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RETRACTED: Green Synthesis of Zinc Oxide Nanoparticles: Fortification for Rice Grain Yield and Nutrients Uptake Enhancement

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Abstract: Applications of metal oxide nanoparticles in the agriculture sector are being extensively included as the materials are considered superior. In the present work, zinc oxide nanoparticle (ZnO NPs), with a developing fertilizer, is applied in the fortification of rice grain yield and nutrient uptake enhancement. To evaluate the role of ZnO NP, two field experiments were conducted during the 2018 and 2019 seasons. ZnO NPs were small, nearly spherical, and their sizes equal to 31.4 nm, as proved via the dynamic light scattering technique. ZnO NPs were applied as a fertilizer in different concentrations, varying between 20 and 60 mg/L as a foliar spray. The mixture of $ZnSO_4$ and ZnO NP_{40} ameliorated yield component and nutrients (N, K, and Zn) uptake was enhanced compared to traditional $ZnSO_4$ treatment. Nevertheless, the uptake of the phosphorous element (P) was adversely affected by the treatment of ZnO NPs. Thus, treatment via utilizing ZnO NPs as a foliar with a very small amount (40 ppm) with of basal $ZnSO_4$ led to a good improvement in agronomic and physiological features; eventually, higher yield and nutrient-enriched rice grain were obtained.

Keywords: foliar spray zinc nanoparticles; growth parameters; yield attributes; nutrients uptake; rice

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1. Introduction

Work is underway to improve the nutritional quality of food to reduce the depletion of food security, particularly in the rural regions where around 80% of undernourished people reside [1]. Food production requires the availability of balanced content of nutrients, which are classified as macro, meso, and micronutrients [2]. In particular, the element zinc (Zn) is an essential micronutrient that is involved as a cofactor in more than 300 enzyme systems [3]. In addition, Zn plays a vital role in increasing the content of chlorophyll, proteins, and carbohydrates. Zinc deficiency (Zn D) is widespread in the developing countries, and it is primarily induced via poor dietary intake. Especially pregnant women and pre-school children in these countries are suffering from Zn D, and they need Zn to improve and promote growth of the human body [4,5]. Zn D can potentially impair the immune system, lead to physical disability, and increase exposure to several diseases, such as diarrhea and pneumonia [6]. Additionally, cultivable soils are suffering from Zn D that was varied and depended on the soil types to induce a yield loss of up to 30%. The presence of Zn D is accompanied by increasing pH, and the content of bicarbonate salts that reduce the production yield [7,8]. Generally, poor soil micronutrients have a negative effect on the productivity and quality of all crops, and they are critical challenge to be addressed with both quantity and quality of the yield. Rice (*Oryza sativa* L.,) is the predominant major crop that feeds nearly 75% of people worldwide. It delivers 50–80% of daily calorie requirements [9]. For rice grains, Zn D is much more popular than most other field crops.

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Moreover, in rice grains, genotype variation of the Zn element content is well established, because these grains are mostly categorized as a very poor source of Zn content. Otherwise, $ZnSO_4$, with the appropriate dose, is a broadly traditional soil application that functions to intensify the amount of Zn in tissues and maximize both the growth and yields [10,11]. Preventing the problem of Zn binding [12] leads to the increased probability of obtaining nutrients, notably when a cultivable soil condition restricts root uptake [13]. Moreover, increasing the Zn content in both edible and grain parts [14], besides the foliar application, are considered good ways to compensate for Zn disorder.

Nanotechnology has been identified in this new era as the fifth revolutionary technology that ensures sustainable agriculture, after the biotechnology branch [15]. The micronutrients assessed in fertilizers are increasingly efficient in the agro-sector both quantitatively and qualitatively through the use of nanoparticles (less than 100 nm). Via these modifications, it is expected to produce positive results in terms of both plant growth and the micronutrients assessed in fertilizers, which are increasingly quantitatively and qualitatively efficient in the agro-sector [16,17]. In particular, foliar treatment with Zn fertilizers as ZnO NPs achieved promising results in improving the nutritional efficiency of the grain under both natural and stress conditions [18], increasing the yield of grains, the amount of spikelets per spike, the number of tillers per hill, and the weight of 1000 grains [19,20]. They induce a dramatic increase of root and shoot length and mass in the leaf area index of up to 69% (both fresh and dry) when rice plants are exposed to 25, 50, 75, 100 and 150 mL of ZnO NPs [21]. There are many methods used for the preparation of ZnO NPs, beside increasing their dispersion in aqueous system to prevent their agglomerations. One of these methods is the precipitation method, which uses polymer as a stabilizing agent to cover these prepared particles and prevent them from agglomeration. In the present work, the aim was to use an environmentally benign polymer, and economically cost-effective and abundant brown algae named Phaeophyta. Brown algae are algal organisms distinguished by their brown or greenish-brown color that contains fucoxanthin, beta-carotene, and chlorophyll a and c. These are mostly influenced by multiple factors of algae that are often tailored to the marine environment [22]. Thus, in the agriculture sectors, nanoscience provides a significant solution to enhance crop production, reduce nutrient-related losses, and increase yields. To produce adequate germination, increase plant growth, boost seed quality, numerous metal oxide nanoparticles have been examined as nutrients and fertilizers. In foliar applications, that is produced using bio-inspired brown algae (Turbinaria ornata) [23]. Therefore, the present research aims to prepare algae-based biogenic ZnO NPs using brown algae, and evaluate their effectiveness in improving the seed quality parameters and performance characteristics of rice plants. The effect of zinc in the form of $ZnSO_4$ as a basal application, foliar application of ZnO NPs suspensions at different concentrations, and its combination on rice growth, yield parameters, and essential nutrient uptake (N, P, K, and Zn) are other goals of the present work.

2. Materials and Methods

2.1. Chemicals, Experiment Location and Rice Cultivar

Zinc sulfate heptahydrate (ACS reagent, 99%) was purchased from Sigma-Aldrich, St. Louis, MO, USA. All other chemicals are of analytical grade and used as received. Brown algae (Phaeophyta) was collected and extracted [24]. The extracted solution was used for ZnO NP synthesis. Two field experiments were conducted at the Experimental Farm of Rice Research and Training Center (RRTC), Sakha, Kafrelsheikh, Egypt during the 2018 and 2019 rice seasons. Giza179 rice cultivar was used in this study.

2.2. Physical and Chemical Soil Analysis

Representative soil samples were taken from the site at the depth of 0–30 cm. Samples were air-dried then ground to pass through 2 mm sieve and well mixed for homogeneity. The procedure of soil analysis followed the methods described earlier [24]. Major chemical and physical properties of the soil in the experimental site are presented in Table 1.

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Table 1. Physical and chemical analysis of the experimental site in 2018 and 2019.

Character	2018	2019
physical analysis:		
Texture	Clayey	Clayey
Sand (%)	13.3	16.2
Silt (%)	32.0	28.0
Clay (%)	54.7	55.8
Chemical analysis:		
pH (1:2.5 soil extract)	8.12	8.25
E.C. (dSm^{-1})	1.80	1.86
Organic matter %	1.51	1.65
Available N (ppm)	17.3	18.2
Available P (ppm)	14.2	15.9
Available K (ppm)	313	318
Available Zn (ppm)	0.80	0.90
Available Mn (ppm)	3.10	3.94
Available Fe (ppm)	2.63	2.95

2.3. Preparation of ZnO Nanoparticles (ZnO NPs)

Zinc oxide nanoparticles (ZnO NPs) were synthesized by the precipitation method. In a typical procedure, 14.37 g of zinc sulfate heptahydrate was dissolved in 50 mL of double distilled water (DDW) and added to the extracted brown algae (10%) under continuous magnetic stirring. Then, sodium hydroxide solution (4 g in 50 mL DDW) was added dropwise under magnetic stirring. The reaction was and continuously stirred for 2 h, and the obtained white suspension was centrifuged at 9000 rpm. Then, the powder was dried at 60 °C for 24 h and calcined at 400 °C for another 2 h.

