*Indian J. Applied & Pure Bio.* Vol. 38(2), 864-871 (2023). **ISSN: 0970-2091**
**A web of Science Journal**

# Effect of Nano Zn and Fe composite on the micronutrient biofortification of rice in coastal Soil

***D. Arul Raja Sekaran and R. Singaravel**

Department of Soil Science and Agricultural Chemistry
Faculty of Agriculture, Annamalai University- 608 002 (India)
*Corresponding author. Email:arulrajasekaran1510@gmail.com

**Abstract**

To evaluate the influence of Biochar and Zeolite based Zn and Fe nanocomposites on the growth, yield, and biofortification of Zn and Fe in rice, a pot experiment was conducted in the Department of Soil Science, Faculty of Agriculture, Annamalai University. The following treatments namely, $T_1$ -RDF (Control), $T_2$ -RDF + $ZnSO_4$ + $FeSO_4$ @ 25 kg $ha^{-1}$, $T_3$ –RDF + Nano ZnO + Nano FeO foliar @ 500 ppm, $T_4$ -RDF + Nano Zeolite composite 1g $kg^{-1}$, $T_5$ -RDF + Nano Biochar composite 1g $kg^{-1}$, $T_6$ - RDF + Nano Zeolite composite + Nano foliar @ 500 ppm, $T_7$ - RDF + Nano Biochar composite + Nano foliar@ 500 ppm were studied in Completely Randomized Design in three replications with rice variety ADT 43. The experimental soil had pH 8.11 and EC 2.53 dS $m^{-1}$. The available N, P, and K status were 109.5, 3.9 and 99.1 mg $kg^{-1}$ respectively. The DTPA extractable Zn and Fe content was 0.66 and 1.53 mg $kg^{-1}$ respectively. The results of the pot experiment showed that the application of recommended dose of fertilizers + Nano Biochar Composite 1g $kg^{-1}$ + Nano Foliar (Zn and Fe) @ 500 ppm excelled all other treatments in increasing the growth characteristics and yield attributes. This treatment recorded a grain and straw yield of 27.7 and 42.1 $g^{-1}$ pot respectively. This treatment also significantly increased the concentration of Zn and Fe in rice grains by recording higher Zn (23.5 mg $kg^{-1}$) and Fe (225 mg $kg^{-1}$).

**Key words :** Nano Zn and Fe, Micronutrient biofortification of rice, Coastal soil.

The coastal agro-high ecosystem's pH and dearth of organic matter result in a zinc and iron deficiency, and crops grown in such soil produce grains of poor nutritional quality. It is common knowledge that zinc is one of the essential nutrients required for plant and animal health. Zn has a vital role in plants, where it is found in enzymes and proteins that are involved in protein synthesis, gene expression, the metabolism of auxin (a growth regulator), the formation of pollen, the preservation of biological membranes, and defence against photo-oxidative damage[3]. In photosynthetic cells, where it is required for the electron transport system, the formation of Fe-S clusters, and the production of cytochromes and other heme molecules, including chlorophyll, over 80% of iron is found[4,6]. Additionally, these nutrients are crucial for a number of basic biological functions. A typical adult's body has 2–3 g of zinc. It is present in every part of the body, including the cells, fluids, bones, tissues, and organs. In India, more than 6,000 children under the age of five each day may away due to iron deficiency, claims Kotecha[8]. Anaemia, which affects around 70% of young children under five and women who are sexually active, occurs when humans are deficient in iron[9].

Fifty percent of the soils used to grow cereal crops are thought to be deficient in zinc and iron, according to estimates from the Food and Agriculture Organization of the United Nations (FAO). Furthermore, it forecasts that in order to feed the planet's more than 9 billion people by 2050, agricultural production must increase by 70%. Nowadays, micronutrient biofortification is required to lower malnutrition in people. The development of low-cost, nutrient-dense, sustainable staple crops is the aim of biofortification. They provide access to locally produced, nutrient-dense foods for those living in rural locations.

Crop micronutrient fertilisation, also known as agronomic fortification, may improve crop productivity for human consumption while simultaneously addressing crop nutritional quality and related dietary micronutrient issues with regard to human health. Nanotechnology-enabled intelligent micronutrient delivery enhances nutrient use and absorption while improving yield and nutrient content in edible parts. These nano fertilisers have a vast surface area and are only required in minute quantities. They have been shown to enhance adsorption and translocation inside the plant, resulting in higher absorption[15]. After realising the more beneficial function of nanonutrients, the present research was carried out to determine the influence of biochar and zeolite-based nanocomposites on the growth, yield, and biofortification of rice.

