Original Research Article

Impact of fortified nano zinc and iron composite capsules on growth, yields and nutrients accumulation in cabbage (*Brassica oleracea* var. *capitata* L.) and Cauliflower (*Brassica oleracea* var. *botrytis* L.)

Abstract: Synthesized composites were characterized through UV-spectrophotometer, XRD, SEM, EDX and FTIR analysis. SEM and EDX images confirmed surface morphology of ordinary mesoporous nano silica (mNs) and Fe & Zn embedded mNs. In XRD pattern of mNs peaks absence indicate that nano silica synthesized by sol-gel method was amorphous whereas reduced graphene oxide (rGO) synthesized in crystalline form. FTIR spectra of Zn and Fe loaded mNs and rGO showed that encapsulation of zinc and iron by mNS and rGO was successful. Results of experiment indicate, twice foliar application of 60 ppm Zn+ 30 ppm Fe through mNs (T6) and 40 ppm Zn+20 ppm Fe through rGO (T8) exhibited significantly higher economic and biological yields of both crops over conventional and Control. With increasing doses of nano zinc and iron through mNs composite capsules, significant increase in nutrients content and uptake by cabbage and cauliflower was observed in comparison to control. Whereas, increasing doses of nano zinc and iron application through rGO lead to a considerable reduction in nutrient content and thus hamper their uptake. Thus, T6 and T8 treatments were best pronounced in terms of yields, nutrients uptake and enriching biomass by iron and zinc content in cabbage and cauliflower, respectively. Compared to control, quality of cabbage head and cauliflower curd biomass in terms of Fe and Zn content, protein and phenol content were significantly more with 40 ppm Zn+20 ppm Fe (T8) and 60 ppm Zn+30 ppm Fe (T6) through rGO and mNs , respectively. Available zinc and iron in soil was unaffected by application of zinc and Fe through mNs and rGO in crops.

(Key words : Nano Iron, Nano Zinc, Composites, Sprays, Cabbage, Cauliflower)

1.Introduction

Our nation is fortunate to have a wide variety of agro-climates with unique seasons, enabling the cultivation of a variety of vegetables that are significant component of Indian agriculture and nutritional security due to their short lifespan, high output, nutrient-dense composition, economic viability, and capacity to create both on- and off-farm employment. The second largest producer is India in the worldwide production of fruits and vegetables. Horticulture crops including vegetables contributes 30 % of GDP in agriculture and 52% export share of the market. Total area under horticultural crops is 21.83 million hectare and production is of 240.53 million tonnes. The percentage share of vegetables in total horticultural production ranges from 58.7 to 59.2% during past five years, 2013-18 (Directorate of Economics and Statistics, 2018).

Cabbage (*Brassica oleracea* var. *capitata* L.) is a prominent vegetable widely grown in India and other nations. It was introduced in India from Portugal in the 15th century (Singh *et al*., 2005). Similarly, Cauliflower (*Brassica oleracea* var. *botrytis* L.) and cabbage (*Brassica oleracea* var. *botrytis* L.) are also cole crops grown in India which was originated in ancient Asia minor in north eastern part of the Mediterranean. Cabbage contains vitamin A and vitamin C (124 mg) per 100 g edible part. It is rich in minerals including phosphorus (44 mg), potassium (114 mg), calcium (39 mg), sodium (14.1 mg) and iron (0.8 mg) (Fageria *et al*., 2003). Whereas fresh raw 100 g edible portion of cauliflower contains 25 kcal energy, 92.7 % water, 4.97 g carbohydrate, 0.28 g total fat, 2.0 g dietary fiber, 57µg folate, 0.507 mg niacin, 0.667 mg pantothenic acid, 0.184 mg pyridoxine and traces of minerals (USDA., 2018).

To meet the needs and demands of increasing population globally, there is a need to increase the production and productivity of vegetable crops by utilizing the limited resources available Gödecke *et al.* (2018). Nanotechnology is a new perspective of precision farming which maximizes the output from crops while minimizing the inputs such as fertilizers, pesticides, fungicides and herbicides (Dey *et al.* 2018). The use of nano fertilizers in place of conventional ones is thought to be a possible solution to the various issues caused by conventional ones (Naderi and Shahraki, 2013; Iavicoli *et al*., 2017). The site-targeted, controlled administration of nutrients with better crop protection is made possible by nanoparticles as special nanocarriers, enable the direct and intended applications in the precise management and control of wastage of inputs. Without any doubt, nanotechnology has made it possible to use nanoscale or nanostructured materials as fertiliser carriers, such as Mesoporous Nano-silica, graphene, and other controlled-release vectors, to create "smart fertiliser" as a novel innovation to improve fortification, nutrient use efficiency.

2.Materials and Methods

2.1 Synthesis of Iron and Zinc Composites

Laboratory studies on characterization and loading of nano-composites were conducted in the Department of Biophysics (Bio-Nanotechnology Unit), College of Basic Science and Humanities (CBSH) G. B. Pant University of Agriculture and Technology, Pantnagar. Nano Iron and Zinc was purchased from the standard sellers of nano-materials. For synthesis of nano composites, the following methods given in the table will be followed.

Chart 1 List of Nanocomposites

Sr. no.	**Nanocomposites**	**Standard Method Given by**
1	Iron oxide entrapped Mesoporous nano silica	Akram *et al*., 2017
2	Iron oxide ingrained Graphene	Guo *et al*., 2012
3	Zinc oxide entrapped Mesoporous nano silica	Shen *et al*., 2018
4	Zinc oxide entrapped Graphene	Zang *et al*., 2014

The loading efficiency of nano Iron and Zinc by Nanocomposites were determined by method described as above – UV-Vis Spectroscopy. The characterization of nanocomposites was done by taking help from IIT Roorkee or IIT Kharagpur. For which, XRD, SEM, TEM images were taken.

