International Journal of Agriculture Sciences
ISSN: 0975-3710&E-ISSN: 0975-9107, Volume 9, Issue 6, 2017, pp.-3795-3798.
Available online at http://www.bioinfopublication.org/jouarchive.php?opt=&jouid=BPJ0000217

Research Article

BIO EFFICACY OF NANO ZINC SULPHIDE (ZnS) ON GROWTH AND YIELD OF SUNFLOWER (*Helianthus annuus* L.) AND NUTRIENT STATUS IN THE SOIL

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Received: January 12, 2017; Revised: January 17, 2017; Accepted: January 19, 2017; Published: February 06, 2017

Abstract- A pot experiment was conducted at IABT polyhouse, UAS, Dharwad, Karnataka to assess the performance of sunflower to different concentration of nano zinc sulphide and nutrient dynamics in soil. The treatments comprised foliar application of nano ZnS with different concentrations (100, 200, 300, 400 and 500 ppm) at 35 and 55 DAS. Nano ZnS 500 ppm sprayed at 55 DAS recorded significantly higher seed yield (5.27 g plant^{-1}) and yield attributes which was on par with 400 ppm nano ZnS sprayed at 35 DAS (4.87 g plant^{-1}). While, nano ZnS 400 ppm nano sprayed at 35 DAS recorded significantly highest plant height at 40 & 70 DAS and harvest (67.85, 120.90 and 124.73 cm, respectively), number of green leaves plant^{-1} (13.67), leaf area (356 cm^2), leaf area index (0.198), leaf area duration (8.79 days) over water spray and soil application of zinc sulphate.

Keywords- Foliar application, Nano ZnS, sunflower, Nutrient dynamics.

Citation: Meena Dharam Singh and B. N. Aravinda Kumar (2017) Bio Efficacy of Nano Zinc Sulphide (ZnS) on Growth and Yield of Sunflower (*Helianthus annuus* L.) and Nutrient Status in the Soil. International Journal of Agriculture Sciences, ISSN: 0975-3710 & E-ISSN: 0975-9107, Volume 9, Issue 6, pp.-3795-3798.

Academic Editor / Reviewer: Dr HM Jayadeva

Introduction

The global population increasing astronomically and the cultivated area is decreasing day by day due to the urbanization and industrialization. To nourish the increasing people there is need to concern more yield per unit area in per unit time with maintaining the economic, social and ecological sustainability. Similar to the other issues it is analysed that in the world and Indian soil zinc is the most wide spread deficient micronutrient. This is particularly the case in areas of oilseeds production, which affects the growth, yield and quality parameters of crop and result low zinc content in agricultural products, which is below the zinc requirement for human and animal consumption. Zinc and sulphur (S) are essential nutrient which require for metabolic reactions functioning in the plant system like zinc require for synthesis of indole acetic acid (IAA), synthesis of protein, chlorophyll production, pollen germination and pollen development [1-3]. Similarly sulphur (S) play an important role in synthesis of oil, protein, improve flavours, odour and quality of oil in oilseed crops. However, the deficiency of sulphurin soil and plant decrease the growth, yield and quality of oilseeds crop. According to Tandon [4], each unit of sulphur applied on sulphur deficient soils can augment the supply of edible oils considerably. There is need supply balance nutrient to achieve full yield potential of crop with enhance ecological, social and economical sustainability which is possible by increase fertilizer nutrient use efficiency.

Hence, to increase nutrient use efficiency nano fertilizers being preferred because the nano nutrient particles easily penetrate into the plant from applied surface, require less doses and also provide more surface area for different metabolic reaction in the plant system which enhance growth and development of crop.

Sunflower is most popular crop because of its good edible quality oil and high market prices of sunflower oil and seeds. It is a sulphur and zinc responsive crop. Hence, if there is deficiency of these nutrients in the soil and plant it reduce growth and yield of the crop drastically. In the absence of sulphur, carbohydrates are not fully utilized for the formation of oil [5]. Now days nano fertilizers are being used for site specific nutrient management to reduce the doses of fertilizer, cost of nutrient management and increase yield and nutrient use efficiency. Nano particles also being proven for better disease management. Sahayaraj *et al.* [6], reported that Aqueous solutions of Ag+and Au+ drastically reduced the body weight of *P. ricini*larvae. In view of the above facts present study entitled "Bio Efficacy Of Nano Zinc Sulphide (Zns) On Growth And Yield Of Sunflower (*Helianthus annuus* L.)And Nutrient Status in The Soil".