To assess the effects of nano fertilisers on the growth, yield, and biofortification of Zn and Fe in rice grown in coastal saline soil, a separate pot experiment involving rice was carried out at the Department of Soil Science, Faculty of Agriculture, Annamalai University. The experiment used a variant of ADT-43 with a completely random design, seven treatments, and three replications. The coastal soil collected from the farmers' field at vadakku Pichavaram, was used for this study. Initial soil characteristics such as texture -*Typic Udipsamments,* pH 8.11 and EC 2.53 ds $m^{-1}$, available N, P, K status was 109.5, 3.99, and 86.2 mg $kg^{-1}$. The DTPA extractable Zn and Fe content were 0.66 and1.53 mg $kg^{-1}$ respectively. Each pot was filled with 10 kg of soil. The treatment details are $T_1$ -RDF (Control), $T_2$ -RDF + $ZnSO_4$ + $FeSO_4$ @ 25 kg $ha^{-1}$, $T_3$ –RDF + Nano ZnO + Nano FeO foliar @ 500 ppm, $T_4$ -RDF + Nano Zeolite composite 1g $kg^{-1}$, $T_5$ -RDF + Nano Biochar composite 1g $kg^{-1}$, $T_6$ - RDF + Nano Zeolite composite + Nano foliar @ 500 ppm, $T_7$ - RDF + Nano Biochar composite + Nano foliar@ 500 ppm. The calculated amount of fertilizer dose using a schedule of 120:40:40 kg $ha^{-1}$ of N: $P_2O_5$:$K_2O$ were applied through urea, Di ammonium phosphate, and muriate of potash respectively to all the pots. The entire dose of $P_2O_5$ and $K_2O$ and 50 percent of nitrogen were applied as basal. The remaining 50% N was top dressed at tillering and panicle initiation stages.

*Preparation of Nano Zeolite :*

In order to achieve a decrease in size to the nanoscale, determined amounts of zeolite were milled in a ball mill under the same parameters (speed, time, and ball-to-powder ratio). To lower the particle size while maintaining the crystallinity of the zeolite, nano Zn oxide and nano Fe oxide were added to the zeolite and milled for six hours. (Alireza and Gholamhosein, 2012; Subramanian and Sharmila Rahale, 2012). The fine powder was characterized using XRD.

*Preparation of Nano biochar :*

Biochar was prepared by the low-cost portable drum (kiln) method of ICAR. Paddy Straw cut into pieces of less than 12 inches were sun-dried and used for charring into biochar. Using the slow pyrolysis method, the biochar was prepared at 450°C for 1.2 h from the biomass. After preparing biochar, they were dried in a hot air oven at $110^0$ C for 24 h [17]. To the biochar, the calculated amount of nano Zn oxide and Fe oxide were added and ball milled for six hours by maintaining the milling speed to obtain biochar nanocomposite. The fine powder was characterized using XRD[18].

In the soil, 1g $kg^{-1}$ of nanocomposite was well mixed. Rice was treated with foliar applications of nano Zn and nano Fe @ 500 ppm at the tillering and blooming stages. At harvest, a variety of growth variables were recorded, including plant height, DMP, LAI, the number of tillers at the flowering and harvest stages, and yield components, including the number of productive tillers $m^2$, 1000 grain weight, grain yield, and straw yield. Using an atomic absorption spectrophotometer, the samples of grain and straw were examined for the presence of Fe and Zn in a di acid extract of (7:1 $HNO_3$: $HClO_4$), as described by Jackson[7].

*Characterization of Nano Zeolite- XRD :*

By using XRD methods, the nano zeolite's XRD pattern was studied. The crystal structure and two theta values of the material were determined using the X-ray diffraction method. For the XRD examination, powdered nano zeolite was utilised. The XRD patterns can be indexed for diffraction from the different angles 531, 622, 840, 640, 642, 644, 884, and 664 planes as shown in the figure. The peaks at 2 theta values are 21.2°, 22.6°, 24.8°, 26.9°, 28.3°, 35.0°, 37.2°, and 43.5° (a total of 8 prominent peaks) were observed for nano zeolite as shown in figure (1). The average crystalline size of nano zeolite is 29.9 nm. These findings are supported by previous XRD analysis of nano zeolite by Mohanraj *et al.*[11], who observed the XRD spectrum of nano zeolite well matched with CCDC No- 01-074-1183 of sodium aluminum silicate and two theta values of the mineral.