2.2 Evaluation of nano composite materials

Pantnagar is located in Uttarakhand Sub Himalayan Region (Tarai) at 29° N latitude and 79.3° E longitude, at an altitude of 243.8 m above mean sea level. Hot and humid subtropical climate is found here. The average daily temperature of the region during the coldest months ranges from 1.0 to 9.0°C but in summers it goes up to a maximum temperature of 30 to 45°C. The soils of this region have developed from the alluvial flood brought down from Himalayan mountains by streams flowing through the *Bhabhar* and *Tarai* regions. The soils of *Tarai* region are highly productive and are silty and silty loam in nature with good moisture storage capacity. For conducting experiment soils were collected from a plot of AICRP on Long Term Fertilizer Experiments in which zinc and Fe fertilizers were not added in rice and wheat both crops since inception of experiment (Kharif 1971). This treatment details are as follows: **T1**: 1% $ZnSO_4$ solution + 0.5% $FeSO_4$ solution; **T2**: 1.8% nano silica **T3**: 1.8% rGO solution; **T4**: 20 ppm Zn+10 ppm Fe through mNs composites; **T5**: 40ppm Zn+20ppm Fe through mNs composites; **T6**: 60ppm Zn+30ppm Fe through mNs composites; **T7**: 20ppm Zn+10ppm Fe through rGO composites; **T8**: 40 ppm Zn+20 ppm Fe through rGO composites; **T9**: 60ppm Zn+30ppm Fe through rGO composites. Half dose of recommended nitrogen, full dose of phosphorus and potassium were applied as basal before transplanting of cabbage and cauliflower by Urea, SSP and MOP fertilizers, respectively. Remaining half dose of nitrogen was applied after 30 days of planting. Graded levels of iron and zinc were applied as per treatments through encapsulated fabricated mNs and rGO composites.

From these composite capsules, a 1000 ppm solution of iron and zinc was prepared as a stock solution for foliar delivery of iron and zinc from nanocomposites capsules. This solution was used to make aqueous spray solutions for various treatments combination. The spray of these solution was done at 30 and 45 days after transplanting of cabbage and cauliflower seedlings. Above treatments were applied through synthesized nano composites of nano Fe and Zinc. The synthesis process and characterization along with other details for nano composites can be viewed in methodology of research paper published in Journal of Nanomaterials Volume 2022, Article ID 5120307, 13 pages https://doi.org/10.1155/2022/5120307.

3. Results and Discussion

3.1 Synthesis of nano composites of Iron and Zinc: Since the current work expects to explore the readied nanocomposites, The FTIR spectra of the nano composites of silica-iron oxide, silica-zinc oxide, graphene-iron oxide and graphene zinc oxide nanoparticles, were carried out using PERKIN ELMER FTIR C94012. The particular outcomes are presented in the fig. 1. a, b, c, and d. The FTIR spectra of the silica-iron oxide, silica-zinc oxide, graphene-iron oxide and graphene zinc oxide nanoparticles unmistakably demonstrated the successful modification of the silica and graphene surface with Iron oxide and zinc oxide nano particles. The FTIR spectra presented in Fig. 1. a and b exhibited a number of characteristic spectral bands, such as the peaks at 1,150, 870 and 650 cm −1 because of the lopsided stretching vibration, symmetric stretching vibration and bending vibration of Si–O–Si, separately, which are the particular groups of the silica nanoparticles Comparable outcomes were also recorded for by Wanyika *et al.* (2013). A generally sharp peak was noticed for Si-C at 970.95 cm^{-1}. The presence of this peak can additionally affirm the holding of silicon and dynamic carbons because of the calcinations of mNs. The trademark FTIR range of rGO nanosheets is portrayed in Fig.1. b and d. In the FTIR range of rGO, oxygen bunches are observed in which the principle ingestion band at around 3410 cm−1 is appointed to the O-H group extending vibrations. Results also found in accordance with **Ciplak *et al*. (2014).** In the fig1 a and c obviously vibrations of Fe–O bond (602 cm–1) which is in agreement with the writing results of Durgude, *et al.* 2021).

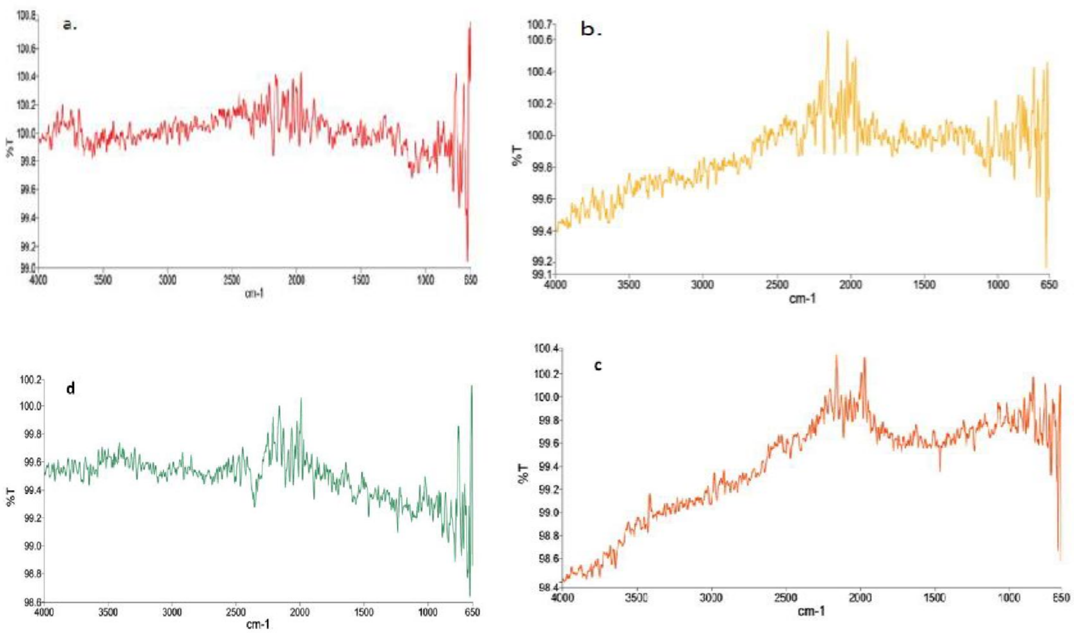
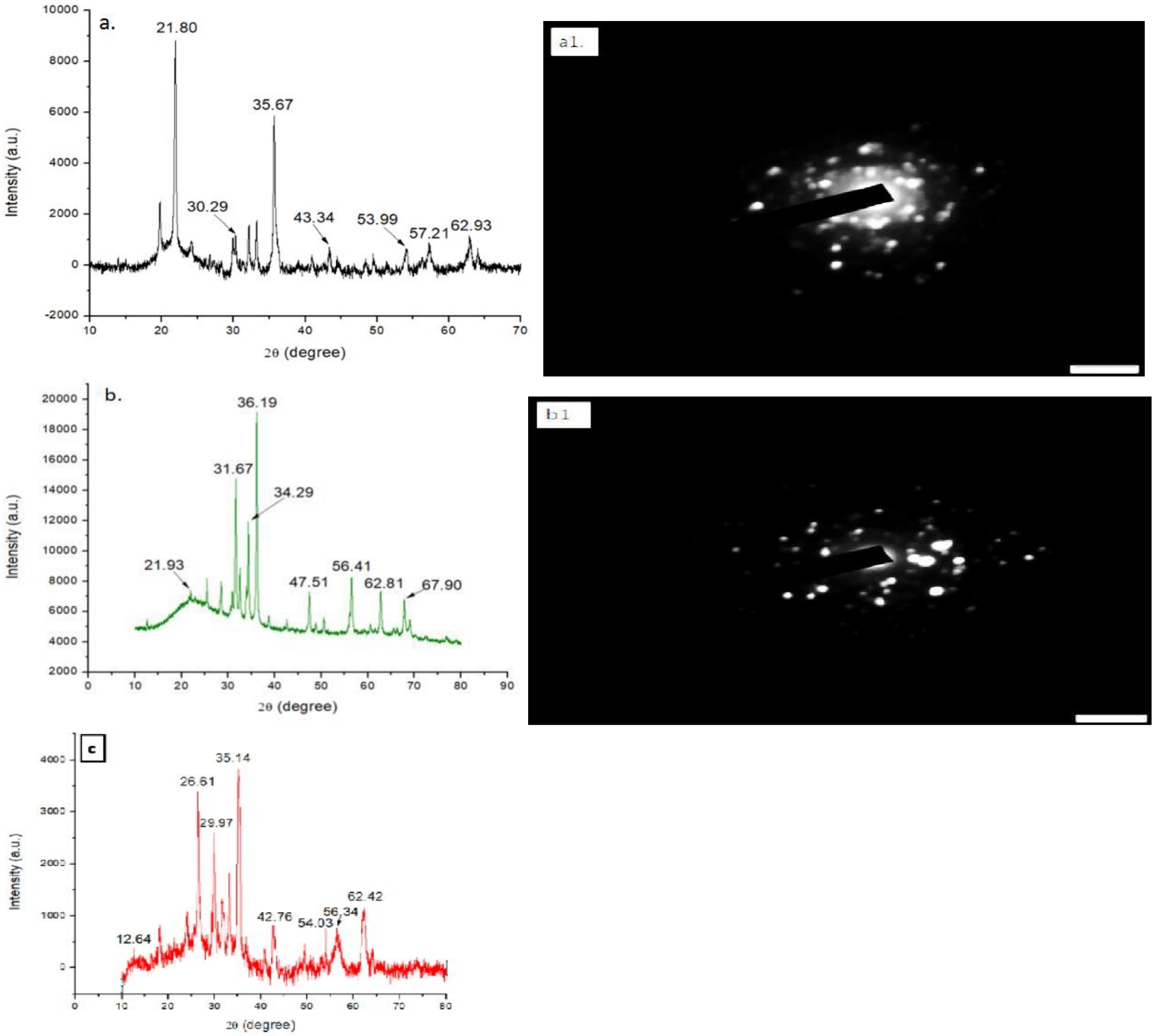