2.4. Characterization of ZnO NPs

The crystalline and phase structure of the synthesized ZnO NPs was studied using an X-ray diffractometer (XRD, X'Pert Pro, PANalytical, Almelo, The Netherlands). The particle shape was determined by transmission electron microscopy (TEM, Tecnai G20, FEI, Eindhoven, The Netherlands). The prepared ZnO NPs (0.1 g) was dispersed in 50 mL of DDW and sonicated for 15 min at room temperature. Then, the dispersed particles were placed on the copper-coated carbon grid before particle shape evaluation. Selected area diffraction (SAED) was examined using a TEM image. The distribution of particles in terms of average hydrodynamic particle size was assessed via dynamic light scattering (DLS using Zetasizer Nano ZS, Malvern Instruments Ltd., Worcestershire, UK). Additionally, the polydispersity index (PDI) was obtained as a numerical value. As known, PDI is ascribed for the width of particle size distribution. PDI value closest to 0 described the monodispersity of particles. A PDI value near to 1 identified the particles as polydispersity form. Zeta potential measurements were carried out using Zetasizer Nano ZS, Malvern Instruments Ltd. (Worcestershire, UK), to provide us with information about the stability of particles. The particle morphology of the prepared ZnO NPs was scanned using a field emission scanning electron microscope (FESEM, ZEISS GeminiSEM 360; Mladá Boleslav, Czech Republic).

2.5. Experimental Design and Treatments

The experiment was laid out in a completely randomized block design with four replications. The plot size was 15 cm (5 × 3 cm). Foliar spray application with ZnO NPs was carried out using two equal batches at mid-tailoring and panicle initiation. The treated

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materials were used as suspension by using ultrasonic baths to produce a high-powered ultrasonic intensity throughout the entire oscillating tank (Badelin SONOREX Digital 10P, Berlin, Germany). The treatments included Zn0 control (the treatment was carried out in the absence of zinc in any form), and $ZnSO_4$ at the full recommended rate of conventional fertilizer of $ZnSO_4$ (24 Kg/ha). The mixed ratio of $ZnSO_4$ + $ZnONP_{20}$ was the full recommended rate of conventional fertilizer of $ZnSO_4$ (24 Kg/ha) + foliar application of ZnO NPs at the rate of 20 ppm. The $ZnSO_4$ + ZnO NP_{40} and $ZnSO_4$ + $ZnONP_{60}$ were based on the full recommended rate of conventional fertilizer of $ZnSO_4$ (24 Kg/ha) + foliar application of ZnO NPs at the rate of 40 ppm and 60 ppm, respectively. The composition $ZnONP_{20}$, $ZnONP_{40}$, and $ZnONP_{60}$ are foliar applications of ZnO NPs at a rate of 20 ppm, 40 ppm, and 60 ppm, respectively.

2.6. Crop Management

Pre-germinated seeds were broadcasted in the nursery on 2 and 5 of May in the 2018 and 2019 seasons, respectively. Seeds at the rate of 140 kg/ha were soaked more than water for 24 h, and further incubated for another 48 h to enhance germination. Three seedlings 30 days old were transplanted at a 20 × 20 cm distance between hills and rows. Weeds were controlled chemically using Saturn 50% at the rate of 5 L/ha at four days after transplant. Nitrogen in the form of urea (46% N) at the rate of 165 kg N/ha was applied as recommended in two doses: 2/3 basal application + 1/3 at panicle initiation. The recommended phosphorous and potassium fertilizers in the form of calcium superphosphate (15% P_2O_5) at a rate of 37 kg P_2O_5/ha and potassium sulfate (48% K_2O) at the rate of 50 kg K_2O kg/ha was applied. Zinc fertilizer applied at the rate of 24 $ZnSO_4$ kg/ha was mixed with sand and manually broadcasted before transplanting (except 1, 6, 7, and 8 treatments).

2.7. Studied Topics and Traits

2.7.1. Plant Growth Characteristics

At the heading stage, plants of five hills were randomly taken from each plot to estimate chlorophyll content (SPAD value), leaf area index, and dry matter production. Total chlorophyll content was determined in ten flag leaves using a chlorophyll meter (Model–SPAD502; Minolta Camera Co. Ltd., Japan). The leaf area index is the ratio between the leaves areas (cm^2) of the plant divided by the ground area occupied by the plant. Dry matter production (g/m^2) was estimated according to earlier works [25,26].

2.7.2. Yield and its Attributes

At the harvest stage, plant height was measured. Panicles of five random hills from each plot were counted, then converted to the number of panicles/m^2. Ten panicles were randomly collected from each plot to determine panicle weight (g), the number of filled grains/panicle, and unfilled grains/panicle and1000-grain weight (g). Grain yield was measured from an area of 12 m^2 (3 × 4 m), which was harvested from each plot at random avoiding the border effects. Grain yield was adjusted to 14% moisture content, determined according to the reported method [27].

2.7.3. Nutrients Uptake by Grain and Straw

All samples were oven-dried to a constant weight at 70 °C, then ground to powder and digested. The total N was determined by the Micro Kjeldahl method, K estimated by the flame photometer using the atomic absorption method. P was calorimetrically estimated by ascorbic acid [28] and Zn by using the atomic absorption method. Nutrients of N, P, and K (kg/ha) and Zn uptake (g/ha) in grain were calculated.

2.8. Statistical Analysis

The obtained data were subjected to analysis of variance [29]. Treatment means were compared by Duncan's multiple range test [30]. All statistical analyses were performed

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using the analysis of variance technique employing the "COSTATC" computer software package.

3. Results and Discussion

The ZnO NPs was capped with using environmentally benign compounds via the precipitation method. The calcination step was conducted to convert zinc hydroxide to ZnO NPs via evaporation of water. The calcined NPs were easily dispersed in water via stirring and ultrasonication tool. The second target is to evaluate the effect of ZnO NPs (different concentrations; 20, 40 and 60 mg/L) as a foliar spray, compared with other traditional fertilizers, to outline the role of NPs. The characteristics of ZnO NPs and their utilization as a foliar spray for rice grain are discussed in the forthcoming section.

3.1. Characterization of ZnO NPs

Figure 1 represents the XRD diffractogram that outlines the crystal phase of the synthesized ZnO NPs. The assigned peaks at 2θ = 31.77°, 34.4°, 36.26°, 47.54°, 57.60°, 63.86°, 63.38°, 67.95°, 69.09°, 73.57°, and 76.97°, which, ascribed to the facet (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202), respectively, indicate the crystalline structure of ZnO NPs [31]. The previous crystalline peaks suggest a hexagonal phase structure of the wurtzite (Zincite, JCPDS 5-0664). The crystallite size was measured according to Scherrer's principle as follows:

$$D = \frac{k}{\beta_{1/2} \cos} \quad (1)$$

where K is the Scherer constant (0.9 to 1), λ is the wavelength of the X-ray, β is the full width of the XRD peak at half maximum, and θ is the Bragg angle. The determined average crystalline size of ZnO nanoparticles was 31.4 nm. The crystalline sizes determined by Scherrer's equation (1) cannot used to estimate the particle sizes, due to the contribution of the lattice strain to line broadening, which produces errors in the peak fitting and width calculation. Therefore, XRD patterns do not give a precise calculation of the nanoparticle crystal sizes, but provide an order of magnitude for nanoscale-sized crystals in bones [32].