Material and Methods

Nano zinc sulphide (ZnS). Nano zinc sulphide was synthesized by following the standard procedure of one-step colloidal synthesis of biocompatible water-soluble ZnS quantum dot/chitosan nano-conjugates Ramanery *et al.* [7] in nanolab of IABT Department, University of Agricultural Sciences, Dharwad. The procedure allows estimating the dimensions of nano-particles in diluted colloidal suspensions in situ based on band gap energy value of UV vis spectrophotometer and the average size of the ZnS nano-crystals was estimated using the empirical model published in the literature [8,9].

Dharwad sunflower hybrid-3 (DSFH-3): The special feature of this variety is a short duration (95–98 days) with yielding capacity of 18 to 20 quintal ha^{-1} and having an oil content of 38 to 39 per cent.

Nutrient management: The recommended dose of nitrogen, phosphorus and potassium were applied at the rate of 35:50:35 kg N, P_2O_5 and K_2O per hectare in the form of urea, diammonium phosphate and muriate of potash after taking into consideration of N and P from DAP. Farm Yard Manure was incorporated 15 days before sowing in all the pots as per recommended dose (8 t ha^{-1}). Per plant nutrient requirement determined based on total plant population in one hectare.

Intercultural operations (thinning)- Initially 3 seeds were sown in each pot and maintained single plant per pot thinning was done at 15 days after sowing. The pots were arranged at a spacing of 60 X 30 cm.

Harvesting and threshing: The crop was harvested when the dorsal side of the capitulum turned to lemon yellow colour. The heads from the pots were cut, and seed yield was recorded after thorough drying. The stalks were left in pots for a week and were cut at ground level with the help of sickle and weight was recorded.

Plant observations: For recording various biometric observations, a sample size consisting of the single plant from each pot was selected. From the samples, observations on various growth, morphological, yield and yield components were recorded at different stages of plant growth (40, 70 DAS and at harvest). Observations on seed oil content were recorded in the harvested samples.

Leaf area (cm^2): Leaf area per plant was measured by the indicator leaf product method Schneiter [10].

Leaf area Index (LAI): Leaf area index was worked out by dividing the leaf area per plant by the land area occupied by the plant [11].

Harvest index. Harvest index was defined as the ratio of economic yield to biological yield and expressed in percentage. Harvest index was estimated as per the formula suggested by Donald [12].

$$\text{Harvest index (HI)} = \frac{\text{Economic yield (g plant}^{-1})}{\text{Biological yield (g plant}^{-1})} \times 100$$

Statistical analysis of data. The experiment was laid out in CRD (Completely Randomized Design) with three replications. Fisher method of analysis of variance applied to the statistical analysis and interpretation of data as given by Gomez and Gomez [13]. The level of significance used in F and t test was P=0.05. Critical difference was calculated wherever F test was significant.

Result

In this present experiment it is reported that nano zinc sulphide different concentration foliar sprayed at 35 and 55 DAS recorded significantly higher growth and yield compare to water spray and soil application which indicate more uptake of nano scale form nanoZnS compare to bulk $ZnSO_4$. Similar results with the use of nano-Zn oxide were observed in groundnut, which was conducted in the field [14].

