observed [27]. Figure 4(c) also depicts the SAED pattern. The bright spots in the electron diffraction pattern are connected with the crystalline structure of zinc oxide nanoparticles.

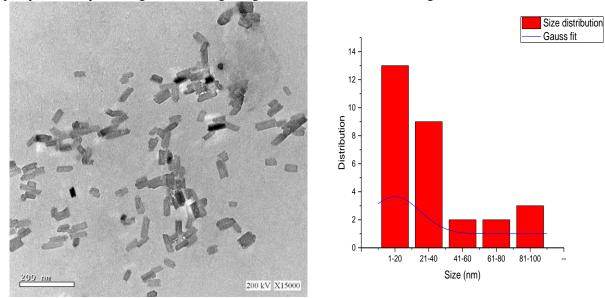
The produced nanoparticles have a polycrystalline structure as revealed by the SAED pattern.

FTIR is a helpful tool to determine chemical composition which can analyze the chemical makeup of a material, by examining the chemical bonds.

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Both organic and inorganic materials can be investigated and identified using FTIR. Within a substance, it also detects covalent bonding pairs and functional groups. The IR spectra of PVP nanoparticles incorporating potassium hydrogen phosphate nanoparticles generated using the gamma irradiation approach are shown in Fig. 5. The interaction between PVP, phosphoric acid, and glycerol, filled with potassium hydrogen carbonate, was determined using FT-IR analysis, which results in considerable changes in the functional groups of the PVP nanostructure gel.

(b)



(a)

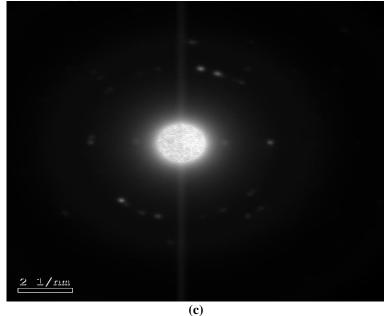


Fig. 4: (a) HRTEM of zinc nanoparticles, (b) Size distribution by histogram of zinc nanoparticles, (c) SAED pattern of zinc nanoparticles.

Table (2) summarizes the vibrational groupings discovered. A strong broad band in between 3245-3471 cm⁻¹ is attributed to O-H stretching (intermolecular bonded). The band at about 2948.5 cm–1is assigned to –CH asymmetric stretching vibration. Also, there is another band at 2884.7 cm⁻¹ for bending and scissoring vibrations of CH₂.

Moreover, the band at 1650 cm⁻¹ confirm the stretching vibration of O-H [41]. The bands corresponding to CH₂ bending vibration and C-H bending appear at about 1467 cm⁻¹and 859.2 cm⁻¹, respectively. The band corresponding to stretching C=O and O-H occurs at about 1423 cm⁻¹, a strong band at about 999 cm⁻¹ is attributed to C=C stretching

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[42], the band at 859.2 cm⁻¹ is assigned to C-H bending. The band at about 676 cm⁻¹ is assigned to C=C bending of alkene (disubstituted (cis) [43]. The characteristic band at 1180.6 cm⁻¹ refers to C-N stretch. Additionally, the stretch vibration of C–O appeared at 1110.6 and 1028 cm⁻¹. Finally, the observed peak at 492 cm⁻¹ is attributed to out of plane ring bending [44].

The FT-IR spectrum of PVA/ acetic acid/ ethanol solution contains zinc oxide is presented in Fig.6, the large band observed at 3338.17 cm⁻¹ is linked to the stretching O-H from the intermolecular and intramolecular hydrogen bonds. The vibration band at 2848.38 cm⁻¹ refers to the stretching C-H from alkyl groups [45]. The peak at 1703 cm⁻¹ is due to the stretching C=O from carboxylic acid. The band at about 1640.94 cm⁻¹ is assigned to C=C stretching from alkene. The bands corresponding to O-H bending from carboxylic acid and alcohol appear at about 1398.35 cm^{-1} and 1388.97 cm^{-1} . The band corresponding to CH₂ symmetric twisting occurs at about 1274 cm^{-1} . The assignment of the main bands of FTIR spectra displayed in FT-IR spectrum are summarized and listed in Table (3). [46].