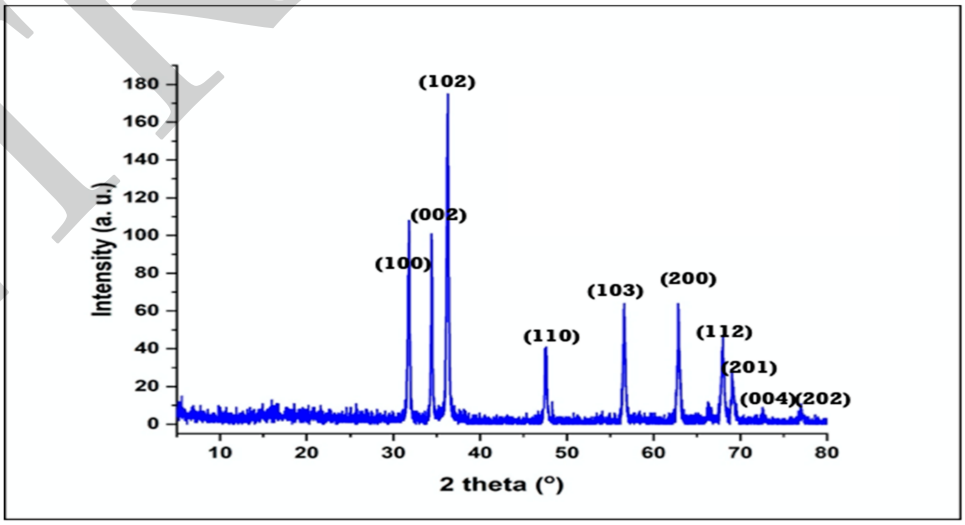


Figure 1. X-ray diffractometer (XRD) of the as-synthesized zinc oxide nanoparticles (ZnO NPs).

For affirming, TEM was used to evaluate and examine the particle shape of ZnO NPs and the obtained image was represented in Figure 2A. As shown, it is revealed that the shape and size of ZnO NPs prepared by precipitation techniques [33] exhibit a nearly nano-sized, spherical shape. The amazing part observed in the TEM image is that the particles tend to form small spheres, which are dispersed in view and collected like a map.

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These particles tend to assemble with each other, owing to the precipitation procedure. Other explanations for the agglomeration may be related to the exhibited high surface area of the synthesized particles. However, these agglomerated particles still exhibit a small cluster size [34]. Figure 2B outlines the selected area diffraction (SAED) pattern of ZnO NPs taken from the particle. It is observed that ZnO NPs typically exhibit diffraction of a ring pattern, with certain lighter and more distinctive points around the ring. This observation suggested the existence of certain larger crystallites, although the rings were still relatively continuous, and confirms that the crystallites were in the nanometer sizes. Hexagonal crystalline-structured zinc oxide with a space group P63mc (JCPDS card No. 00-00-036-1451), confirmed from Figure 2B, agrees with the data obtained from the XRD spectrum (Figure 1).

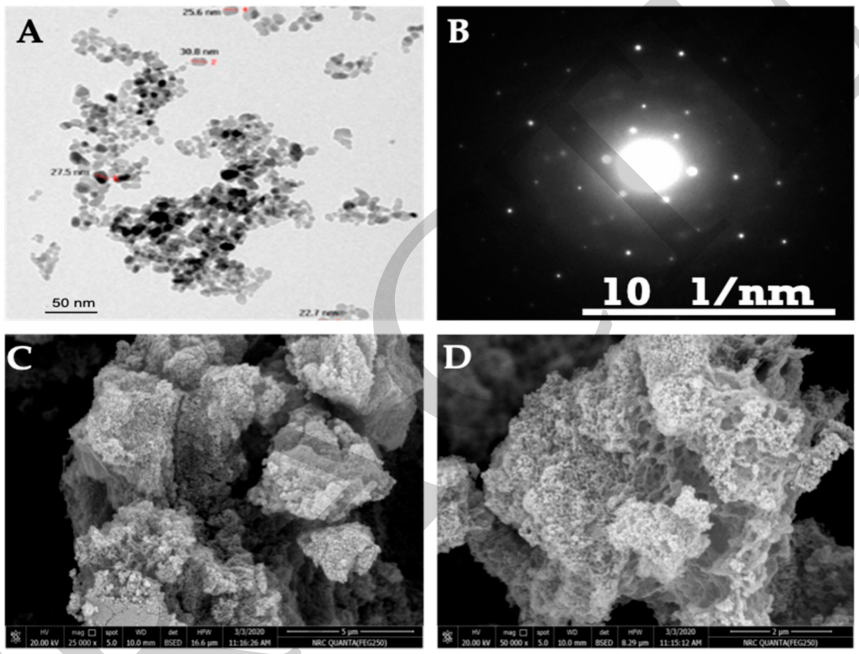


Figure 2. (**A**) transmission electron microscopy (TEM), (**B**) selected area diffraction (SAED), (**C**,**D**) scanning electron microscope (SEM) at low and high magnifications of ZnO NPs.

The surface topographical morphological feature of ZnO NPs were further examined using FESEM, as shown in Figure 2C,D. It is well known that the morphology of particle sizes determined by TEM (Figure 2A) included the internal structure, while the FESEM can be used just to evaluate the surfaces topographical of particles with either rough or smooth morphologies. It is observed that ZnO NPs (Figure 2C,D) are formed with fine regular particles contains definite edges. Additionally, it is worth seeing that the particles are considered as small dots accumulated on each other. The ZnO NPs will apply in the present work as suspensions, and for this reason it is necessary to evaluate their dispersion stability and particles sizes from their DLS measurements, as represented in Figure 3A,B. The data for the average hydrodynamic size of ZnO NPs is shown in Figure 3A as 41 nm, and their PDI is 0.264. The increase of particle sizes of ZnO NPs determined in an aqueous solution (41 nm), compared to that determined from XRD data in dry solution (31 nm), elucidates that the ZnO NPs adsorb water as hydrated water on their surfaces, which increases their sizes [35]. Moreover, the single peak obtained (Figure 3A) suggests that the consistency of the ZnO NPs synthesized via brown algae was reasonable. In addition, brown algae synthesized ZnO NPs were almost monodispersed in a small scale, indicating that brown algae are a good dispersing agent, capable of producing particles with good dispersion, implying the importance of brown algae in preventing the aggregation of particles [22].

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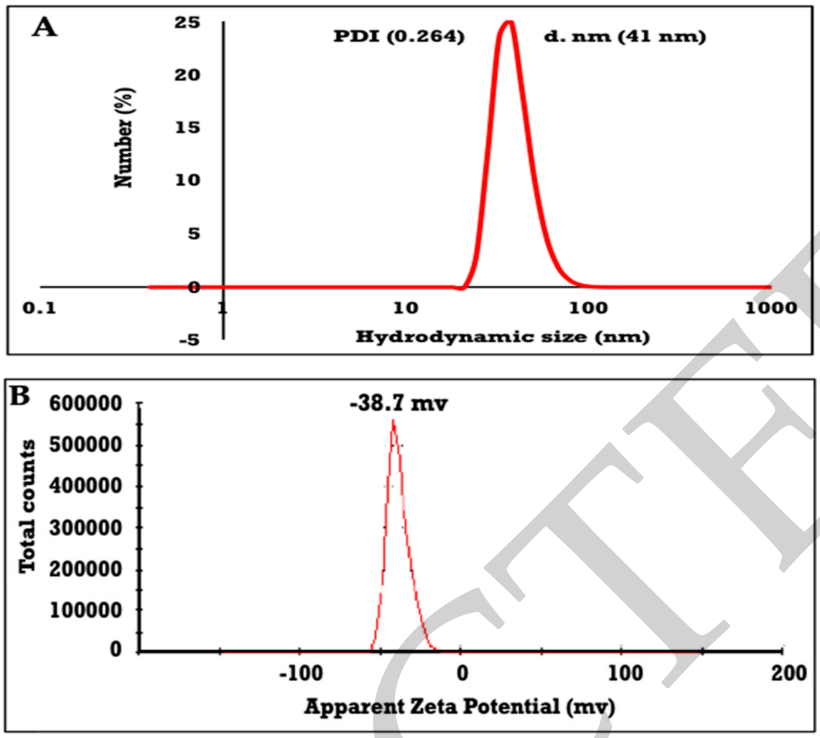


Figure 3. (**A**) hydrodynamic size and (**B**) zeta potential of ZnO NPs.