Fig. 1: FTIR spectra of a. mNs – Iron oxide nanocomposite, b. mNs – Zinc oxide nanocomposite, c. rGO – Iron oxide nanocomposite, d. rGO – Zinc oxide nanocomposite.

Another XR Diffraction peaks at 31.670, 34.190, 36.190, 47.510, 56.410, 62.810 and 67.900 were observed in fig. 2 b, while characterization of mNs –ZnO nanocomposite. The peaks are the clear evidence of presence of ZnO nanoparticles in the same nano composite with crystal size of 30.08 nm (d spacing 2.48 A0). The presence of crystalline ZnO in rGO – ZnO nanocomposite was confirmed with the intense peaks at 26.470, 31.670, 34.430, 47.530, 56.410, 62.710 and 67.760 (fig.2 d). All the observed peak could be indexed as ZnO as per JCPDS data card no. 36-1451. Crystalline size of 19.90 nm was reported with d spacing of 2.48 A0. The crystalline nature of both zinc oxide nanomaterials is confirmed with SAED TEM images of respective nanocomposites (fig. 2 b1 and d1). The results found attendant with the results of Kanjana *et al.* (2019)


a.
21.80
35.67
30.29
43.34
53.99
57.21
62.93
Intensity (a.u.)
2θ (degree)
a1.
b.
36.19
31.67
34.29
21.93
47.51
56.41
62.81
67.90
Intensity (a.u.)
2θ (degree)
b1
c
35.14
26.61
29.97
42.76
54.03
56.34
62.42
12.64
Intensity (a.u.)
2θ (degree)

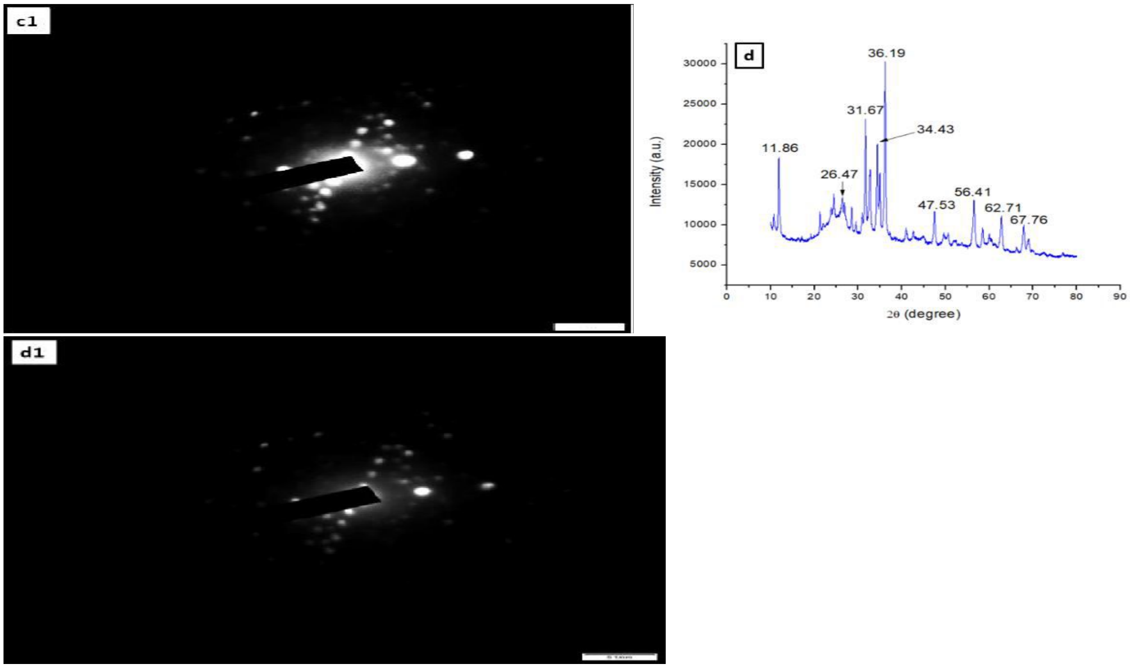
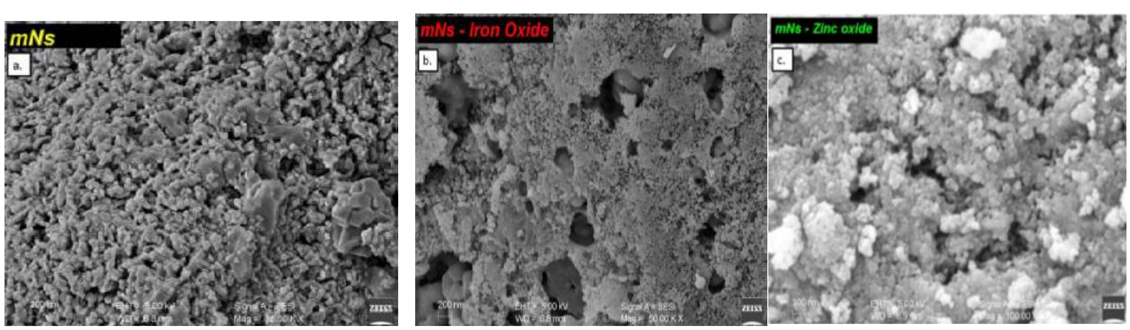