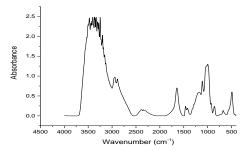


Figure 5: FTIR spectra of PVP/phosphoric acid /glycerin containing potassium hydrogen phosphate nanoparticles.

Table (2): Summarize the FT-IR bands of PVP/ phosphoric acid/ glycerol, filled with potassium hydrogen carbonate.

Band (cm ⁻¹)	Description
3245-3471 (broad band)	O-H stretching (intermolecular bonded)
2948.5	-CH asymmetric stretching vibration
2884.7	Bending and scissoring vibrations of CH ₂ .
2369.56	Symmetric axial deformation of the CO ₂
1650	Stretching vibration of O-H
1467	CH ₂ , bending vibration
1423	Stretching C=O and O-H
1180.6	C-N stretch (amine)
1110.6	C–O stretch
1028	C–O stretch
999	C=C bending
859.2	C-H bending
676	C=C bending of alkene (disubstituted (cis)
492	Out of plane ring bending

Table (3): FT-IR bands of PVA/ acetic acid/ ethanol solution containing zinc oxide

Wavenumber (cm ⁻¹)	Band assignment
3338.17	Stretching O-H from the intermolecular and intramolecular hydrogen
	bonds.
2848.38	Stretching C-H
1703	C=O stretching from carboxylic acid
1640.94	C=C stretching from alkene
1398.35	O-H bending from carboxylic acid and alcohol
1388.97	O-H bending from carboxylic acid and alcohol
1274.37	CH ₂ symmetric twisting
1095.7	C-O stretching for secondary alcohol
1044.98	C–O–C stretching
1015.90	C–O–C stretching
876.8	C-H bending
609	δ(COO ⁻)

On the other hand, there is a peak at 1095.7 cm⁻¹ refers to C-O stretching for secondary alcohol. Furthermore, the bands appeared at 1044.98 and 1015.90 cm⁻¹ are attributed to C–O–C stretching. The characteristic absorption peak of the C–H bending band presented at 876.8 cm⁻¹. [47, 48].

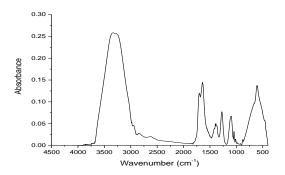


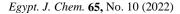
Figure 6: FT-IR spectrum of PVA/ acetic acid/ ethanol solution containing zinc oxide.

UV measurements

UV spectra of potassium hydrogen phosphate and zinc oxide nanoparticles were recorded on UV- spectrophotometer. The experiment was conducted out at a wavelength of 200-1400 nm. The formation of potassium hydrogen phosphate and zinc oxide nanoparticles was confirmed by UV spectral analysis. The principle of UV spectroscopy suggests that a molecule can absorbs UV radiation owing to presence of either or both conjugated pi (π) bonding systems (π - π * transition) and nonbonding electron system (n- π^* transition) in the compound. The UV absorption phenomena occurred when electrons moved from low energy orbital (i.e., σ , n, and π) to high energy orbital (i.e., σ^* and π^*). There is an energy gap between σ - σ^* , σ - π^* , π - π^* and n- π^* orbitals. When this energy gap was changed, the wavelength (max) was changed as well [49].

The UV spectra of PVP/ potassium mono hydrogen phosphate nanostructure is shown in Fig.7. The nanostructure exhibited an absorbance maxima (λ max) at 290 nm. The UV absorption occurred due to transition of electron i.e., bonding (π - π * transition) or nonbonding (n- π * transition) from ground state to excited state [50].

Fig.8 shows the absorption spectrum of ZnO prepared in PVA/ acetic acid/ ethanol solution via gamma radiation. The UV–Vis. spectrum shows two bands at 276 nm and 294 nm, assigned to exciton transitions in small ZnO clusters [40].As declared in previous reports [51], five stated absorption features are typically reported, located near 210, 230, 270, 320 and 360 nm. These electronic transitions confirm the appearance of preferentially stable "magic sizes" from the II–VI-semiconductor cluster chemistry.



