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Designing and scanning electron enumeration of micronutrient nanofertilizers utilizing mesoporous nanosilica based altered nanocomposites

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Abstract
Considering nutrient conveyance and micronutrient use efficiency issues, mesoporous nano silica (mNs) nanomaterial-based micronutrient fertilizer designing was done specifically for iron and zinc at Govind Ballabh Pant University of Agriculture and Technology, Pantnagar, Uttarakhand, India. The nanocomposites arranged were described by Scanning Electron Microscopy (FE-SEM) and Atomic Absorption Spectroscopy (AAS). FE-SEM uncovered the changed surface of mesoporous nano silica by the expansion of designated micronutrient (with average crystal size of 30-70 nm). AAS analysis revealed the higher elemental composition in the acid diluted nanocomposites sample than the samples diluted in distilled water. In acid diluted nanocomposites the 21.3% Fe and 27.6% Zn were reported in the nanocompsites of mNs – FeO and mNs – ZnO respectively. The modification of nanosilica with iron and zinc found successful with the given efforts. The radied nanocomnposites within optimum exposure found significant positive impacts on seed germination and seed vigour in Wheat seed.

Keywords: Nanocomposites, silica, iron, zinc

Introduction

Micronutrient deficiency is far and wide in numerous Asian nations because of the calcareous nature of soils, high pH, low organic matter, salt pressure, continuous drought, high bicarbonate content in water system water, and imbalanced use of fertilizers. The shortfall of micronutrient fertilizers brings about insufficient retention of trace elements by plants, which causes substantial yield losses in different crops and forages and in the end brings about chronic weakness in domestic animals and people. Investigation of soil and plant tests has shown that 49% of soils in India are conceivably deficient around 49% in Zn, 12% in Fe, 5% in Mn, 3% in copper (Cu), 33% in boron (B) and 11% in molybdenum (Mo). The crop fertilizer-micronutrient use efficiency of Iron and Zinc is also approximately less than 5% (Dey *et al.*, 2018) [4]. Billions of people and many soils across the planet suffer from micronutrient (MN) deficiencies impairing human health. The soil applied fertilizer-MN use efficiency (MUE) by crops is <5% due to a lack of synchronization between the fertilizer-MN release and their crop demand during growth. (Monreal *et al*., 2015) [8]

By supplying plant nutrients through –Nanotechnology, Nanofertilizer or Nano composites could possibly boost the plant growth (Dey *et al.*, 2018) [4]. Nanomaterials offer a more extensive surface area to fertilizers and pesticides. Furthermore, nanomaterials as remarkable transporters of agrochemicals encourage the site-focused on controlled release of nutrient with increased crop production. Because of their immediate and planned applications in the precise management and control of inputs (fertilizers, pesticides, herbicides), nanotools, for example, nanobiosensors, supports the improvement of innovative agriculture farm (Shang *et al.*, 2019) [9]. Mesoporous nano silica (mNs / MNs) materials become known as a promising competitor that can defeat above issues and produce impacts in a controllable and feasible way. Specifically, mesoporous silica nanoparticles (MSNs) are generally utilized as a delivery agent since silica has positive compound properties like thermal stability, and biocompatibility. The novel mesoporous design of silica encourages powerful loading of target substances and their ensuing controlled release towards the site in question. (Bharti *et al.*, 2015) [1]. Undeniably, nanotechnology has provided the feasibility of exploiting nanoscale or nanostructured materials as fertilizer carriers like Mesoporous Nano-silica, Graphene etc or controlled-release vectors for building "smart fertilizer" as new address to enhance nutrient use. For testing the potential of prepared nanocomposite. A Temporal seed germination trial was conducted which surely will create strong basis for field trials.

Experimental/Material and method

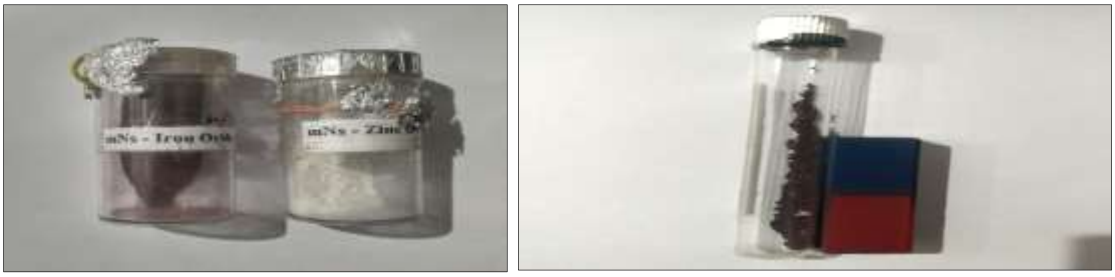
Laboratory experiment on engrafting of Iron and Zinc on mesoporous nanosilica mNs was conducted in the Nanotechnology Unit, GB Pant University of Agriculture and Technology Pantnagar, India. For evaluation, nanocomposites were synthesized by the reference method outlined by Guo *et al.*, 2018 [6], Chen *et al.*, 2016 [3], Chaneac *et al.*, 2017 [2], and Shen *et al.*, 2018 [10] etc.