Fig. 2 : XRD spectrum of a. mNs – Iron oxide nanocomposite, b. mNs – Zinc oxide nanocomposite, c. rGO – Iron oxide nanocomposite, d. rGO – Zinc oxide nanocomposite. and Selected Area Electron Diffrection (SAED) micrographs of a1. mNs – Iron oxide nanocomposite, b1. mNs – Zinc oxide nanocomposite, c1. rGO – Iron oxide nanocomposite, d1. rGO – Zinc oxide nanocomposite.

Nanocomposites were subjected to surface analysis using field emission scanning electron microscopy (FE - SEM). FE – SEM was performed using CARL ZEISS SUPRA 55 operating at 10 kv.



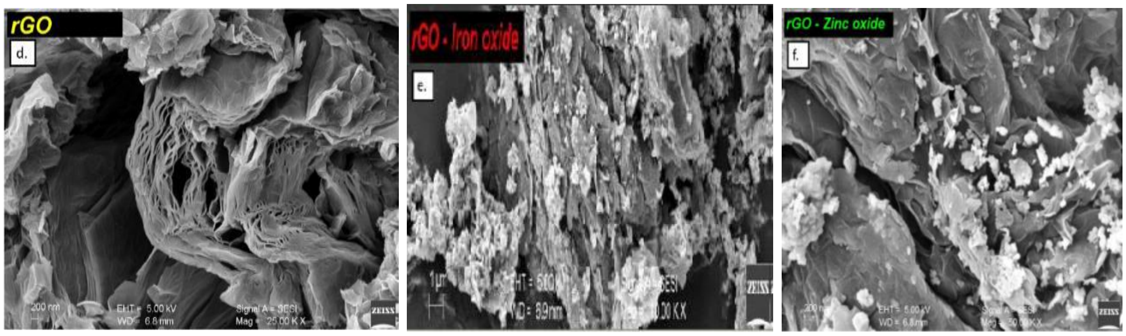


Fig. 3 : FE SEM micrographs of radied nanocomposites a. black sample of mesoporous nanosilica, b. mNs engrafted with iron oxide nanoparticles and c. mNs engrafted with Zinc oxide nanoparticles.c. rGO – Iron oxide nanocomposite, d. rGO – Zinc oxide nanocomposite

SEM analysis revealed the surface morphology of spheroidal nanoparticles of silica with little aggregation (fig. 3 a). Nano silica particles were porous providing the average space of 40 – 50 nm. The SEM micrograph revealed that the addition of FeO nanoparticles significantly altered the morphology of silica nanomaterial. The engrafting of FeO nanoparticles over silica is clearly visible (fig. 3 b) Average diameter of iron oxide nano particle is ranging from 30 - 40 nm), grain sized is analysed using Image J image processor. The mesoporous silica and zinc oxide microspheres were evident from the gray worm like structure doped with ZnO nano particles appearing as a complex mixture. ZnO nanoparticles were capsulated onto pore opening and the edges of silica particles with the average grain size ranging from 30-50 nm (fig. 3 c). these results found accompanying with the results of Qureshi *et al.* (2018)

Nanocomposites were subjected to elemental analysis using AAS was performed using a Pin AAcle series Atomic Absorption Spectrometer. The results of analysis are presented in table

Chart 2 Elemental analysis using AAS

S.N.	**Elemental composition**	**Element %**
	Dilution with acidified water	
1	Mesoporous silica implanted Iron oxide (mNs – Fe nanocomposite)	21.3 Fe
2	Mesoporous silica implanted zinc oxide (mNs	27.6 Zn

	– Zn nanocomposite)	
3	Graphene oxide implanted Iron oxide (rGO – Fe nanocomposite)	23.4 Fe
4	Graphene oxide implanted zinc oxide (rGO – Zn nanocomposite)	38.1 Zn
Dilution with deionized water		
1	Mesoporous silica implanted Iron oxide (mNs – Fe nanocomposite)	9.8 Fe
2	Mesoporous silica implanted zinc oxide (mNs – Zn nanocomposite)	15.4 Zn
3	Graphene oxide implanted Iron oxide (rGO – Fe nanocomposite)	11.3 Fe
4	Graphene oxide implanted zinc oxide (rGO – Zn nanocomposite)	24.6 Zn

3.2 Growth attributes: The data regarding growth parameters indicate that plant height at maturity in cabbage and cauliflower was not affected significantly by the applied doses of iron and zinc through mesoporous nano silica (mNs) and reduced graphene oxide (rGO) capsules but numerically maximum plant height was found in treatment (T5) that received 40 ppm Zn+30 ppm Fe through rGO composite capsules as foliar sprays (Table 1). Maximum number of leaves per plant in cauliflower and maximum leaf length was attained by T8 in cabbage and T7 in cauliflower, respectively. Increase in growth qualities could be owing to the fact that, in addition to its role nano Zn and Fe in chlorophyll synthesis, regulated cell division, tissue meristematic activity, cell expansion and cell wall development**.** These finding are in accordance with Balyan and Joginder, 1994.