Moreover, Hu *et al.* [52] have analyzed the progressive spectral between 300 and 360 nm which is associated with nanoparticle size range between 2 and 6 nm.

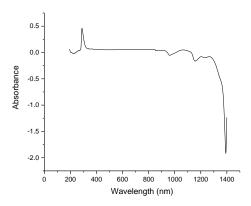


Figure 7: UV spectra of PVP/ potassium hydrogen phosphate nanostructure.

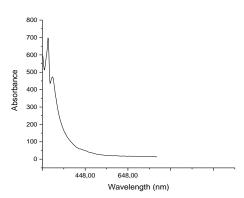


Figure 8: UV spectra of PVA/ acetic acid/ ethanol containing zinc oxide nanoparticles. Vegetative growth characters

Data presented in Table (4) show that the highest concentrations 8 ml / 1 and 9 ml / 1 of both potassium phosphate and zinc oxide nano composites scored the highest values of plant height, fresh and dry weight of plant haulm as well as number of stems per plant. Regarding the effect of the interaction between both foliar application treatments, it was observed that 8 ml / 1 of potassium phosphate and 6 ml / 1 as well as 9 ml / l of zinc nano composites gave higher values for all previous characters than other treatments. Concerning nano potassium phosphate composite similar result was obtained by Abd El-All [53] who stated that the highest concentration of nano phosphorus and potassium scored the highest plant height and shoot dry weight of pepper and Mahdieh et al. [54] who reported that nano zinc has an effective role on enhancing vegetative growth characters of pinto bean plants. The simulative effect of nano phosphorus might be related to the role of phosphorus in the installation of energy compounds such as ATP and ADP which reflect on enhancing growth

parameters [55], respiration and photosynthesis process [8]. Also, it participates in the structure of phospholipids nucleic acids, coenzymes [9,10] which reflect on the amelioration of growth characters.

increasing the process of photosynthesis rate [57] Also the activation of photosynthesis process might be referred to the involvement of zinc in the structure as catalytic component of protein and enzymes which is

Table (4): Effect of nano potassium phosphate and nano zinc oxide foliar application on plant height (cm), fresh	
and dry weight of plant haulm (g) as well as number of stems per plant of potato during 2019 and 2020 seasons.	