The prediction about the stability of the synthesized ZnONPs was also evaluated and set in Figure 3B. Firstly, the prepared nanoparticles were dispersed in deionized water, and the solution was submitted to ultrasonication before characterization to ensure the dispersion of particles. It is proved that the obtained zeta potential value of ZnO NPs stabilized via the steric and electrostatic repulsive force effects of brown algae is −38.7 mV, with a single peak signifying the presence of repulsion among the synthesized nanoparticles, as depicted in Figure 3A. As the literature documented, the particles in suspension have a large negative zeta potential tend to repel with each other, and there will be no tendency of the particles to assemble [35]. As shown in Figure 3B, ZnO NPs have high zeta potential values, thus, excellent force originates from brown algae, to act as a stabilizing agent to prevent the particles from coming together and flocculating and increases the stability of the prepared ZnO NPs. Thanks to the helpful role of brown algae for long-term stability, ZnO NPs exceeded the recommended zeta potentials for the stable suspensions at above +25 or −25 mV [35].

3.2. Plant Growth Characteristics

After the successful preparation and the full characterization of the prepared nanoparticles, ZnO NPs are ready to be used and compared or blended with other traditional compounds for agricultural domains. Table 2 shows all tested growth parameters, such as chlorophyll content, leaf area index, and dry matter production, and the data were significantly higher than that of the control sample. The main observation noted that $ZnSO_4$ + $ZnONP_{40}$ and $ZnSO_4$ + $ZnONP_{60}$ treatments give the highest value of chlorophyll content (39.83, 40.81, and 39.66, 40.90, respectively) in both years, without any statistical difference among them. The same trend was observed in the leaf area index that both treatments gave 6.65, 6.82, and 6.70, 6.81, respectively. The highest production of dry matter (g/m^2) was obtained from the $ZnSO_4$ + $ZnoNP_{40}$, $ZnSo_4$ + $ZnONP_{60,}$ and $ZnONP_{60}$ treatments without significant difference between them, but the highest one was the $ZnSO_4$+ $ZnONP_{60}$ treatment, which gave 1587.6 and1585.8 g/m^2 in the 2018 and 2019 seasons, respectively. High regression in chlorophyll content, leaf area index, and dry matter production were recorded under control treatment followed by $ZnSO_4$ at the recommended dose (24 Kg/ha)

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except first year, dry matter production under $ZnONP_{20}$ occupied the second rank in this regression (1381.5 g/m^2). It was previously reported that ZnO NPs (200 ppm) were used to increase the chlorophyll contents of non-photoperiod sensitive rice cultivars, and researchers found that these particles did not show a statistically significant difference for the photosynthetic pigment contents [36]. They also reported that the accumulation of the antioxidant enzyme activities inhibits the damage of the photosynthetic pigments, due to the toxicity of ZnO NPs.

Table 2. Influence of traditional zinc application, foliar ZnO/NPs at different concentrations and its combination on chlorophyll (SPAD value), leaf area index, and dry matter production (g/m^2) of Giza179 rice variety during the 2018 and 2019 seasons.

Traits / Treatments	Chlorophyll Content (SPAD Value)		Leaf Area Index (LAI)		Dry Matter Production (g/m^2)	
	2018	2019	2018	2019	2018	2019
Zn_0	35.76 ^{d}	37.4 ^{d}	4.91 ^{d}	5.16 ^{d}	1360.5 ^{c}	1379.6 ^{c}
$ZnSO_4$	37.66 ^{c}	38.33 ^{cd}	5.25 ^{c}	5.55 ^{c}	1383.2 ^{bc}	1398.3 ^{c}
$ZnSO_4$ + $ZnONP_{20}$	38.16 ^{bc}	39.50 ^{bc}	6.02 ^{b}	6.10 ^{b}	1428.9 ^{bc}	1446.8 ^{bc}
$ZnSO_4$ + $ZnONP_{40}$	39.83 ^{a}	40.81 ^{ab}	6.65 ^{a}	6.82 ^{a}	1563.4 ^{a}	1574.1 ^{ab}
$ZnSO_4$ + $ZnONP_{60}$	39.66 ^{a}	40.90 ^{a}	6.70 ^{a}	6.81 ^{a}	1587.6 ^{a}	1585.8 ^{a}
$ZnONP_{20}$	37.83 ^{bc}	38.70 ^{cd}	5.26 ^{c}	5.58 ^{c}	1381.5 ^{bc}	1400.1 ^{c}
$ZnONP_{40}$	38.36 ^{bc}	39.36 ^{bc}	5.83 ^{b}	6.00 ^{b}	1421.8 ^{bc}	1436.6 ^{c}
$ZnONP_{60}$	39.06 ^{b}	39.52 ^{bc}	6.10 ^{b}	6.17 ^{b}	1493.7 ^{ab}	1501.2 ^{ab}
F. test	**	**	**	**	**	**

*, ** and NS indicate $p < 0.05$, $p < 0.01$ and not significant, respectively. Zn_0: Control, $ZnSO_4$: $ZnSO_4$ at 24 Kg/ha, $ZnSO_4$ + $ZnONP_{20}$: $ZnSO_4$ (24 Kg/ha) + ZnONP in the rate of 20 ppm, $ZnSO_4$ + $ZnONP_{40}$: $ZnSO_4$ at 24 Kg/ha + ZnONP in the rate of 40 ppm, $ZnSO_4$ + $ZnONP_{60}$: $ZnSO_4$ at 24 Kg/ha + foliar ZnONP at a rate of 60 ppm, $ZnONP_{20}$: ZnONP at a rate of 20 ppm, $ZnONP_{40}$: ZnONP at a rate of 40 ppm And $ZnONP_{60}$: ZnONP at a rate of 60 ppm. Values are the average of five repetitions. Means (n = 5). Different letters (a, ab, b, c, bc, d, cd) in each column means that the treatments were statistically different (Tukey, $p \leq 0.05$).

3.3. Yield and its Attributes

3.3.1. Plant Height, Number of Panicles/m^2, and Panicle Weight

Plant height, number of panicles/m^2, and panicle weight have meaningful change under various Zn treatments as shown in Table 3. During the 2018 and 2019 seasons, these yield attributes are greater for $ZnSO_4$ + $ZnONP_{40}$, $ZnSO_4$ + $ZnONP_{60,}$ and $ZnONP_{60}$ treatments, compared with control and other treatments. The tallest rice plants are noted with treatments using $ZnSO_4$ + $ZnONP_{60}$ treatment (93.0 cm) in first season, but $ZnSO_4$ + $ZnONP_{40}$ recorded highest plants (94.2 cm) in second season. During the 2018 season, the number of panicles/m^2 significantly increases by 5.6, 6.0 and 3.2% under $ZnSO_4$ + $ZnONP_{40}$, $ZnSO_4$ + $ZnONP_{60,}$ and $ZnONP_{60}$ treatments, respectively, while ratios became 9.0, 8.7 and 5.9%, respectively, in the second season, compared with the recommended dose treatment ($ZnSO_4$). However, there was no significant difference between $ZnSO_4$ + $ZnONP_{40}$ and $ZnSO_4$+ $ZnONP_{60}$ in both seasons. A significantly higher panicle weight was obtained under the applications of $ZnSO_4$ + $ZnONP_{40}$, $ZnSO_4$ + $ZnONP_{60}$, and $ZnONP_{60}$ than $ZnSO_4$ treatment by 28.4, 29.9 and 17.3% in the 2018 season and 33.5, 33.0 and 18.1%, respectively, in the 2019 season. The lowest value of these studied characters was located where no zinc fertilizers were added (Zn_0).