Table 1 Effect of nano Fe and Zn through mNs and rGO nanocomposites on growth parameters of Cabbage and Cauliflower.

Treatments	**Cabbage**			**Cauliflower**		
	Plant height at maturity	**Number of leaves**	**Leaf length**	**Plant height at maturity**	**Number of leaves**	**Leaf length**
T1: 1% $ZnSO_4$ + 0.5% $FeSO_4$	14.73	12.69	9.27	21.78	11.66	13.78
T2: 1.8% mNs	13.60	12.33	8.07	23.15	11.33	14.65
T3: 1.8% rGO	14.00	12.63	10.06	23.28	11.33	14.39

T4:20ppmZn (mNs) + 10 ppm Fe (mNs)	16.96	15.03	11.04	24.18	11.33	15.16
T5: 40 ppm Zn (mNs) + 20 ppm Fe (mNs)	17.96	14.36	11.04	24.25	14.33	17.97
T6: 60 ppm Zn (mNs) + 30 ppm Fe (mNs)	18.13	14.66	11.40	24.66	15.00	18.13
T7: 20 ppm Zn (rGO) +10 ppm Fe (rGO)	18.00	14.43	12.07	24.96	14.33	17.82
T8: 40 ppm Zn (rGO) + 20 ppm Fe (rGO)	18.16	15.06	11.74	25.43	16.33	18.27
T9: 60 ppm Zn (rGO) + 30 ppm Fe (rGO)	17.40	14.83	11.07	24.36	13.34	17.93
SEm± LSD (p=0.05)	1.224 NS	1.241 NS	1.12 NS	0.645 NS	1.19 NS	1.46 NS

3.3 Crop yields: On the application of various doses of zinc and Fe through nanocomposites on cabbage and cauliflower, significant effect on yield were observed (Table 2). The maximum head and curd yields in cabbage and cauliflower was found as 485.15 and 495.42 g pot^{-1} respectively, with application of 60 ppm Zn + 30 ppm Fe through mNs composites (T6) which was statistically at par with T8 (40 ppm Zn + 20 ppm Fe through rGO composite) which yielded 483.15g pot^{-1} and 490.42g pot^{-1} in cabbage and cauliflower respectively. This increase might be due to Nano zinc and Fe absorption helped in translocation of photosynthates from one part to another (Choudhary *et al.*, 2018). However**,** treatment T6 which received 60 ppm Zn and 30 ppm Fe through mNs composites solution as foliar sprays gave maximum biological yields as 644.35g pot^{-1} in cabbage, while in cauliflower treatment T8 (40 ppm Zn and 20 ppm Fe through rGO) gave maximum yield (660.48) g pot^{-1}. Higher doses of Nano Zn and Fe through rGO composites (T9) showed significantly lower curd yields of cabbage and head of cauliflower compared to T8 treatment in which 40 ppm Zn +20 ppm Fe through rGO was applied. The reduction in head and curd yield of cabbage and cauliflower might be ascribed due to the toxic effect on metabolic activities of plants. These findings are in accordance with (Palanog *et al.*, 2019; Durgude *et al.*, 2021).

Table 2: Effect of nano Fe and Zn through mNs and rGO nanocomposites on biological and economic yield of Cabbage and Cauliflower.

Treatments	Cabbage		Cauliflower	
	Head (gm)	Biological yield (gm)	Curd (gm)	Biological yield (gm)
T1: 1% ZnSO4 + 0.5% FeSO4	388.72	532.95	405.35	556.99
T2: 1.8% mNs	450.17	600.77	425.84	595.01
T3: 1.8% rGO	457.5	608.1	438.81	612.91
T4: 20 ppm Zn (mNs)+10 ppm Fe (mNs)	468.27	632.7	449.59	628.06
T5: 40 ppm Zn (mNs) + 20 ppm Fe (mNs)	474.41	643.58	466.26	647.16
T6: 60 ppm Zn (mNs) + 30 ppm Fe (mNs)	485.15	644.35	495.42	668.28
T7: 20 ppm Zn (rGO) +10 ppm Fe (rGO)	471.95	634.68	464.89	641.6
T8: 40 ppm Zn (rGO) + 20 ppm Fe (rGO)	483.18	643.51	490.42	660.48
T9: 60 ppm Zn (rGO) + 30 ppm Fe (rGO)	474.63	636.69	470.45	644.78
SEm±	1.24	1.17	1.54	0.042
LSD (p=0.05)	3.71	3.5	4.62	0.126

3.4 Nutrients Composition and Uptake

The nutrient content varied significantly with the application of various doses of Fe and Zn nanocomposites through mNs and rGO (table 3). Treatment T8, gave maximum and significantly greater nitrogen content in cabbage and cauliflower. Phosphorus content in plants was found maximum in treatment T5 (40 ppm Zn+20 ppm Fe through mNs) in both crops whereas the potassium content was found maximum with the application of treatment T8. The different treatments of iron and zinc application through mNs and rGO via foliar mode recorded significantly higher nutrient content and uptake by cabbage and cauliflower, registering the nitrogen uptake of (10.23 and 11.59 gm pot^{-1}) with T8 treatment in cabbage and cauliflower. However, phosphorus uptake was recorded maximum with T5 and T6 respectively. K uptake was 8.57 gm pot^{-1} and 8.74 $gpot^{-1}$ in cabbage and cauliflower, respectively and significantly differed with various treatments of iron and zinc application through mNs and rGO via foliar application. The increase in nitrogen content might be due to synergetic impact with nitrogen in which zinc plays a significant function in nitrogen metabolism and its translocation. These results are in agreement with the findings of Chethana and Naveen (2019) who observed an increment of (2.56%) nitrogen content over traditional application. The higher potassium content in cabbage and cauliflower could be owing to the synergistic action of zinc-potassium.