		First s			_	r plant of pol	~	season	
Treatn	nents	Plant height	Fresh weight of plant haulm	Number of stems /plant	Dry weight of plant haulm	Plant height	Fresh weight of plant haulm	Number of stems /plant	Dry weight of plant haulm
				Potassiu	m phospha	te			
	Control	65.6 D	290.4 D	3.32 D	54.1 D	65.4 D	297.4 D	3.2 D	55.4 D
Potassium	2 ml / L	72.0 C	300.8 C	3.8 C	58.1 C	67.8 C	306.3 C	3.5 C	60.5 C
phosphate	4 ml / L	80.7 B	306.9 B	3.9 B	68.4 B	73.8 B	313.2 B	3.9 B	73.2 B
	8 ml / L	85.4 A	330.3 A	4.6 A	70.4 A	79.9 A	325.6 A	4.1 A	78.5 A
					Zinc				
	Control	71.8 D	289.1 D	3.4 D	58.5 D	67.7 D	300.2 D	3.3 D	63.0 D
	3 ml / L	74.6 C	302.5 C	3.7 C	61.0 C	70.0 C	306.6 C	3.5 C	65.7 C
Zinc	6 ml / L	76.5 B	312.1 B	4.0 B	64.6 B	72.9 B	312.5 B	3.8 B	68.0 B
	9 ml / L		324.6						
	> mi ; L	81.0 A	А	4.4 A	66.9 A	76.3 A	323.2 A	4.1 A	71.0 A
	~				eraction				
	Control	62.4 g	275.5 g	2.8 g	48.6 h	61.2 g	282.3 h	2.9 f	51.2 i
Control	3 ml / L	64.5 f	282.4 f	3.1 f	51.4 g	63.2 f	294.5 g	3.1 e	54.4 h
	6 ml / L	66.7 e	293.5 e	3.5 e	56.7 f	67.6 e	301.3 e	3.3cd	56.5 g
	9 ml / L	69.1 de	310.4 c	3.9 d	59.8 e	69.7 d	311.6 c	3.6 c	59.8 f
	Control	67.6 e	286.6 f	3.2 f	53.6 g	64.5 f	299.7 f	3.2 d	55.6 g
2 ml / L	3 ml / L	69.6 de	298.7 e	3.7 d	55.7 f	66.7 e	301.5 e	3.4 cd	59.7 f
2 m / L	6 ml / L	71.4 d	302.5 d	4.1 c	59.8 e	68.8 d	309.8 c	3.6 c	61.3 f
	9 ml / L		315.6						
		79.6 c	bc	4.4 b	63.5 de	71.3 c	314.5 c	3.9 b	65.5 e
	Control	77.5 d	293.4 e	3.5 e	65.6 c	68.7 d	307.6 d	3.5 c	69.7 de
	3 ml / L	79.7 c	303.5 d	3.8 d	67.3 bc	72.3 c	310.9 c	3.8 b	71.2 c
4 ml / L	6 ml / L	81.3 c	311.2 c	3.9 d	69.6 b	75.5 bc	314.5 c	4.1 ab	74.4 bc
	9 ml / L		319.8						
		84.6 b	bc	4.5 b	71.2 ab	78.7 b	319.9 b	4.4 ab	77.7 b
	Control	79.8 c	301.2	4.1 c	66.5 bc	76.6 b	311.5 c	3.7 bc	75.6 bc
	3 ml / L	84.6 b	325.4 b	4.4 b	69.7 b	77.8 b	319.8 b	3.9 b	77.6 b
8 ml / L	6 ml / L		341.2						
		86.7 ab	ab	4.8 ab	72.3 ab	79.7 ab	324.5ab	4.2 ab	79.8 ab
	9 ml / L	90.8 a	353.4 a	5.1 a	73.4 a	85.7 a	346.8 a	4.8 a	81.3 a

Means followed by different letters are significantly different at $P \le 0.05$ level; Duncan 's multiple range test.

Concerning the effect of nano potassium on the enhancement of growth parameters of potato plants, it might be referred to its role on enhancing the physiological process in plant such as enzymatic and vital reactions and regulating hormones production [56]. Regarding the effect of nano zinc oxide composite on increasing vegetative characters, it might be related to the effective role of zinc on increasing the metabolism of carbohydrates via necessary for the activation process [58]. From another point, it has an important role in the oxidationreduction process through its role as catalytic agent which reflect on enhancing auxin content in plants [59] In addition to the above, zinc nano composite has a critical role in the activation of merisitimic tissues, increasing cell division and cell elongation which affect plant length [57], increasing the synthesis of IAA through activating the amino acid tryptophan[60].