Table-1. Effect of Zinc and Iron nano Composite on the growth components of rice

| Treatments | Plant height (cm) | | | LAI | | Chlorophyll content (Spade value) | DMP (g $Pot^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | Tiller. | Flower. | Harv. | Flower. | Harv. | | Flower. | Harv. |
| $T_1$ | 19.3 | 55.1 | 77.2 | 3.9 | 4.1 | 30.3 | 35.2 | 45.3 |
| $T_2$ | 25.7 | 67.3 | 82.7 | 4.4 | 4.6 | 33.1 | 40.1 | 51.5 |
| $T_3$ | 30.2 | 73.1 | 92.5 | 5.0 | 5.1 | 35.8 | 45.5 | 57.6 |
| $T_4$ | 36.6 | 79.0 | 100.4 | 5.2 | 5.3 | 35.9 | 51.0 | 63.0 |
| $T_5$ | 43.3 | 85.9 | 109.6 | 6.0 | 6.1 | 39.0 | 59.2 | 70.7 |
| $T_6$ | 38.0 | 80.0 | 101.8 | 5.4 | 5.5 | 36.1 | 53.3 | 64.8 |
| $T_7$ | 45.8 | 86.1 | 111.0 | 6.2 | 6.3 | 39.8 | 61.8 | 72.1 |
| SEd | 2.12 | 2.32 | 3.28 | 0.20 | 0.13 | 1.23 | 1.9 | 2.1 |
| C.D (0.05) | 4.61 | 5.04 | 7.10 | 0.44 | 0.42 | 2.66 | 4.1 | 4.5 |

Table-2. Effect of Zinc and Iron nano Composite on the yield and yield attributes of rice

| Treatments | Productive Tillers $Hill^{-1}$ | No. of. Tillers $Hill^{-1}$ | | 1000 grain weight (g) | Grain Yield (g $Pot^{-1}$) | Straw Yield (g $Pot^{-1}$) |
|---|---|---|---|---|---|---|
| | | Flower. | Harv. | | | |
| $T_1$ | 11.1 | 11.6 | 13.2 | 15.0 | 12.8 | 23.2 |
| $T_2$ | 14.3 | 14.0 | 16.3 | 15.2 | 16.7 | 27.5 |
| $T_3$ | 17.4 | 16.5 | 19.1 | 15.5 | 19.3 | 31.4 |
| $T_4$ | 20.7 | 19.2 | 22.0 | 15.7 | 22.6 | 35.3 |
| $T_5$ | 24.6 | 22.0 | 26.2 | 15.9 | 26.4 | 40.5 |
| $T_6$ | 21.8 | 19.3 | 23.7 | 16.0 | 23.6 | 36.6 |
| $T_7$ | 25.9 | 23.1 | 27.8 | 16.2 | 27.7 | 42.1 |
| SEd | 1.26 | 1.08 | 1.24 | NS | 0.67 | 1.04 |
| C.D (0.05) | 2.73 | 2.34 | 2.51 | NS | 1.46 | 2.25 |

Table-3. Effect of Zinc and Iron nano Composite on the Zn and Fe biofortification of rice

| Treatments | Zn content (mg $kg^{-1}$) | | Fe content (mg $kg^{-1}$) | |
|---|---|---|---|---|
| | Grain | Straw | Grain | Straw |
| $T_1$ -RDF (Control) | 12.6 | 33.9 | 172 | 183 |
| $T_2$ -RDF + $ZnSO_4$ + $FeSO_4$ @ 25 kg $ha^{-1}$ | 15.4 | 37.6 | 185 | 195 |
| $T_3$ –RDF + Nano ZnO + Nano FeO foliar @ 500 ppm | 16.9 | 40.8 | 195 | 206 |
| $T_4$ -RDF + Nano Zeolite composite | 18.7 | 44.1 | 205 | 218 |
| $T_5$ -RDF + Nano Biochar composite | 22.4 | 49.2 | 221 | 235 |
| $T_6$ - RDF + Nano Zeolite composite + Nano foliar @ 500 ppm | 19.9 | 45.6 | 209 | 223 |
| $T_7$ - RDF + Nano Biochar composite + Nano foliar @ 500 ppm | 23.5 | 50.7 | 225 | 241 |
| SEd | 0.7 | 0.76 | 3.39 | 4.73 |
| C.D(0.05) | 1.3 | 2.33 | 7.34 | 9.51 |