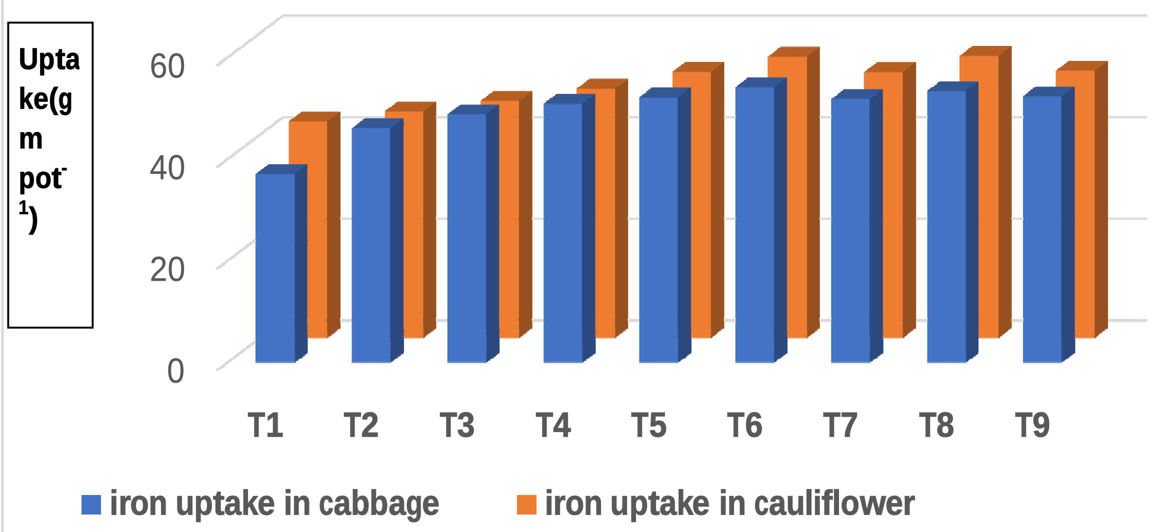
Table 3: Effect of nano Fe and Zn through mNs and rGO nanocomposites on nutrients content and uptake of Cabbage and Cauliflower.

Treatments	Cabbage			Cauliflower			Cabbage			Cauliflower		
	Nutrient Content (%)						Nutrient Uptake (Kg ha^{-1})					
	N	P	K	N	P	K	N	P	K	N	P	K
T1	1.95	0.31	1.70	1.88	0.33	1.74	7.57	1.22	6.62	7.63	1.32	7.07
T2	1.96	0.35	1.72	1.90	0.34	1.75	8.81	1.59	7.76	8.11	1.43	7.47
T3	1.99	0.35	1.73	1.92	0.34	1.75	9.09	1.61	7.93	8.44	1.47	7.69
T4	2.01	0.36	1.72	1.94	0.36	1.76	9.40	1.67	8.07	8.74	1.60	7.93
T5	2.06	0.35	1.74	2.02	0.39	1.76	9.76	1.70	8.27	9.44	1.80	8.22
T6	2.11	0.34	1.77	2.09	0.38	1.77	10.18	1.65	8.57	10.16	1.82	8.61
T7	2.09	0.34	1.74	2.06	0.39	1.74	9.85	1.62	8.23	9.59	1.79	8.11
T8	2.12	0.34	1.77	2.09	0.37	1.78	10.23	1.65	8.57	10.26	1.79	8.74
T9	2.09	0.33	1.76	2.08	0.37	1.75	9.90	1.58	8.37	9.80	1.72	8.25
SEm±	0.01	0.01	0.01	0.01	0.01	0.01	0.12	0.04	0.15	0.15	0.10	0.15
LSD (p=0.05)	0.04	0.03	0.03	0.02	0.04	0.02	0.36	0.13	0.44	0.44	0.29	0.43

3.5 Zn and Fe fortification of biomass

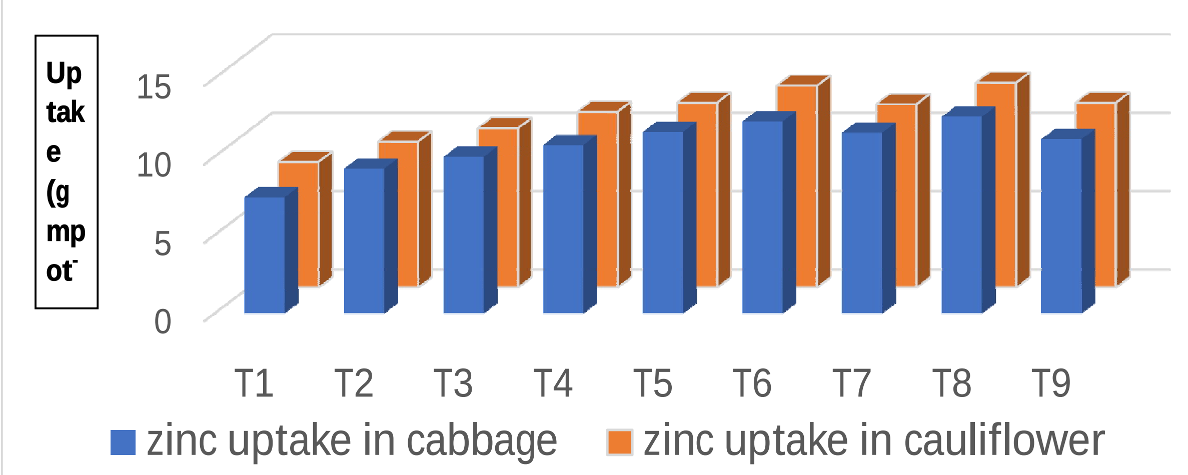
The data representing iron and zinc content is presented in table 4 and fig 4 & 5. Iron content and uptake in cabbage and cauliflower was affected significantly by the application of 60 ppm Zn + 30 ppm Fe through mNs registering maximum iron uptake of 54.13mg pot^{-1} and 55.32mg pot^{-1} respectively. A significant increase in uptake of iron was observed with increasing doses of zinc and Fe through mNs in both the crops but the higher doses of Zn and Fe nanocomposites through rGO leads to a considerable reduction in iron uptake by cabbage and cauliflower. The slow release features of silica and graphene might have a good impact on plant iron uptake, providing long-term benefits over crop requirements. This has been reported by (Chethana and Naveen, 2019; Shubham *et al.* 2022). Zinc content and uptake was significantly affected by the application of T8 (40 ppm Zn +20 ppm Fe through rGO) with the corresponding values of 12.53 and 13.06 mg pot^{-1} in cabbage and cauliflower respectively. +41.11% and +38.67% increase in zinc uptake was recorded with T8 treatment over T1 treatment in cabbage and cauliflower respectively. The increase in uptake of zinc might be ascribed due to higher absorption of nanosized Zn particles by plant parts which enhances every metabolic activity of plants (Gopali *et al*. 2020). The significant reduction in zinc uptake in both crops by the application of nano Zinc and Fe through rGO might be ascribed due to phytotoxic action of

Fig 4 Effect of nano composit capsules on Iron uptake by Cabbage and Cauliflower



reduced graphene oxide which hampers the zinc absorption that ultimately leads to zinc uptake reduction (Lin and Xing, 2008).