	Fir	st season				Second seas	on
Treatments		Number of tubers /plant	Average tuber weight	Total yield (Ton/fed.)	Number of tubers /plant	Average tuber weight	Total yield (Ton/fed.)
			(g)	-		(g)	
			Potas				
	Control	4.5 D	114.4 D	13.8 D	4.6 D	133.5 D	13.2 D
Potassium	2 ml / L	5.0 C	129.1 C	15.9 C	4.8 C	138.8 C	16.0 C
phosphate	4 ml / L	5.6 B	138.2 B	17.8 B	5.4 B	168.2 B	18.1 B
	8 ml / L	6.8 A	159.1 A	18.8 A	6.8 A	176.1 A	19.0 A
			Zir				
Zinc	Control	4.9 D	116.8 D	14.6 D	5.0 D	132.5 D	15.0 D
	3 ml / L	5.3 C	128.6 C	16.3 C	5.2 C	148.3 C	16.0 C
	6 ml / L	5.6 B	142.1 B	17.2 B	5.5 B	162.9 B	17.1 B
	9 ml / L	6.1 A	153.3 A	18.2 A	6.0 A	172.9 A	18.3 A
			Intera	ction			
	Control	3.9 g	99.8 h	12.3 h	4.2 g	110.2 g	11.5 h
Control	3 ml / L	4.3 f	102.3 gh	13.4 g	4.5 f	124.3 f	12.6 g
	6 ml / L	4.7 e	123.2 f	14.2 f	4.7 ef	146.3 e	13.5 f
	9 ml / L	5.1 d	132.3 e	15.4 e	5.1 e	153.3 d	15.5 d
	Control	4.6 f	112.3 g	14.3 f	4.5 f	120.9	14.5 e
2 ml / L	3 ml / L	4.9 e	126.4 f	15.4 e	4.7 ef	138.7 ef	15.5 d
	6 ml / L	5.1 d	136.5de	16.4 d	4.9 e	142.4 e	16.5 c
	9 ml / L	5.6 c	141.2 d	17.6 c	5.4 de	153.4 d	17.6 bc
	Control	4.9 e	120.9 f	15.4 e	4.9 e	144.5 e	16.6 c
	3 ml / L	5.3 d	132.3 e	17.7 c	5.2 de	165.6 c	17.6 bc
4 ml / L	6 ml / L	5.8 c	146.5 d	18.7 b	5.7 d	175.3 b	18.5 b
	9 ml / L	6.5 bc	153.3 c	19.7 ab	6.1 c	187.4 ab	19.8 ab
	Control	6.3 bc	134.4 de	16.5 d	6.4 bc	154.4 d	17.6 bc
	3 ml/L	6.7 b	153.4 c	18.7 b	6.7 b	164.7 b	18.5 b
8 ml / L	6 ml / L	6.9 ab	162.3 b	19.8 ab	6.9 ab	187.8 ab	19.9 ab
	9 ml / L	7.3 a	186.6 a	20.4 a	7.5 a	197.8 a	20.3 a

Table (5): Effect of nano potassium phosphate and nano zinc oxide foliar application on number of tubers per plant, tuber weight (g) and total yield per feddan (ton) of potato during 2019 and 2020 seasons

Means followed by different letters are significantly different at $P \le 0.05$ level; Duncan 's multiple range test.Vield and its componentsper plant. As for average tuber weight, it was observed

Concerning tuber yield, data tabulated in Table (5) show that plants sprayed with 8 ml / 1 of potassium phosphate and 9 ml / 1 of zinc oxide nano composites gave higher number of tubers per plant, average tuber weight and total yield per feddan than other foliar application treatments in both seasons. Similar finding was obtained by Abd El-Azeim *et al.* [61] who found that the highest concentration of both nano phosphorus and potassium foliar application scored the highest economical yield and tubers dry weight of potato plants. Also Marzouk *et al.* [62] who found that the foliar application of zinc nano particles increase pod fresh and dry weight as well as total yield of snap bean plants.

Respecting the interaction between both nano elements and their effect on tuber yield, data revealed that the combination between 8 ml / 1 of potassium phosphate and 6 ml / 1 as well as 9 ml / 1 of zinc oxide nano composites led to the highest number of tubers

that 8 ml / 1 of potassium phosphate nano composite combined with 9 ml / 1 of zinc oxide nano composite scored the highest value of tuber weight in both seasons. On the other side, data illustrated that the foliar application of 4 ml / 1 of potassium phosphate nano composite combined with 9 ml / 1 of zinc oxide nano composite and 8ml/l of potassium phosphate nano composite combined with 6 ml/l and 9 ml/l of nano zinc oxide yielded higher tuber yield per feddan in both seasons. Respecting the effect of nano potassium and phosphorus on increasing tuber yield, it could be concluded that both nano elements have an important role in increasing plant vegetative growth which increase the chance to utilize solar radiation and essential minerals which reflect on photosynthesis and plant yield[61].Concerning the effect of nano potassium on the enhancement of tubers yield of potato plants, it might be referred to the important role of nano potassium in the translocation of the output of the photosynthesis process and carbohydrates from