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Table 3. The influence of traditional zinc application, foliar nano zinc at different concentrations and its combination on plant height, number of panicles/m^2, and panicle weight of the Giza179 rice variety during the 2018 and 2019 seasons.

Traits / Treatments	Plant Height (cm)		Number of Panicles (m^{-2})		Panicle Weight (g)	
	2018	2019	2018	2019	2018	2019
Zn_0	86.7 ^{c}	88.1 ^{d}	453.4 ^{d}	448.8 ^{d}	2.44 ^{c}	2.38 ^{c}
$ZnSO_4$	89.9 ^{b}	90.3 ^{c}	482.2 ^{bc}	472.6 ^{cd}	2.71 ^{bc}	2.75 ^{bc}
$ZnSO_4$+ $ZnONP_{20}$	91.4 ^{ab}	92.0 ^{b}	490.8 ^{bc}	492.8 ^{bc}	2.97 ^{b}	3.03 ^{ab}
$ZnSO_4$+ $ZnONP_{40}$	92.3 ^{ab}	94.2 ^{a}	509.3 ^{a}	515.3 ^{a}	3.48 ^{a}	3.67 ^{a}
$ZnSO_4$+ $ZnONP_{60}$	93.0 ^{a}	93.8 ^{a}	511.2 ^{a}	513.6 ^{a}	3.52 ^{a}	3.66 ^{a}
$ZnONP_{20}$	90.2 ^{ab}	90.0 ^{c}	480.7 ^{c}	485.0 ^{bc}	2.64 ^{bc}	2.78 ^{bc}
$ZnONP_{40}$	91.5 ^{ab}	91.1 ^{bc}	493.0 ^{b}	491.2 ^{bc}	2.85 ^{bc}	2.98 ^{bc}
$ZnONP_{60}$	92.4 ^{ab}	92.8 ^{ab}	497.6 ^{b}	500.6 ^{b}	3.18 ^{ab}	3.25 ^{ab}
F. test	*	**	**	**	**	**

*, ** and NS indicate $p < 0.05$, $p < 0.01$ and not significant, respectively. Zn_0: Control, $ZnSO_4$: $ZnSO_4$ at 24 Kg/ha, $ZnSO_4$ + $ZnONP_{20}$: $ZnSO_4$ (24 Kg/ha) + ZnONP at a rate of 20 ppm, $ZnSO_4$ + $ZnONP_{40}$: $ZnSO_4$ at 24 Kg/ha + ZnONP in the rate of 40 ppm, $ZnSO_4$ + $ZnONP_{60}$: $ZnSO_4$ at 24 Kg/ha + foliar ZnONP in the rate of 60 ppm, $ZnONP_{20}$: ZnONP at a rate of 20 ppm, $ZnONP_{40}$: ZnONP at the rate of 40 ppm and $ZnONP_{60}$: ZnONP at a rate of 60 ppm. Values are the average of five repetitions. Means ($n = 5$). Different letters (a, ab, b, c, bc, d, cd) in each column means that the treatments were statistically different (Tukey, $p \leq 0.05$).

3.3.2. Number of Filled Grains, Number of Unfilled Grains, and Thousand-Grain Weight

As seen in Table 4, a significant difference among treatments on the number of filled grains/panicles that impart the highest number was found under $ZnSO_4$ + $ZnONP_{40}$ and $ZnSO_4$ + $ZnONP_{60}$ (128.40, 134.31 and 127.60, 136.23), respectively, in both seasons. Under different treatments in this current study, a large difference appears on the sterility character (number of unfilled grains). The highest unfilled grains number is obtained under Zn_0 (13.12 and11.00), respectively. On the contrary, the lowest number (3.01 and 3.71) is obtained under $ZnSO_4$ + $ZnONP_{40}$, followed by $ZnSO_4$ + $ZnONP_{60}$ (3.13 and 4.10, respectively). For thousand-grain weight, implications implied that the maximum weight of 1000 grain is realized under $ZnSO_4$ + $ZnONP_{40}$, $ZnSO_4$ + $ZnONP_{60}$, $ZnONP_{60}$, and $ZnONP_{40}$ (27.45, 27.42, 26.94 and 26.66 g, respectively) in the first season, without a statistical difference among these treatments. However, in the season of 2018, $ZnSO_4$+ $ZnONP_{60}$ exhibited the highest weight of 1000 grains, followed by $ZnSO_4$ + $ZnONP_{40}$ and $ZnONP_{60}$ (27.60, 27.28, and 27.02). Additionally, there was no significant difference between these treatments.

3.3.3. Grain Yield, Straw Yield, and Harvest Index

It is noticed from Table 5 that both grain and straw yields responded positively to the different Zn applications. Grain yield was higher in $ZnSO_4$ + $ZnONP_{40}$ and $ZnSO_4$ + $ZnONP_{60}$ treatments by 15.8 and 17.4% than those in $ZnSO_4$, respectively, in the first season. the increment is 13.6 and 13.9%, respectively, compared with $ZnSO_4$ in the 2019 season. During the 2018 season, a similar trend was observed in straw yield, it was larger under the $ZnSO_4$ + $ZnONP_{40}$, $ZnSO_4$ + $ZnONP_{60}$, $ZnONP_{60}$, and $ZnONP_{40}$ treatments by 14.8, 11.4, 10.7 and 7.6%, respectively, compared to $ZnSO_4$ treatment. However, the ratio of the increment is 15.1, 14.9, 7.7 and 11.6%, respectively, in the second year. Concerning the harvest index (HI), no significant effect is exerted by the studied treatments in both seasons. The highest value of HI is obtained under $ZnSO_4$ + $ZnONP_{60}$ in the first season and $ZnSO_4$ + $ZnONP_{40}$ in the second season. So, there is no significant difference between all treatments in the two studied seasons.

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Table 4. Influence of traditional zinc application, foliar ZnO/NPs at different concentrations and its combination on several filled grains/panicle, number of unfilled grains/panicles, and 1000-grain weight of Giza179 rice variety during the 2018 and 2019 seasons.

Traits / Treatments	Number of Filled Grains/Panicle		Number of Unfilled Grains/Panicles		1000-Grain Weight (g)	
	2018	2019	2018	2019	2018	2019
Zn_0	93.66 ^{d}	97.41 ^{e}	13.12 ^{a}	11.00 ^{a}	25.50 ^{c}	25.61 ^{d}
$ZnSO_4$	101.02 ^{cd}	106.00 ^{d}	8.30 ^{b}	7.51 ^{b}	25.89 ^{bc}	25.97 ^{cd}
$ZnSO_4$+ $ZnONP_{20}$	114.38 ^{b}	128.0 ^{b}	5.11 ^{cd}	6.22 ^{c}	26.21 ^{bc}	26.61 ^{bc}
$ZnSO_4$+ $ZnONP_{40}$	128.40 ^{a}	134.31 ^{a}	3.01 ^{d}	3.71 ^{d}	27.45 ^{a}	27.28 ^{ab}
$ZnSO_4$+ $ZnONP_{60}$	127.60 ^{a}	136.23 ^{a}	3.13 ^{d}	4.10 ^{d}	27.42 ^{a}	27.60 ^{a}
$ZnONP_{20}$	103.33 ^{cd}	107.10 ^{c}	6.20 ^{bc}	6.55 ^{c}	26.15 ^{bc}	26.33 ^{bc}
$ZnONP_{40}$	110.01 ^{bc}	115.24 ^{c}	4.53 ^{cd}	5.21 ^{cd}	26.66 ^{ab}	26.74 ^{bc}
$ZnONP_{60}$	115.00 ^{b}	122.5 ^{b}	4.26 ^{cd}	4.00 ^{d}	26.94 ^{ab}	27.02 ^{ab}
F. test	**	**	**	**	**	**