Table-1 *Effects of different concentrations of nano ZnS on plant height, no. of leaves and leaf area of sunflower*

Treatment	Plant height (cm)			No of green leaves			Leaf area (cm^2)		
	40 DAS	70 DAS	H	40 DAS	70 DAS	H	40 DAS	70 DAS	H
1: T_1C_1	61.7	110.33	117.33	12.17	13.67	12.00	341.98	516.17	405.33
2: T_1C_2	62.5	114.02	119.37	12.17	14.33	12.33	342.33	570.67	451.33
3: T_1C_3	63.0	115.47	120.37	12.33	14.83	12.67	344.33	620.50	480.33
4: T_1C_4	67.5	120.90	124.73	13.67	16.17	14.67	356.00	698.83	537.67
5: T_1C_5	66.2	118.23	123.00	13.33	15.17	15.00	354.33	657.17	520.00
6: T_2C_1	59.8	110.07	116.93	12.17	13.83	12.33	310.17	508.00	417.33
7: T_2C_2	58.3	111.15	119.40	12.00	13.80	12.67	315.17	556.00	428.67
8: T_2C_3	59.3	113.88	121.47	12.17	14.00	13.00	322.83	568.00	445.33
9: T_2C_4	58.3	115.18	122.67	11.83	14.50	13.33	320.83	596.67	458.67
10: T_2C_5	60.0	115.98	124.47	12.00	15.20	14.67	324.33	668.67	511.00
11. WS @ two stages	58.8	102.83	113.87	11.67	12.33	11.00	311.33	433.17	356.00
12. RPP + WS @ two stages	65.7	114.72	117.70	13.00	13.67	11.67	353.00	546.83	417.67
S.Em±	0.51	1.44	0.82	0.27	0.45	0.68	4.89	12.97	8.41
CD at (p=0.01)	1.48	4.21	2.41	0.78	1.31	1.99	14,28	37.84	24.55

H: Harvest

Note:T1 - Vegetative stage (35 DAS), T2 - 50 % flowering stage (55 DAS and C1 - nano- Zinc sulphide @ 100 ppm, C2 - nano- zinc sulphide @ 200 ppm, C3 - nano-zinc sulphide @ 300 ppm, C4- nano zinc sulphide @ 400 ppm, C5 - nano zinc sulphide @ 500 ppm. The recommended package of practices (RPP) – FYM @ 8 t. ha-1 + 35: 50: 35 kg N: P2O5: K2O ha-1+10 kg ZnSO4 and from treatment 1 to 11 RPP followed except the application of $ZnSO_4$baised on RPP nutrient requirement per pot calculated.

Growth parameters of sunflower: In the present investigation result reported that among the different concentration of nano zinc sulphide 400 ppm sprayed at 35 DAS recorded highest plant height (67.85 cm, 120.90 cm, 124.73 cm), number of green leaves (13.67, 16.17, 14.67 $plant^{-1}$) at 40, 70 and harvest respectively which were on par with 500 ppm nano zinc sulphide sprayed at 55 DAS and 500 ppm nano zinc sulphide sprayed at 35 DAS [Table-1]. This might be due to more availability on nutrient to the crop during initial growth period, which enhance growth rate of these growth parameters by more photosynthesis. Similar result reported that nano-TiO_2 treated seeds produced plants recorded 73% more dry weight, three times higher photosynthetic rate, and 45% increase in chlorophyll-a formation compared to the control over germination period of 30 days [15]. Similar results reported that the application of the apatite nanoparticles increased the growth rate of soybean 32.6 per cent, above ground biomass productions 18.2% and 41.2% below-ground biomass production over control [16]. Similarly, 400 ppm nano zinc sulphide sprayed 35 DAS recorded significantly higher leaf area (356.00, 698.83, 537.67 cm^2 $plant^{-1}$), leaf area index (0.197, 0.365, 0.289) at 40, 70 and harvest respectively [Fig-1] and leaf area duration (8.79 and 5.13) at 70 and harvest which were on par with 500 ppm nano zinc sulphide sprayed at 35 and 55 DAS [Table-2]. These results are in accordance with the findings of Rani *et al.*[17]. The leaf area and leaf area index are major factors for determining the solar radiation interception, canopy photosynthesis and ultimately growth and development rate of the crop. In the present investigation, significantly higher plant height and LA at all the growth stages was noticed under 400 ppm nano-ZnS sprayed at 35 DAS over control [Table-1]. This might be due to the direct effect of sulphur and zinc on increasing the availability to the crop plant. Similar result reported that the shoot length, root lengths, leaf area, chlorophyll, carbohydrate and protein contents of the two tested crop common bean (*Phaseolus vulgaris* L.) and corn (*Zea mays* L.) were increased significantly with increase the concentration of silver nanoparticles from 20 to 60 ppm over control [18]. Hence, higher the value of these growth parameters over control indicate more availability of zinc and sulphar to the plants from foliar applied nano zinc sulphide with higher concentration which indicating more uptake and penetration of nutrient from nanoZnS over control.