leaves to different storage organs which reflect on tuber yield and its components [63]. Phosphorus is an essential element for lucrative potato yield, taking into account that there is no abundant amount in soil and potato crop need a high requirement of phosphorus which could not be obtained from soil[6].thus the foliar application of phosphorus led to obtain the sufficient requirement which participate in different metabolic process such as respiration, the transfer of cellular energy and photosynthesis[8]. It participates in the structure of phospholipids, coenzymes and the structure of ATP and ADP and the storage of nutrients in seeds as phytic acid in storage organs such as seeds [10], thus all previous roles play an important role on total yield. As for the effect of zinc on enhancing yield, it could be referred to its positive effect on controlling the internal plant hormone specially indole acetic acid content which has a relation with cell elongation and plant development, it has an important role in the synthesis of protein and carbohydrates which reflect on plant yield [64].

Chemical constituents of tubers

As for the effect of both potassium phosphate and zinc oxide nano composites foliar application and their influence on chemical constituents of potato tubers, results obtained and presented in Table (6) show that 8 ml / 1 of nano potassium phosphate and 9 ml / l of nano zinc oxide gave the highest percentage of dry matter, specific gravity, total carbohydrates and starch percentage in potato tubers during the two successive seasons. This finding agree with that obtained by Abd El-All [53] who found that the highest concentration of nano phosphorus and potassium led to the highest content of pepper fruits carbohydrates content; Mijwel and Muhsin [65] who declared that the highest levels of nano phosphorus, potassium and zinc scored the highest percentage of starch in potato tubers, also Amin and Badwy[66] who stated that high levels of nano zinc resulted high carbohydrates content in common bean seeds. Similarly, Al-Juthery et al. [63] found that spraying potato plants with nano phosphorus, potassium and zinc with high levels led to an increase in tubers dry matter.

Concerning the interaction between both nano elements and their influence on chemical constituents of potato tubers, data show that 8 ml / l of potassium phosphate nano composite combined with 6 ml / l and 9 ml / l of zinc oxide nano composite gave the highest values of dry matter percentage and total carbohydrates percentage in potato tubers during the two successive seasons. While, it was observed that the interaction between 8 ml / 1 of potassium phosphate and 9 ml / 1 of zinc oxide nano composites gave higher specific gravity and starch percentage than other treatments through the twice seasons.

The effect of phosphorus ,potassium and zinc nano composites on chemical constituents of tubers might be related to the fact that they have an important role in stimulating the photosynthesis rate and the activation of enzymes which affect the synthesis carbohydrates in leaves [67], the highest percentage of starch in tubers might be related to the role of potassium in increasing the translocation of synthesized carbohydrates from leaves to tubers [68].From another point ,the simulative effect of nano zinc oxide might be related to its important role in activating different enzymes which are responsible of photosynthesis, biosynthesis and transformation of carbohydrates.

Regarding phosphorus and potassium percentage and zinc concentration in tubers, data tabulated in Table (7) show that the highest concentration of both nano fertilizers composite (potassium phosphate and zinc) 8 ml / 1 and 9 ml / 1 gave the highest values for phosphorus, potassium percentage and zinc concentration in potato tubers in both seasons. Regarding the interaction between both nano fertilzers and their effect on phosphorus and potassium percentage and zinc concentartion in potato tubers, it was found that 8 ml / 1 of potassium phosphate combined with 6 and 9 ml / 1 of zinc oxide nano composite led to the highest percentage of phosphorus and potassium as well as zinc concentration in potato tubers during the two successive seasons. Similar finding was obtained by Amin and Badwy [66] who found that the highest concentration of nano zinc scored the highest content of phosphorus and potassium in dry seeds of common bean, Marzouk et al. [62] who found that snap bean plants sprayed with nano zin oxide had high content of phosphorus, potassium and zinc in green pods, Abd El-Azeim et al.[61] who found that potato plants sprayed with nano phosphorus and potassium had high concentration of phosphorus and potassium in tubers.