1. Synthesis of Mesoporous nano silica (mNs) – Iron oxide nano-composite

Simply added in 50 mL $FeCl_3$ solution were 6 g mesoporous silica (0.45 M). The 1 h 0.25 m sodium borohydride solution was stirred (at 800 rpm) with the addition of a drop wise solution. The solvent is purified and washed with water and ethanol twice after completing mixing before transparent filtration is achieved. The resultant powder was dried for 2 hours in the oven at 60 °C.

2. Synthesis of MNs-Zinc oxide nano-composites

A wet impregnation procedure has been used to load zinc oxide nanoparticles onto mesoporous silica. Set the zinc nitrate solution for a total of 50 mL (100 mmoL). Add 500 mg Salicylaldimine Mobile Matter no.41 or MCM-41 with 24 hour stirring at 30 0C. After filtering, washing and drying, Zn/Sal-MCM-41 and Zn/MCM-41 were collected. Since calcination in the air at 550 ^{0}C for 6 h. It's got ZnO-Silica**.**



a b

Fig 1: a. Readied nanocomposite b. Magnetic property of iron oxide in mNs.

Characterization of nanocomposites

Characterization of all prepared nanocomposites were done at Bombay, Indian Institute of Technology (IIT), India, through *Spring Testing Solutions*. For characterization advanced techniques FE SEM (using CARL ZEISS SUPRA 55 operating at 10 kv) was used. The elemental analysis was done with the help of AAS (model of PinAAcle series) at Micronutrient research scheme, MPKV Rahuri, Maharashtra.413722, India.

Another detailing study on seed germination was performed in department of soil science, GBPUA & T, Pantnagar, UK, India.

Results and Discussion

FE SEM

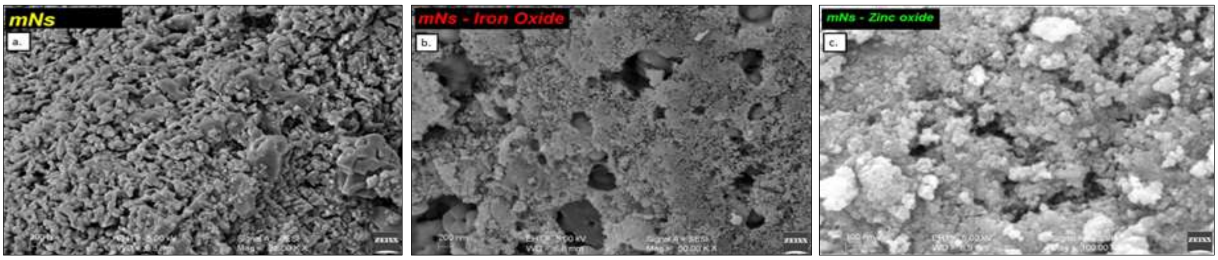


Fig 2: FE SEM micrographs of radied nanocomposites a. black sample of mesoporous nanosilica, b. mNs engrafted with iron oxide nanoparticles and c. mNs engrafted with Zinc oxide nanoparticles.

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.

SEM analysis revealed the surface morphology of spheroidal nanoparticles of silica with little aggregation (fig.2a). Nanosilica 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.2b) (Average diameter of iron oxide nanoparticleis ranging from 30 - 40 nm), grain sized is analyzed using Image J image processor. The mesoporous silica and zinc oxide microspheres were evident from the gray worm like structure dopped with ZnO nanoparticles 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.2c). The results found accompanying with the results of Chaneac *et al.*, (2017) [2] and Donnadio *et al.*, (2019) [5].

AAS

Nanocomposites were subjected to elemental analysis using AAS. AAS was performed using a PinAAcle series Atomic Absorption Spectrometer.