*, ** and NS indicate $p < 0.05$, $p < 0.01$ and not significant, respectively. Zn_0: Control, $ZnSO_4$: $ZnSO_4$ at 24 Kg/ha, $ZnSO_4$ + $ZnONP_{20}$: $ZnSO_4$ (24 Kg/ha) + ZnONP at a rate of 20 ppm, $ZnSO_4$ + $ZnONP_{40}$: $ZnSO_4$ at 24 Kg/ha + ZnONP at a rate of 40 ppm, $ZnSO_4$ + $ZnONP_{60}$: $ZnSO_4$ at 24 Kg/ha + foliar ZnONP at a rate of 60 ppm, $ZnONP_{20}$: ZnONP at a rate of 20 ppm, $ZnONP_{40}$: ZnONP at the rate of 40ppm and $ZnONP_{60}$: ZnONP at a rate of 60 ppm. Values are the average of five repetitions. Means (n = 5). Different letters (a, ab, b, c, bc, d, cd) in each column means that the treatments were statistically different (Tukey, $p \leq 0.05$).

Table 5. Influence of traditional zinc application, foliar ZnO/NPs at different concentrations and its combination on grain yield, straw yield, and harvest index of the Giza179 rice variety during the 2018 and 2019 seasons.

Traits / Treatments	Grain Yield (T/ha)		Straw Yield (T/ha)		Harvest Index (HI)	
	2018	2019	2018	2019	2018	2019
Zn_0	8.31 ^{d}	8.24 ^{d}	11.80 ^{c}	11.36 ^{c}	42.23	42.20
$ZnSO_4$	8.83 ^{cd}	9.15 ^{cd}	12.14 ^{bc}	12.29 ^{bc}	42.40	42.52
$ZnSO_4$+ $ZnONP_{20}$	9.44 ^{bc}	9.67 ^{bc}	12.63 ^{bc}	13.12 ^{ab}	43.03	42.78
$ZnSO_4$+ $ZnONP_{40}$	10.23 ^{a}	10.40 ^{a}	13.94 ^{a}	14.15 ^{a}	43.10	43.12
$ZnSO_4$+ $ZnONP_{60}$	10.37 ^{a}	10.43 ^{a}	14.08 ^{a}	14.13 ^{a}	43.13	43.11
$ZnONP_{20}$	9.22 ^{bc}	9.37 ^{bc}	12.77 ^{bc}	12.77 ^{bc}	42.34	42.39
$ZnONP_{40}$	9.59 ^{bc}	9.78 ^{bc}	13.07 ^{ab}	13.24 ^{ab}	42.56	42.61
$ZnONP_{60}$	9.98 ^{b}	10.05 ^{b}	13.45 ^{ab}	13.72 ^{ab}	43.05	42.83
F. test	**	**	**	**	N.S	N.S

*, ** and NS indicate $p < 0.05$, $p < 0.01$ and not significant, respectively. Zn_0: Control, $ZnSO_4$: $ZnSO_4$ at 24 Kg/ha, $ZnSO_4$ + $ZnONP_{20}$: $ZnSO_4$ (24 Kg/ha) + ZnONP in the rate of 20 ppm, $ZnSO_4$ + $ZnONP_{40}$: $ZnSO_4$ at 24 Kg/ha + ZnONP in the rate of 40 ppm, $ZnSO_4$ + $ZnONP_{60}$: $ZnSO_4$ at 24 Kg/ha + foliar ZnONP at a rate of 60 ppm, $ZnONP_{20}$: ZnONP at a rate of 20 ppm, $ZnONP_{40}$: ZnONP at a rate of 40 ppm And $ZnONP_{60}$: ZnONP at a rate of 60 ppm. Values are the average of five repetitions. Means (n = 5). Different letters (a, ab, b, c, bc, d, cd) in each column means that the treatments were statistically different (Tukey, $p \leq 0.05$).

3.3.4. Nutrient Uptake by Grain and Straw

The data about N, P, K, and Zn uptake in grains are presented in Table 6. In both seasons, a significant difference is noted among treatments related to N uptake by grains. The highest value of N uptake by grains (140.92 and 151.12 Kg/ha) was obtained under $ZnSO_4$+$ZnONP_{60}$, on par with $ZnSO_4$+$ZnONP_{40}$ (137.12 and 130.10 Kg/ha), respectively. In addition, there is no statistical difference between $ZnSO_4$+$ZnONP_{60}$, $ZnSO_4$+$ZnONP_{40}$,

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and $ZnONP_{60}$ treatments in the 2018 and 2019 seasons. The lowest value of N uptake by grains (91.33 and 90.23 Kg/ha) is obtained from Zn_0. On the other hand, P uptake by grains is found to decline with the application of Zn fertilizers. The highest value of P uptake by grains (30.16 and 35.44 Kg/ha) is seen under the Zn_0 treatment. However, the lowest value of P uptake (26.71 and 29.06 Kg/ha), respectively, is recorded under $ZnSO_4$+$ZnONP_{60}$. The highest uptake of K (49.15 and 51.10 Kg/ha) is represented by the treatments $ZnSO_4$+$ZnONP_{40}$ first and $ZnSO_4$+$ZnONP_{60}$ s, respectively. From the prolific results, no significant difference is found among $ZnSO_4$+$ZnONP_{20}$, $ZnSO_4$+$ZnONP_{40}$ $ZnSO_4$+$ZnONP_{60}$, $ZnONP_{20}$, $ZnONP_{40}$ and $ZnONP_{60}$ in the 2018 and 2019 seasons. The treatment of $ZnSO_4$+$ZnONP_{60}$ recorded the highest value (460.31 and 471.42 g/ha) of Zn uptake by grains, followed by $ZnSO_4$+$ZnONP_{40}$ treatment (447.13 and 462.85 g/ha), respectively, in both seasons. The treatment of $ZnSO_4$ occupied the second rank (349.46 and 385.32 g/ha) at the least uptake of Zn after control treatment (265.22 and 336.31 g/ha), respectively, in both seasons.

Table 6. Influence of traditional zinc application, foliar nano zinc at different concentrations and its combination on N, P, K, and Zn uptake in grains of the Giza179 rice variety in the 2018 and 2019 seasons.

Traits / Treatments	N Uptake (Kg/ha)		P Uptake (Kg/ha)		K Uptake (Kg/ha)		Zn Uptake (g/ha)	
	2018	2019	2018	2019	2018	2019	2018	2019
Zn_0	91.33 ^{d}	90.23 ^{d}	33.16 ^{a}	35.44 ^{a}	43.65 ^{c}	42.80 ^{c}	265.22 ^{d}	336.31 ^{d}
$Znso_4$	109.85 ^{c}	115.18 ^{c}	30.88 ^{ab}	34.25 ^{b}	45.01 ^{bc}	45.56 ^{b}	349.46 ^{c}	385.32 ^{c}
$Znso_4$+$ZnoNP_{20}$	125.14 ^{b}	130.10 ^{b}	30.11 ^{ab}	32.54 ^{ab}	47.84 ^{ab}	49.06 ^{a}	405.17 ^{ab}	430.16 ^{b}
$Znso_4$+$ZnoNP_{40}$	137.12 ^{a}	148.07 ^{a}	29.60 ^{ab}	29.94 ^{b}	49.15 ^{a}	50.77 ^{a}	447.13 ^{a}	462.85 ^{a}
$Znso_4$+$ZnoNP_{60}$	140.92 ^{a}	151.12 ^{a}	26.71 ^{b}	29.06 ^{b}	48.94 ^{a}	51.10 ^{a}	460.31 ^{a}	471.42 ^{a}
$ZnoNP_{20}$	112.22 ^{c}	124.51 ^{bc}	30.23 ^{ab}	33.46 ^{ab}	46.88 ^{ab}	48.75 ^{ab}	374.82 ^{bc}	391.36 ^{bc}
$ZnoNP_{40}$	121.2 ^{bc}	131.18 ^{b}	28.91 ^{ab}	32.11 ^{ab}	47.26 ^{ab}	49.91 ^{a}	390.44 ^{ab}	431.61 ^{b}
$ZnoNP_{60}$	130.84 ^{ab}	143.28 ^{a}	28.30 ^{ab}	31.74 ^{ab}	49.07 ^{a}	50.41 ^{a}	435.16 ^{ab}	450.00 ^{ab}
F. test	**	**	*	*	**	**	**	**