Yield of sunflower: Present experiment was conducted in sulphar deficient soil to know the response of sunflower crop to different concentration of foliar sprayed nano zinc sulphide particles [Table-2]. The result indicated the significance response of sunflower crop to the nano-ZnS application this might be due to more synthesis of chlorophyll due to more availability of sulphur and Zinc. Chatterjee *et al.* [19], reported similar result that response of sunflower crop to the nano-ZnS application this might be due to more synthesis of chlorophyll due to more availability of sulphur Among the different concentration of nano zinc sulphide 500 ppm nano-ZnS sprayed at 55 DAS recorded significantly higher yield (5.27g plant^{-1}) superior over rest of the treatments, which was on par with seed weight (4.87 g plant^{-1}) 400 ppm at 35 DAS. Rattan and Ruiqiang [16], reported a similar result that application of the nano-particles phosphorus increased the growth rate and seed yield of soybean by 32.6 per cent and 20.4 per cent respectively over control. The data are presented in the [Table-2].

Table-2 *Effects of different concentrations of ZnS on LAI, LAD and seeds yield of sunflower.*

Treatment	LAI			LAD		Seeds yield plant^{-1} (g)
	40 DAS	70 DAS	H	70 DAS	H	
1: T_1C_1	0.181	0.287	0.225	7.15	3.82	2.97
2: T_1C_2	0.190	0.317	0.251	7.61	4.24	3.07
3: T_1C_3	0.191	0.345	0.267	8.04	4.57	3.37
4: T_1C_4	0.198	0.388	0.299	8.79	5.13	4.87
5: T_1C_5	0.197	0.365	0.289	8.43	4.88	4.40
6: T_2C_1	0.172	0.282	0.232	6.82	3.83	3.00
7: T_2C_2	0.175	0.309	0.238	7.26	4.08	3.20
8: T_2C_3	0.179	0.316	0.247	7.42	4.20	3.43
9: T_2C_4	0.178	0.331	0.255	7.65	4.38	4.60
10: T_2C_5	0.180	0.371	0.284	8.28	4.89	5.27
11. WS @two stages	0.170	0.241	0.198	6.33	3.27	2.47
12. RPP +WS @ two stages	0.196	0.304	0.232	7.37	4.00	3.07
S.Em±	0	0.010	0	0.08	0.05	0.14
CD at (p=0.01)	0.01	0.030	0.01	0.34	0.15	0.41

H: Harevest LAI: Leaf area index LAD: Leaf area duration

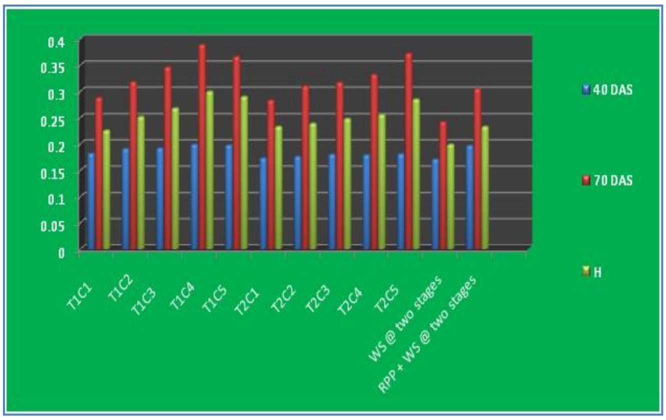

Fig-1 Effects of different concentrations of ZnS on Leaf area index of sunflower.