Fig 5 Effect of nano Composites on Zn uptake by cabbage and cauliflower.



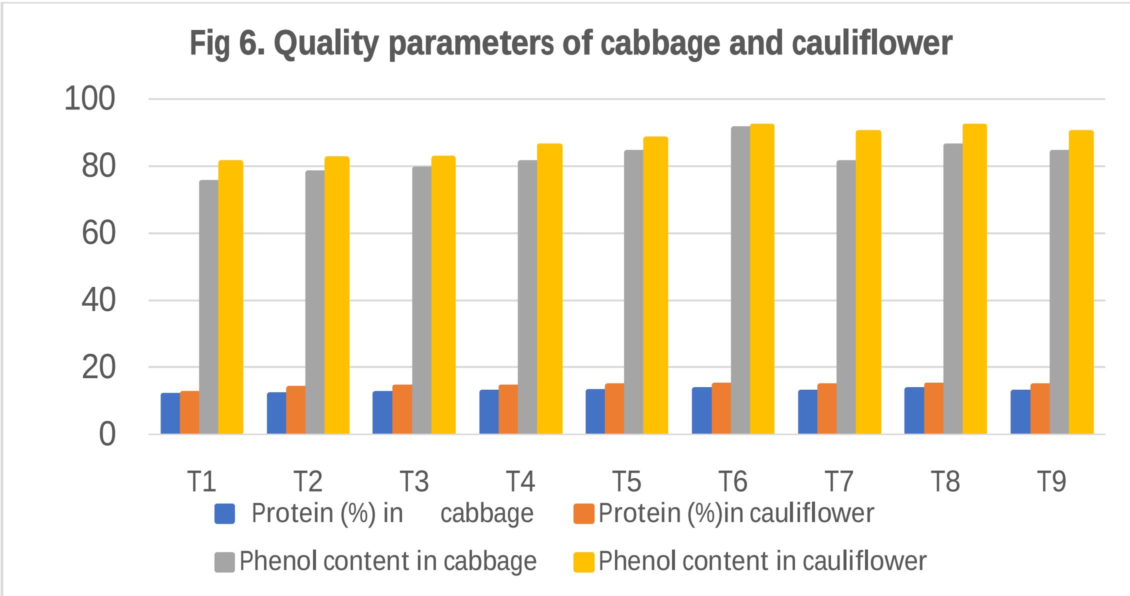
Treatment	Cabbage		Cauliflower		Cabbage		Cauliflower	
	Fe content (mg kg^{-1})	**Zn content (mg kg^{-1})**	**Fe content (mg kg^{-1})**	**Zn content (mg kg^{-1})**	**Iron uptake (mg pot^{-1})**	**Zinc uptake (mg pot^{-1})**	**Iron uptake (mg pot^{-1})**	**Zinc uptake (mg pot^{-1})**
T1	100.61	18.98	103.01	19.41	41.08	7.38	42.53	8.01
T2	101.99	20.47	103.39	21.61	46.08	9.21	44.50	9.30
T3	105.98	21.78	105.27	22.94	48.83	9.97	46.57	10.15
T4	107.94	22.92	107.55	24.61	50.89	10.73	48.95	11.20
T5	109.64	24.37	110.67	24.94	52.19	11.56	52.29	11.78
T6	112.72	25.94	115.57	26.88	54.13	12.23	55.32	12.86
T7	109.01	24.39	110.36	24.67	51.79	11.51	52.24	11.68
T8	111.05	25.31	114.67	27.01	53.38	12.53	55.48	13.06
T9	110.34	23.39	111.66	25.04	52.37	11.10	52.53	11.78
LSD (p=0.05)	2.75	1.17	2.28	0.08	2.34	0.57	2.10	0.42
SEm±	0.92	0.39	0.76	0.03	0.78	0.19	0.70	0.14

Table 4 Effect of nano Fe and Zn through mNs and rGO nanocomposites on Fe and Zn content and uptake in Cabbage and Cauliflower

3.6 Quality Parameters

Different treatment of iron and zinc through mNs and rGo via foliar mode significantly affected the protein and phenol content of cabbage and cauliflower crop respectively. Treatment T8, which received 40 ppm Zn + 20 ppm Fe through rGo as foliar spray, had a much greater protein content as compared to control (T1). T8 showed an increment of +8% and +9% in protein percent over T1 in cabbage and cauliflower respectively. Treatment T6 (60 ppm Zn + 30 ppm Fe through mNs) resulted considerable higher phenol content over all other treatments. 11 % increase in phenolic content was recorded with T6 treatment compared to T1 treatment in cabbage and cauliflower respectively. Cabbage and cauliflower when treated with different doses of zinc and iron nanoparticles differed non-significantly with respect to antioxidant activity, but numerically the highest value was reported in T4 and T6 in which 20 ppm +10 ppm

Fe and 60 ppm Zn +30 ppm Fe was applied through mNs. The corresponding values were 96.02% in case of cabbage and 98.20% in cauliflower with treatment T6. Similarly, application of mesoporous silica and graphene based nanocomposites of Fe and Zn, showed non-significant impact on anti-inflammatory activity of both crops. However, highest anti-inflammatory activity was observed with treatment T6 whereas, treatment T8 resulted in maximum anti-inflammatory with corresponding value of 79.12% in cauliflower and with T6 (78.39%) in cabbage.



3.7 Studies on phytotoxicities

3.7.1 Observation of stomatal apparatus and cellular structures in cabbage and cauliflower

Since, scanning electron microscopy requires verification of spectroscopy for elemental or material identification in the live tissue sample but electron microscopy was performed to asses phytotoxic accumulation in the plant leaves. The outputs were particularly studied for analysis of cell arrangement and mass accumulation of nanoparticles in the stomata. Particularly, where the graphene nanoforms were sprayed showed kind of abnormalities in the stomatal apparatus. Little undefined mass aggregation of microscale material was observed in the leaf tissue of cabbage and cauliflower Leaf samples treated with reduced graphene oxide showed deformations in the stomata and trichome morphology. The ***image J 8.0*** quantification results indicated an decrease in area of stomata (fig: B. rGO-NP -treated leaves), than the control (fig A.), whereas size reduction was noted in both the crops. Interestingly, the plants treated with mesoporous nano silica and predefined higher concentrations of iron and zinc showed no significant deformities in both the crop (Qureshi, *et al.* (2018). The respective impacts were not originated from the application of nanoparticles of iron and zinc. The plant tissues were analyzed for the respective nutrient concentrations through absorption spectroscopy. No significant concentrations (nano Fe and Zn) or no evidence of what we can call a toxicity factor has been found.