*, ** and NS indicate $p < 0.05$, $p < 0.01$ and not significant, respectively. Zn_0: Control, $ZnSO_4$: $ZnSO_4$ at 24 Kg/ha, $ZnSO_4$ + $ZnONP_{20}$: $ZnSO_4$ (24 Kg/ha) + ZnONP at a rate of 20 ppm, $ZnSO_4$ + $ZnONP_{40}$: $ZnSO_4$ at 24 Kg/ha + ZnONP in the rate of 40 ppm, $ZnSO_4$ + $ZnONP_{60}$: $ZnSO_4$ at 24 Kg/ha + foliar ZnONP at a rate of 60 ppm, $ZnONP_{20}$: ZnONP at a rate of 20 ppm, $ZnONP_{40}$: ZnONP at the rate of 40ppm and $ZnONP_{60}$: ZnONP at a rate of 60 ppm. Values are the average of five repetitions. Means (n = 5). Different letters (a, ab, b, c, bc, d, cd) in each column means that the treatments were statistically different (Tukey, $p \leq 0.05$).

Means of N, P, K, and Zn uptake in straw, as affected by traditional zinc application, foliar ZnO NPs at different concentrations, and its combination, are represented in Table 7. General observations indicated that all parameters are significantly increased by the addition of ZnO NPs, except P uptake, which declined under different treatments of Zn applications. The highest value of N uptake in straw came from $ZnSO_4$+$ZnONP_{60}$ (66.13 K/ha) in the 2018 season, and $ZnSO_4$+$ZnONP_{40}$ (76.95 K/ha) in the 2019 season. Nonetheless, no noticeable statistical difference among $ZnSO_4$+$ZnONP_{20}$, $ZnSO_4$+$ZnONP_{40}$, $ZnSO_4$+$ZnONP_{60}$, $ZnONP_{40}$, and $ZnONP_{60}$ was observed. Control treatment (Zn_0) displays the lowest amount of N uptake (57.47 and 55.65 K/ha), respectively, in both seasons. In contrast

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to the previous statement, the highest value of P uptake (20.14 and 19.30 K/ha) is depicted under Zn_0. The addition of $ZnSO_4$+ZnO NP_{60} occupied the lowest value (14.30 and 12.95 K/ha), respectively, in both seasons relative to the other treatment. For K uptake, a high amount of K uptake is indicated under $ZnSO_4$+$ZnONP_{60}$ treatment (238.14 and 247.86 K/ha), followed by ZnSO4+$ZnONP_{40}$ (230.20 and 244.15 K/ha), respectively, in both seasons. No statistical difference is remarked among $ZnSO_4$+$ZnONP_{60}$, $ZnSO_4$+$ZnONP_{40}$, and $ZnONP_{60}$ in the 2018 and 2019 seasons. Almost the same trend is displayed on the Zn uptake value, increasing the amount of Zn uptake up to 475.82 and 488.95 g/ha under $ZnSO_4$+$ZnONP_{60}$ treatment, respectively, in both seasons. The lowest Zn uptake (392.73 and 394.01 g/ha) is seen under Zn_0, followed by $ZnSO_4$ (413.93 and 421.81g/ha), respectively, in both seasons.

Table 7. Influence of traditional zinc application, foliar nano zinc at different concentrations and its combination on N, P, K, and Zn uptake in the straw of the Giza179 rice variety during the 2018 and 2019 seasons.

Traits / Treatments	N Uptake (Kg/ha)		P Uptake (Kg/ha)		K Uptake (Kg/ha)		Zn Uptake (g/ha)	
	2018	2019	2018	2019	2018	2019	2018	2019
Zn_0	57.47 ^{c}	55.65 ^{c}	20.14 ^{a}	19.30 ^{a}	193.05 ^{e}	190.66 ^{d}	392.73 ^{e}	394.01 ^{d}
$Znso_4$	59.47 ^{bc}	60.81 ^{b}	17.33 ^{ab}	15.06 ^{ab}	201.48 ^{de}	218.81 ^{c}	413.93 ^{d}	420.81 ^{c}
$Znso_4$+$ZnoNP_{20}$	63.78 ^{ab}	65.89 ^{ab}	16.87 ^{ab}	15.56 ^{ab}	213.94 ^{bc}	230.39 ^{b}	446.38 ^{bc}	468.68 ^{ab}
$Znso_4$+$ZnoNP_{40}$	65.86 ^{a}	67.95 ^{a}	14.30 ^{b}	13.76 ^{ab}	230.20 ^{ab}	244.15 ^{a}	465.22 ^{ab}	479.56 ^{a}
$Znso_4$+$ZnoNP_{60}$	66.13 ^{a}	67.10 ^{a}	14.65 ^{b}	12.95 ^{b}	238.14 ^{a}	247.86 ^{a}	478.82 ^{a}	489.95 ^{a}
$ZnoNP_{20}$	61.39 ^{bc}	62.03 ^{bc}	16.15 ^{ab}	16.63 ^{ab}	209.74 ^{cd}	224.60 ^{bc}	431.83 ^{c}	442.45 ^{bc}
$ZnoNP_{40}$	63.24 ^{ab}	65.23 ^{ab}	14.65 ^{b}	15.68 ^{ab}	215.43 ^{bc}	233.05 ^{b}	454.17 ^{ab}	463.72 ^{ab}
$ZnoNP_{60}$	64.91 ^{ab}	67.23 ^{a}	13.14 ^{b}	13.73 ^{ab}	227.31 ^{ab}	242.68 ^{a}	459.24 ^{ab}	478.12 ^{a}
F. test	**	**	*	*	**	**	**	**

*, ** and NS indicate $p < 0.05$, $p < 0.01$ and not significant, respectively. Zn_0: Control, $ZnSO_4$: $ZnSO_4$ at 24 Kg/ha, $ZnSO_4$ + $ZnONP_{20}$: $ZnSO_4$ (24 Kg/ha) + ZnONP at a rate of 20 ppm, $ZnSO_4$ + $ZnONP_{40}$: $ZnSO_4$ at 24 Kg/ha + ZnONP in the rate of 40 ppm, $ZnSO_4$ + $ZnONP_{60}$: $ZnSO_4$ at 24 Kg/ha + foliar ZnONP at a rate of 60 ppm, $ZnONP_{20}$: ZnONP at a rate of 20 ppm, $ZnONP_{40}$: ZnONP at the rate of 40ppm and $ZnONP_{60}$: ZnONP at a rate of 60 ppm. Values are the average of five repetitions. Means ($n = 5$). Different letters (a, ab, b, c, bc, d, cd) in each column means that the treatments were statistically different (Tukey, $p \leq 0.05$).