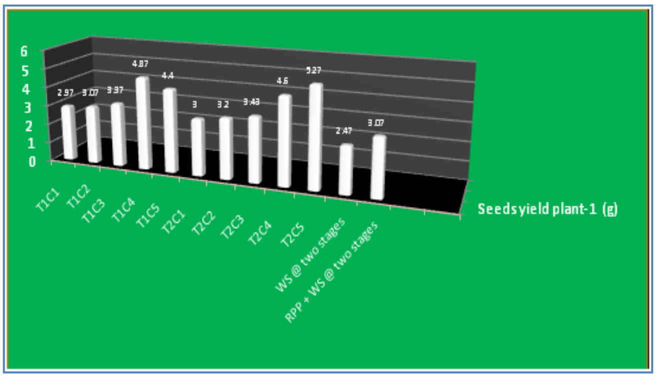

Fig-2 Effects of different concentrations of ZnS on seeds yield of sunflower

The lowest yield (2.47 g plant^{-1}) was recorded under control, which was about 42.93 percent [Fig-2]. This might be due to lower availability of sulphur under water spray treated which leading to improper seed formation and low seed weight and ultimately results in lower seed yield [Table-2]. Similar result reported that the among five concentration of iron (i.e. control, iron 2 g/L, Nano iron with 2, 4 and 6 g/L) nano-iron 6 g/L recorded highest yield (467.7 g/m^2) of feba bean (*Vicia faba* L.) over control Nadi *et al.* [20]. Similar result reported that the treatment of nano zinc oxide recorded 34 per cent higher pod yield per plant compared to chelated zinc sulphate ($ZnSO_4$) Prasad *et al.* [14]

Effect of different concentration of ZnS on uptake of primary nutrients (N, P, K, S and Zn) and available nutrient status (N, P_2O_5, K_2O, S and Zn) in soil after the harvest of sunflower plants.

The uptake of nutrients (N, P and K) by sunflower was significantly affected by the application of sulphur and zinc. The data are presented in [Table-3]. A marked increase in the nitrogen (418.30 and 398.76 mg plant^{-1}), phosphorus (92.51 and 91.68 mg^{-1}) and potassium (357.14 mg and 336.33 mg plant^{-1}) uptake was recorded with the application of 400 ppm nanoZnS sprayed at 35 DAS and 500 ppm nanoZnS at 55 DAS respectively and uptake of sulphur and zinc observed highest in 500 ppm nanoZnS sprayed at 55 DAS followed by 400 ppm nano-ZnS sprayed at 35 DAS.

Table-3 *Effects of different concentrations of nano-ZnS on uptake of primary nutrients (N, P, K, S and Zn) of the sunflower.*

Treatment	N uptake (mg plant^{-1})	P uptake (mg plant^{-1})	K uptake (mg plant^{-1})	S uptake (mg plant^{-1})	Zn uptake (mg plant^{-1})
1. T_1C_1	269.46	57.48	224.59	36.34	0.17
2. T_1C_2	283.98	63.08	239.62	39.72	0.20
3. T_1C_3	311.05	69.20	262.40	43.90	0.23
4. T_1C_4	418.30	92.52	357.15	55.74	0.40
5. T_1C_5	372.76	88.41	309.29	52.00	0.33
6. T_2C_1	275.61	60.90	231.38	38.63	0.20
7. T_2C_2	295.29	65.04	247.04	42.22	0.23
8. T_2C_3	316.97	70.15	266.14	44.60	0.26
9. T_2C_4	355.80	83.25	302.30	49.96	0.31
10.T_2C_5	398.76	91.69	336.33	58.92	0.40
11. WS @ two stages	259.95	53.45	221.06	36.03	0.24
12. RPP+WS @ two stages	300.34	66.89	251.99	42.29	0.22
S.Em±	24.92	2.70	6.06	6.98	0.01
CD(p=0.05)	72.72	7.88	17.70	20.36	0.04

Table-4 *Effect of different concentration of* nano-ZnS *on available nutrient status (N, P_2O_5, K_2O, S and Zn) in soil after the harvest of sunflower plants*