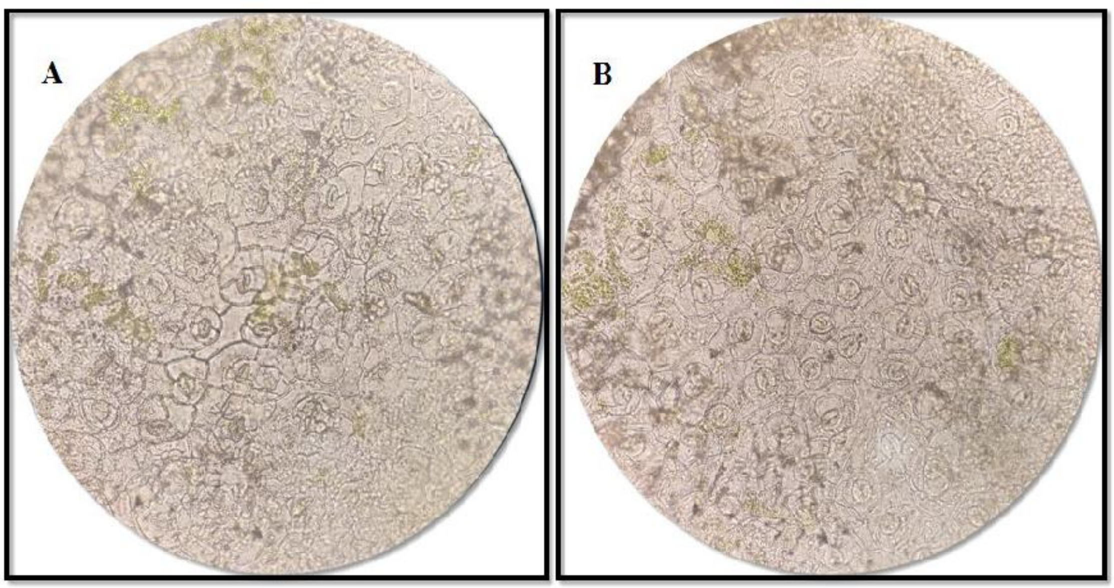


Fig. 7: EVO-40 outputs for the cabbage leaf tissue sample (1mm) A. Control B. Intensively treated with rGO

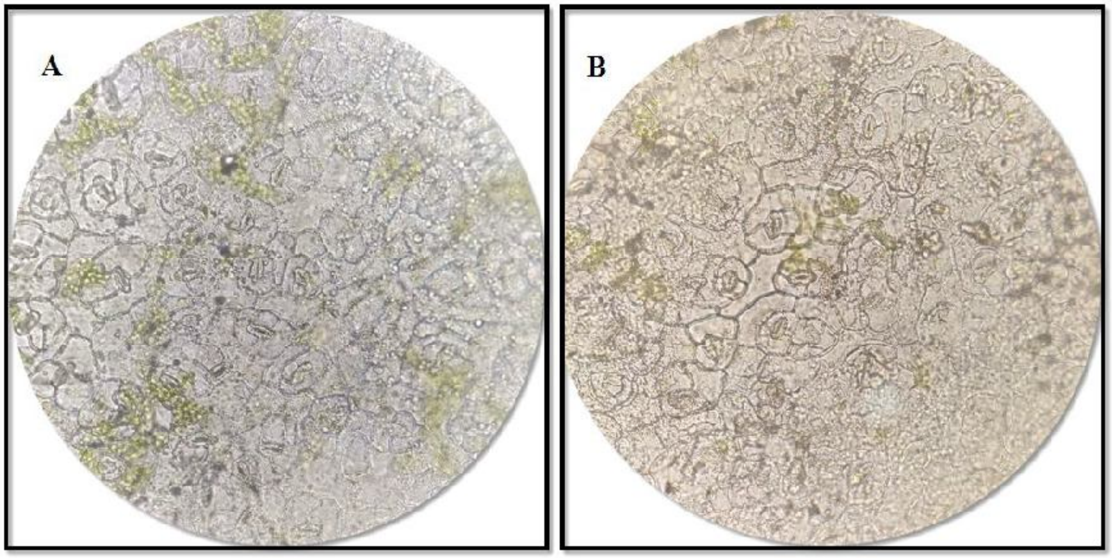


Fig. 8: EVO-40 outputs for the cauliflower leaf tissue sample (1mm) A. Control B. Intensively Treated with rGO

Conclusion

It may be concluded from the findings of studies that twice foliar application of 60 ppm Zn+ 30 ppm Fe through mNs (T6) and 40 ppm Zn+20 ppm Fe through rGO (T8) showed significantly higher economic and biological yields over conventional application of Zn and Fe (T1) in both crops. With increasing doses of nanozinc and iron through mNs , a significant increase in nutrient content and uptake was observed. Whereas, increasing doses of nanozinc and iron application through rGO leads to a considerable reduction in nutrient content and thus hampers their uptake. Thus, Treatment T6 and T8 were best pronounced in terms of yields, nutrient uptake, iron and zinc content in cabbage and cauliflower respectively. However, increasing doses of nano zinc and iron application through rGO leads to significant reduction in yields, nutrients uptake and zinc content in both crops along with phytotoxic accumulation of graphene in leaf tissues. The quality of cabbage and cauliflower in terms of protein and phenol content was significantly influenced with the foliar application of 40 ppm Zn+20 ppm Fe (T8) and 60 ppm Zn+30 ppm Fe (T6) through reduced graphene oxide and mesoporous nano silica respectively.

Abbreviations

mNs : Mesoporous nano silica, rGO : reduced graphene oxide, FTIR : These composites were characterized by using Fourier Transform Infrared Spectroscopy, XRD : X-ray diffractometer , SEM : Scanning electron microscopy, TEM : Transmission electron microscopy, EDX : Energy-dispersive X-ray ,

Data Availability

All data are presented within the article.

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