Table-4. Correlation analysis between Growth characters and micronutrient content with grain yield of rice

| Parameters | Grain yield |
|---|---|
| Plant height | 0.988** |
| LAI | 0.979** |
| DMP | 0.988** |
| No.of tillers | 0.996** |
| Productive Tillers/Hill | 0.996** |
| Zn content | 0.989** |
| Fe content | 0.997** |

*Characterization of Nano Bio char- XRD* **:**

XRD analysis determined the phase presence in nano biochar. XRD results in a pattern of biochar in various profiles of peaks and diffraction angle 2 thetas. The XRD pattern of biochar was recorded in the fraction angle range of 20-80 degrees as shown in the figure. This figure showed a characteristic peak of Silica ($SiO_2$) at 2 theta position 28°. The peaks at 2 theta values are 27.3°, 29.1°, 41.5°, 50.0°, 58.6°, 66.7°, and 74.3° (a total of 7 prominent peaks) were observed for biochar as shown in figure (2). XRD patterns can be indexed for diffraction from the average crystalline size is 49.6 nm. The results were comparable to previously reported XRD analysis of rice straw biochar by El-Hassasin *et al.*[5], who observed a characteristic peak of silica ($SiO_2$) at 2 theta position – 28°. Compared with other materials, rice straw contains low lignin and high $SiO_2$.

*Growth characters and yield attributes:*

In the present study, the application of nano Zn and Fe composite significantly increased all the growth characteristics of rice namely plant height, Leaf area index, No. of tillers and Productive tillers of rice (Table-1). Among the various treatments, the application of $T_7$- RDF+ Nano Biochar Composite 1g $kg^{-1}$ + Nano Foliar @ 500 ppm accounted for recording a significantly higher plant height of (111.06cm), LAI (6.31), no. of. Tillers (27.8) and DMP (72.1 g $pot^{-1}$) at the harvest stage of rice. However, the treatment $T_7$ rated on par with the treatment $T_5$- RDF+ Nano Biochar Composite @ 1g $kg^{-1}$ alone by registering higher plant height of (109.6cm), LAI (6.12), tillers number (26.2) and DMP (70.7 g $pot^{-1}$) at harvest stage. The treatment $T_6$ - RDF+ Nano Zeolite Composite 1g $kg^{-1}$ + Nano Foliar @ 500 ppm and $T_4$ - RDF+ Nano zeolite Composite 1g $kg^{-1}$ alone rated on par and followed $T_7$ and $T_5$. The treatment $T_3$, foliar application also enhanced the growth characteristics of rice when compared to the control. The treatment control registered the lowest plant height (77.2 cm), LAI (3.97), no. of tillers (13.2) and DMP (45.3 g $pot^{-1}$) at harvest. Application of nanocomposites resulted in the slow release of Zn and Fe to maintain the required nutrient during the critical stages of rice crop growth thereby improving all the physiological parameters of rice including the chlorophyll SPAD value, as compared to $ZnSO_4$ applied pots. The results corroborated the earlier report of Yuvaraj and Subramaniyan[20]. Soil application of zeolite and biochar-based nanocomposite increased the availability of Zn and Fe in soil which helped in higher concentration and uptake of this nutrient and promoted the growth characteristics of rice[12,13]. Nano nutrients enhanced better root proliferation and increased the availability and uptake of nutrients by rice and in turn produced higher DMP, Reetu Bala *et al*.[16]. In the present study, Zn and Fe nanocomposites increased the SPAD and indicated higher chlorophyll concentration and photosynthetic efficiency. The earlier work of Sun *et al*.,[19] supports the present findings.