From all the resultant data, it can be concluded that the different responses of studied growth parameters to $ZnSO_4$, ZnO NPs as foliar applications with various concentrations and their combinations were observed. These obtained results may be attributed to the important role of Zn in several physiological issues in a biological system [30]. Generally, Zn is an instituted of carbonic anhydrase, alkaline phosphatase, phospholipase, carboxypeptidase, RNA polymerase, and catalyzed the activity of rubisco (rubulose 1-5 bisphosphate carboxylase oxygenase). The previous enzymes stimulate the diffusion of CO_2 through the plant cell to the chloroplast [37]. Photosynthetic metabolism demands a suitable amount of Zn in plant cells. Owing to the unique properties of ZnO NPs, it can represent a novel agronomic innovation. Highly chlorophyll content under $ZnSO_4$+$ZnONP_{60}$ and $ZnSO_4$+$ZnONP_{40}$ treatments may be due to the availability of enough Zn in the plant tissue leading to an enhanced chlorophyll a:b ratio, which resulted in an improvement of the total

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chlorophyll content in leaves [38]. On the other hand, the Zn application has a positive relationship with improving the concentration of tryptophan (α-amino acid that is used as a precursor in IAA biosynthesis). IAA (indol-3-acetic acid) is an important auxin that plays a critical role in cell division and elongation. Based on the aforementioned data, the addition of ZnO NPs with proper dose enhances the photosynthetic activity, cell elongation resulted in improvement in leaf area index, plant height, and dry matter accumulation as discussed earlier. It has been reported that the application of ZnO NPs with a small concentration (28 ppm) enhanced the root length, plant height, and dry matter production (DMP) in maize plants when compared with $ZnSO_4$ [38,39]. The increase of DMP while using $ZnSO_4$+$ZnONP_{60}$ and $ZnSO_4$+$ZnONP_{40}$ compared to other treatments may be related to the improvement in both root and shoot biomass by ZnO NPs, which consequently lead to more nutrient uptake [40]. In addition, it was found that ZnO NPs enhance the number of panicles/m^2 by developing the absorption and providing several nutrients for various metabolic processes inside plant tissues [41]. The overload of yield component by the impact of ZnO NPs as a foliar application at different concentrations, and its combination with $ZnSO_4$ was demonstrated under field conditions. Increasing in panicle weight, number of filled grains, and 1000-grain weight may be related to the promising role of Zn in improving enzymatic activity, resulting in an effectively enhancement photosynthesis rate and translocation of photo-assimilates to the grain. Many scientists have provided evidence of ZnO NPs in enhancing the other parameters of both growth and yield in cereals [42,43]. The sterility became at least a ratio (63.7 and 50.5%) using $ZnSO_4$ + $ZnONP_{40}$ treatment in comparison with conventional $ZnSO_4$. It was affirmed that Zn D lessens pollen production worked on increasing the proportion of sterility [44]. Such phenomena can be related to the important function of ZnO NPs as reinforcing pollination and fertilization compounds that eventually caused minimize sterility [45]. A significant increase in the number of panicles/m^2, panicle weight, number of filled grains, and 1000-grain weight lead directly to achieving the desired grain yield. In addition to that, the availability of more accessible nutrients using ZnO NPs treatments fortifies the translocation of photosynthetic output from source to sink. Therefore, the increase in the grain portion is a reasonable consequence of the treatment with ZnO NPs [46].

An appraisal of results given in this study revealed that ZnO NPs treatments increased N and uptake in grains and straw yield. Interestingly, N uptake in grains under $ZnSO_4$ + $ZnONP_{60}$ outstripped by 28.3 and 31.2%, compared with $ZnSO_4$. The synergistic role of Zn in RNA and DNA synthesis, carbohydrate, lipids, and protein generating are well documented. The previous functions cause optimization vegetative plant material and more N uptake translocation in rice grain and straw yields. These results are in agreement with the previously reported data [47]. The implications revealed that a negative effect on P uptake with increases in ZnO NPs concentrations. The lowest value of P uptake in grain and straw yield appeared under $ZnSO_4$ + $ZnONP_{60}$ followed by $ZnSO_4$ + $ZnONP_{40}$. This may be returned to the inverse correlation between Zn and p absorption which is known with antagonistic Zn: P effect [48]. The formation of zinc phosphate probably binds p uptake in cultivated soil [49]. Similar findings were found and noted a large inhibition on P accumulation in the sorghum plant under ZnO NPs treatments [49]. This result does not align with that of those who indicated that ZnO NPs stimulates P accumulation. Data concerning K uptake in grain and straw yield showed a positive significant effect on K uptake under basal and foliar ZnO NPs treatment. In rice grains, consequences noted an advanced increase in K uptake by 9.2% under $ZnSO_4$ + $ZnONP_{40}$ in the first season and 12.1% under $ZnSO_4$ + $ZnONP_{60}$ in the second season related to $ZnSO_4$ (traditional treatment). However, the increase was 18.2 and 13.3%, respectively, in both seasons under $ZnSO_4$ + $ZnONP_{60}$ treatment in straw yield rather than $ZnSO_4$. This increase may be due to synergetic relationships among Zn and K, which causes more available and increase in K efflux from the root and shoot to translocate it to sink parts [50]. Generally, N, K, and Zn uptake in both grain and straw yields are markedly increased with Zn sufficiency. The treatment of $ZnSO_4$ + $ZnONP_{60}$ caused an increase of 31.7 and 22.3% Zn uptake

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in rice grain and by 15.6 and 16.4% in straw yield uptake, respectively, in both seasons in comparison with $ZnSO_4$. It was also reported that Zn foliar application increased Zn accumulation in rice grains from 17.7 to 50% in all varieties, which is consonance with the results of the present study [51]. Similarly, it was indicated that the ZnO NPs foliar application showed superiority increase Zn uptake in grain and straw by 14.2 and 16.1%, respectively, compared with soil application. Notably, foliar time application in the maximum tillering and flowering stage caused a marked increase in improvement Zn uptake in rice grain, besides the basal application [52]. Major studies [53] confirmed that Zn transport from vegetative parts (leaf, leaf sheath, and stem) via the phloem of rice plant under flooding conditions. Hence, foliar application methods are considered an excellent route to compensate and fortify plants with Zn especially under Zn D conditions. The efficacy of ZnO NPs is well documented in the agriculture sector, not only as a nutrient in crop production, but also as aids in the cultivated soil recovery of lost macro and micronutrients, and protects the plants during different growth stages from UV radiation, as mentioned previously [54]. By comparing our results with other NPs [54,55] based on Ag, Au, Se, TiO_2, and $Cu/CuSO_4$ that are used for the fortification of plant nutrients and the improvement of crop production, it was found that the lower doses of ZnO NPs below 100 ppm are effective with low toxicity, compared to toxic ions such as Ag^+. Consequently, such ZnO NPs could greatly improve nutritional health and sanitation, food security and sustainability, and the environment, especially in developing countries.

4. Conclusions

The green synthesis of ZnO NPs was obtained using the precipitation method in the presence of a stabilizing agent (brown algae extract). Such a stabilizing agent was used for many reasons, such as being abundant, cost-effective, cheap, and non-toxic. Then, these nanoparticles were used as efficient fertilizer to enhance grain yield outcomes and fortify rice (grain and straw) with nutrients. In addition, as carried out in our research study, Zn application methods (basal, basal + foliar, and foliar) were applied to achieve grain yield and nutrient fortification. It was concluded that the application of basal and foliar $ZnONP_{40}$ exhibited better effects than $ZnSO_4$ (traditional method). ZnO NPs with appropriate dosage leads to a higher change in improving grain yield and consolidation nutrient delivery in rice outcomes than large amounts of conventional or common fertilizer. This change would bring benefits to feeding humans who suffer from malnutrition and feeding animals with a rich nutrient straw. The current study suggests the addition of basal application ($ZnSO_4$) plus foliar treatment of $ZnONP_{40}$ at mid-tillering and panicle initiation can produce ZnO with the desired grain, straw yields, and benign nutrient uptake.

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