The high amount of phosphorus and potassium as well as zinc in tubers might be referred to the large surface area of nano composite which are smaller than stomata size of potato leaves which increase the chance of minerals penetration and improve the absorption and enhance the efficiency of utilizing nutrient which reflect on the content of elements in plant organs [69]

		Firs	st season				Sec	ond season		
Treatments		J		Total Carbohydrates	Starch		Specific gravity	Total Carbohydrates	Starch	
			8-00-00	Potassium ph	osphate	matter	8	0		
	Control	22.6 D	1.03 D	45.7 D	67.0 D	21.8 D	1.033 C	45.7 D	64.8 D	
	2 ml / L	25.6 C	1.04 C	45.9 C	68.5 C	24.1 C	1.03 C	49.9 C	68.3 (
Potassium	4 ml / L	26.7 B	1.06 B	47.3 B	69.7 B	25.2 B	1.05 B	51.8 B	69.5 E	
phosphate	8 ml / L	28.0 A	1.08 A	50.4 A	70.7 A	26.8 A	1.07 A	52.8 A	70.8 A	
				Zinc						
	Control	24.6 C	1.04 D	45.2 D	66.2 D	23.2 B	1.04 D	48.175	65.7 I	
	3 ml / L	25.5 B	1.05 C	46.7 C	68.1 C	24.3 AB	1.04 C	49.575	67.8 0	
Zinc	6 ml / L	26.2 A	1.05 B	47.9 B	69.9 B	25.1 A	1.05 B	50.775	69.2 I	
	9 ml / L	26.6 A	1.06 A	49.5 A	71.7 A	25.4 A	1.06 A	51.85	70.7 A	
				Interact	ion					
	Control	21.2 g	1.02 f	43.3 e	64.3 e	20.2 g	1.02 e	44.3 f	63.2 1	
Control	3 ml / L	22.4 f	1.03 e	45.4 d	66.5 d	21.2 f	1.03 d	45.1 ef	64.2 6	
	6 ml / L	23.5 e	1.03 e	46.5 cd	67.6 bc	23.2 de	1.03 d	46.3 e	65.4 0	
	9 ml / L	23.5 e	1.04 d	47.6 c	69.6 b	22.6 e	1.03 d	47.4 e	66.5c	
	Control	24.3 d	1.04 d	44.4 de	65.5 d	22.3 de	1.03 d	46.5 e	65.5 c	
2 ml / L	3 ml / L	25.5 c	1.04 d	45.4 d	67.6 bc	24.4 d	1.03 d	49.7 de	67.6 0	
	6 ml / L	26.1 b	1.04 d	46.5 cd	69.7 b	24.8 d	1.04 cd	51.2 c	69.7 b	
	9 ml / L	26.6 b	1.05 c	47.6 c	71.3 ab	25.1 c	1.04 cd	52.2 b	70.7 ł	
	Control	25.6 c	1.04 d	45.5 d	66.5 c	24.3 d	1.04 cd	50.7 d	66.7 c	
4 1 / T	3 ml / L	26.5 b	1.05 c	46.5 cd	68.7 b	24.9 d	1.05 c	51.2 c	69.7 b	
4 ml / L	6 ml / L	27.1ab	1.06 bc	47.6 c	71.2 ab	25.3 с	1.06 b	52.3 b	70.4 ł	
	9 ml / L	27.8 ab	1.07 b	49.7 b	72.5 ab	26.4 b	1.06 b	53.3 ab	71.3 ł	
0.117	Control	27.5 ab	1.06 bc	47.6 c	68.6 b	26.1 b	1.06 b	51.2 c	67.6	
	3 ml / L	27.9 ab	1.07 b	49.8 b	69.7 b	26.7 b	1.07 ab	52.3 b	69.7 b	
8 ml / L	6 ml / L	28.1 a	1.08 ab	51.3a b	71.2 ab	27.2 ab	1.08 b	53.3 ab	71.4 ł	
	9 ml / L	28.5 a	1.09 a	53.2 a	73.4 a	27.5 a	1.09 a	54.5 a	74.6 a	

Table (6): Effect of nano potassium phosphate and nano zinc oxide foliar application on dry matter percentage, specific gravity (g / cm^3), total carbohydrates percentage and starch percentage of potato tubers during 2019 and 2020 seasons.