Treatment	Available Nitrogen (mg 10 kg^{-1} soil)	Available Phosphorus (mg 10 kg^{-1} soil)	Available Potassium (mg 10 kg^{-1} soil)	Available Sulphur (mg 10 kg^{-1})	Zn (ppm 10 kg^{-1} soil)
1. T_1C_1	617.06	159.98	1361.78	27.57	0.24
2. T_1C_2	610.30	152.07	1358.22	27.15	0.23
3. T_1C_3	600.60	150.45	1354.67	27.04	0.23
4. T_1C_4	579.66	145.40	1333.33	25.37	0.22
5. T_1C_5	588.19	147.93	1344.00	25.56	0.22
6. T_2C_1	610.21	154.67	1358.22	27.19	0.24
7. T_2C_2	604.36	151.37	1355.73	27.04	0.23
8. T_2C_3	599.35	149.89	1354.11	26.22	0.23
9. T_2C_4	591.14	147.57	1351.56	25.93	0.22
10.T_2C_5	582.41	146.80	1310.67	25.19	0.21
11.WS @ two stages	618.55	167.17	1365.33	27.96	0.24
12.RPP+WS@ two stages	604.58	151.16	1354.67	39.63	3.42
S.Em±	4.40	3.07	6.14	0.90	0.13
CD(P=0.05)	12.84	8.97	17.11	2.63	0.37

This is might be due to higher biomass production lead to higher uptake of nutrients from soil at higher sulphur levels. Rani *et al* [14]. Significantly, lower available nitrogen was recorded with application of 400 ppm nano-oZnS sprayed at 35 DAS followed by 500 ppm nano-ZnS at 55 DAS indicating higher uptake of nitrogen [Table-4]. Similar trend was observed with respect to phosphorus and potassium because of synergistic interaction N, P and K and seed yield at higher levels of sulphur and zinc lead to higher uptake of N, P and K. Fertilizers encapsulated in nano-particles will increase the uptake of nutrients [21].

Discussion

Among the different treatment exposed in the experiment nano-Zn S500 ppm and 400 ppm sprayed at 55 DAS and 35 DAS Recorded significantly higher yield and growth parameters respectively. Which were on par with 500 ppm nano-ZnS sprayed at 35 DAS. However, water sprayed at two stages 35 and 55 DAS recorded significantly lower yield than other treatments. Similarly uptake of nutrients (N, P and K) by sunflower was significantly affected by the application of sulphur and zinc. A marked increase in the nitrogen (418.30 and 398.76 mg plant^{-1}), phosphorus (92.51 and 91.68 mg^{-1}) and potassium (357.14 mg and 336.33 mg plant^{-1}) uptake was recorded with the application of 400 ppm nano-ZnS sprayed at 35 DAS and 500 ppm nano-ZnS at 55 DAS respectively and uptake of sulphur and zinc observed highest in 500 ppm nanoZnS sprayed at 55 DAS followed by 400 ppm nanoZnS sprayed at 35 DAS.

Conclusion

The study shown that application of nano-ZnS recorded more yield and growth of sunflower compare to bulk Zinc Sulphate. Hence, by using a very less quantity of fertilizers may reduce the application doses of fertilizers, wastage of fertilizers, environmental hazards and increase nutrient use efficiency. The present study is a new opportunity for fertilizers industries to produce nano-fertilizers as a plant nutrient. The reduce dose of fertilizer, increase nutrient availability, nutrient use efficiency and reduce the cost of fertilizers the suitable strategy must be devised. Use of nano fertilizers may be an efficient tools for site specific nutrient management in precision farming for correcting nutrient deficiency. There is need to study the effects of nano zinc sulphide particles on soil beneficial microorganisms and different beneficial process like nitrification, nitrogen fixation, decomposition of organic material, mineralization, and immobilization. There is a need to study the toxicity of nano fertilised agricultural products in human/ animal nutrition. There is also need to standardize the nano fertilizers doses for different crop and optimum stage of crop for to achieve better crop production.

Acknowledgement: The authors thank to department of nanotechnology, UAS, Dharawad, Karnataka and the Karnataka University for providing facilities for synthesis and characterization of nano-ZnS.

Funding: None

Author Contributions: All author equally contributed

Abbreviations: All abbreviation mentioned below the tables.

Ethical approval: This article does not contain any studies with human participants or animals performed by any of the authors. While conducting this research author does not included any animal or human participants.

Conflict of Interest: None declared

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