Table 1: Elemental composition of nanocomposites

Sr. no.		Element %
Dilution with acidified water		
1	Mesoporous silica implanted Iron oxide	21.3 Fe
2	Mesoporous silica implanted zinc oxide	27.6 Zn
Dilution with deionized water		
1	Mesoporous silica implanted Iron oxide	9.8 Fe
2	Mesoporous silica implanted zinc oxide	15.4 Zn

Elemental composition of all the nanocomposites is listed in the table 1. AAS analysis revealed the higher elemental composition in the acid diluted nanocomposites sample than the samples diluted in distilled water. In acid diluted nanocomposites the 21.3% Fe and 27.6% Zn were reported in the nanocompsites of mNs – FeO and mNs – ZnO respectively. All this leads to the conclusion that we can graft another metal on the silica and use it as a fertilizer.

Seed germination Test

Table 2: Performance of seed over graded levels of applied nanocomposites engrafted with targeted micronutrient

Treatments	Seed germination	Seed vigour
T1: Absolute control	60	420
T2: $ZnSO_4$+ $FeSO_4$	80	989
T3: 10 ppm Zn (mNs) + 1 ppm Fe (mNs)	60	420
T4: 20 ppm Zn (mNs) + 3 ppm Fe (mNs)	80	1034
T5: 30 ppm Zn (mNs) + 5 ppm Fe (mNs)	90	1260
T6: 50 ppm Zn (mNs) + 10 ppm Fe (mNs)	80	960
T7: 100 ppm Zn (mNs) + 30 ppm Fe (mNs)	60	540
T8: 200 ppm Zn (mNs) + 50 ppm Fe (mNs)	50	302
SE +m	3.953	50.859
CD @ 5%	11.953	153.787

Seed germination and seed vigour in wheat seed were analyzed and found both positive and phytotoxical impacts of prepared nanocomposites on wheat seed. The significant highest seed germination (90%) was recorded for the treatment T5 (corresponding to the 30 ppm of Zinc and 5 ppm of Iron through mesoporous nanosilica) Solanki and Laura, (2018) [11] Further decline in seed germination was observed with increasing exposure of nanoparticles of micronutrient and lowest seed germination (50%) was recorded for treatment T8 (Corresponding to highest i.e. 200 ppm of zinc and 50 ppm of iron dose through mNs). The same trend was observed for seed vigour (fig 3abc).

Fig 3: Wheat seed, seed vigour pictorial a. control, b. 30 ppm Zn (mNs) + 5 ppm Fe (mNs) and c. 200 ppm Zn (mNs) + 50 ppm Fe (mNs)

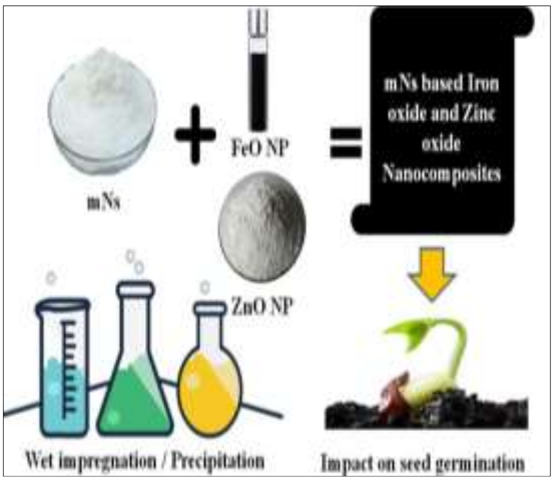


Fig 4: Concept executed (NP = Nano particles, mNs = Mesoporous nanosilica)

The increased seed germination and vigour is might be due to optimum dose of iron and zinc that plant can tolerate the exposure of nanoparticles. Zinc and iron also plays an important role in activation of various enzymes which are essential during the various processes involved in early seed development. The phytotoxicity of nanosilica and higher concentration of nano iron and zinc in treatment T8 is mainly manifested as a delay in seed germination and a severe loss of morphology of the plant seedling. The higher concentration of nano particle may lead to the unnecessary accumulation in the seed organelles causing the various phytotoxical impacts like blocking of pores Wang *et al*., (2019) [12], impaired functioning of embryo.

Conclusion

Mesoporous nanosilica is the material which can successfully be used as a carrier for nutrient (especially iron and zinc micronutrients) because of biocompatible nature of mesoporous nano silica. The surface morphology of silica and allows it to be serve as chelating agent with ability to revolutionize the nutrient delivery system in agriculture. Engrafted nanocomposites within the optimum limit found significant effect of seed germination and seed vigour in wheat seeds.

Acknowledgements
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