Means followed by different letters are significantly different at $P \le 0.05$ level; Duncan 's multiple range test.

Table (7): Effect of nano potassium phosphate and nano zinc oxide foliar application on potassium and phosphorus
percentage as well as zinc concentration (ppm)of potato tubers during 2019 and 2020 seasons

		First season				Second season	
Treatments		Phosphorus (%)	Potassium (%)	Zinc (ppm)	Phosphorus (%)	Potassium (%)	Zinc (ppm)
			Potassiu	n phosphate			
	Control	0.23 D	2.10 D	19.31 D	0.23 D	2.02 D	19.52 D
Potassium	2 ml/L	0.35 C	2.28 C	20.75 C	0.34 C	2.30 C	20.53 C
phosphate	4 ml/L	0.45 B	2.48 B	21.98 B	0.47 B	2.56 B	21.47 B
	8 ml/L	0.57 A	2.71 A	23.10 A	0.57 A	2.75 A	22.51A
			2	Zinc			
Zinc	Control	0.35 D	2.30 D	20.76 D	0.36 D	2.30 D	20.52 D
	3 ml/L	0.38 C	2.36 C	21.19 C	0.38 C	2.37 C	20.94 C
	6 ml/L	0.41 B	2.43 B	21.41 B	0.41 B	2.45 B	21.10 B
	9 ml/L	0.45 A	2.48 A	21.77 A	0.45 A	2.51 A	21.47 A
			Inte	raction			
Control	Control	0.18 i	1.99 i	18.72 h	0.19 i	1.84 h	18.87 g
	3 ml/L	0.22 hi	2.11 h	19.21 g	0.21 h	1.97 g	19.45 f
	6 ml/L	0.25 hi	2.14 g	19.45 f	0.24 g	2.12 f	19.67 f
	9 ml/L	0.29 h	2.17 f	19.87 f	0.28 fg	2.16 f	20.11 e
2	Control	0.31 h	2.19 f	20.12 e	0.30 f	2.21 ef	20.23 de
	3 ml/L	0.33 gh	2.23 e	20.67 e	0.32 e	2.27 e	20.48 d
	6 ml/L	0.37 f	2.35 de	20.98 e	0.35 e	2.32 de	20.53 d
	9 ml/L	0.40 ef	2.38 d	21.23 d	0.41 de	2.41 d	20.89 d
4	Control	0.42 e	2.41 c	21.56 d	0.43 d	2.48 d	21.10 cd
	3 ml/L	0.44 d	2.45 c	21.91 d	0.46 cd	2.53 c	21.43 cd
	6 ml/L	0.47cd	2.52 bc	22.12 c	0.49 cd	2.59 c	21.58 cd
	9 ml/L	0.49 c	2.56 bc	22.34 c	0.51 c	2.64 bc	21.77 c
8	Control	0.52bc	2.62 b	22.67 b	0.52 c	2.67 b	21.89 c
	3 ml/L	0.56 b	2.68 b	22.98 b	0.55 b	2.72 b	22.43 b
	6 ml/L	0.58 ab	2.73 ab	23.10 ab	0.59 ab	2.78 ab	22.63 ab
	9 ml/L	0.62 a	2.84 a	23.67 a	0.63 a	2.85 a	23.12 a

Means followed by different letters are significantly different at $P \le 0.05$ level; Duncan 's multiple range test.

Conclusion

In this work, it was reported that the successful synthesis of potassium mono hydrogen phosphate and zinc oxide nano-fertilizer inside the PVP and PVA networks, respectively, using gamma irradiation. PVA and PVP operate as good stabilizers that control the growth, size, and crystalline phase formation of potassium mono hydrogen phosphate and zinc oxide nanoparticles, according to data acquired from HRTEM, UV-vis spectroscopy, and FTIR. The high concentration of both nano composites 8ml / 1 of potassium mono hydrogen phosphate and 9 ml/l of zinc oxide led to better growth characters which reflect on potato yield and its chemical constituents.

Conflicts of interest.

There are no conflicts to declare

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