*Yield of rice :*

Nano Zn and Fe composite and nano foliar significantly increased the yield parameter and yield of rice (Table-2). Among the various treatments, the application of $T_7$-RDF+ Nano Biochar Composite 1g $kg^{-1}$ + Nano Foliar @ 500 ppm accounted for increased productive tillers $hill^{-1}$ (25.83), grain yield (27.7 g $pot^{-1}$) and straw yield (42.1 g $pot^{-1}$) respectively and rated on par with the treatment $T_5$- RDF+ Nano Biochar Composite 1g $kg^{-1}$ by registering a productive tillers $hill^{-1}$ (24.6), grain yield (26.4 g $pot^{-1}$) and straw yield (40.5 g $pot^{-1}$) of rice. The 1000 grain weight ranged from 16.2 to 15.0 grams and was not influenced by the various treatments evaluated. The treatment $T_3$ -RDF+ Nano Foliar ZnO and FeO @ 500 ppm also significantly enhanced the yield of rice contrasted with the control. Due to an enhancement in the yield-attributing character linked to better biochemical and physiological activities, the ZnO and FeO NPS ensured increased yield. Due to the ultra-small size, simple solubility, and diffusible character of nanonutrients, which boosted its effectiveness in penetrating through the leaf surface and release of ions across the cuticle, the nanocomposite increased the absorption of Zn and Fe in plants. Improved root properties, plant biomass, and yield using nano fertiliser have also been documented by prior researchers Reetu Bala *et al*.,[16] and Ali *et al*.,[1]. Additionally, Peng *et al*.,[14] demonstrated that the use of rice straw biochar might boost rice output by up to 146% when combined with NPK fertiliser. The present findings are supported by an extremely substantial positive association between grain production and productive tillers (r= 0.99**). (Table-4).

*Zinc and Iron biofortification :*

The use of biochar and zeolite-based nano Zn and Fe composite considerably boosted the zinc and Fe fortification of rice grain, which is important given the significance of micronutrient fortification in the current research (Table-3). In comparison to the other treatments, the application of NPK+ nano biochar composite at 1g $kg^{-1}$ + nano foliar spray @500 ppm outperformed them by registering greater Zn and Fe content in grain 23.5 and 225 mg $kg^{-1}$ and 50.7 and 241 mg $kg^{-1}$ in straw respectively. This treatment was contrasted with treatment $T_5$, which measured 22.4 mg $kg^{-1}$ of zinc and 221 mg $kg^{-1}$ of iron in grain, respectively. The lowest Zn and Fe contents were 12.6 and 172 mg $kg^{-1}$ in grain and 33.9 and 183 mg $kg^{-1}$ in straw respectively, when NPK alone was used as the treatment control. By having a better usage efficiency, nanocomposite fertilisers transport the nutrients to the desired rhizosphere on schedule[3]. Micronutrient nanoparticles were shown to have strong adhesion to the root surface, as well as to penetrate the root surface and enter the plant cell, according to Lin and Xing's 2007 research. Nanocomposite fertilisers have a larger surface area-to-volume ratio than traditional fertilisers, which allows them to quadruple the efficiency of the nutrients while

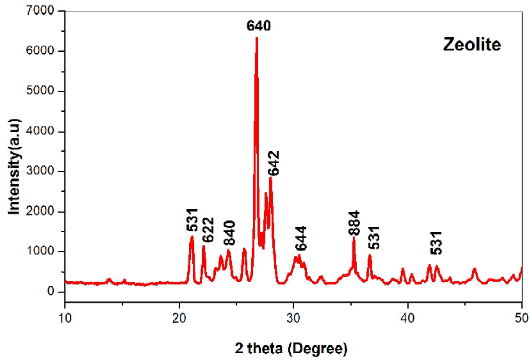


Fig. 1. XRD of Zeolite

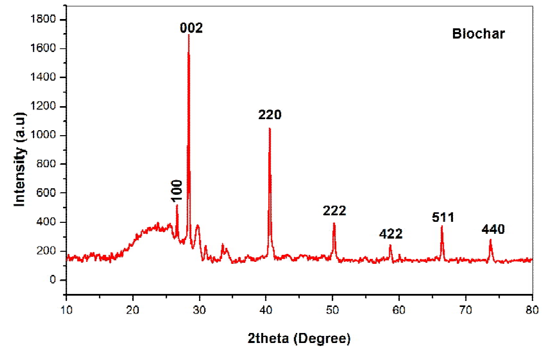


Fig. 2. XRD of Biochar

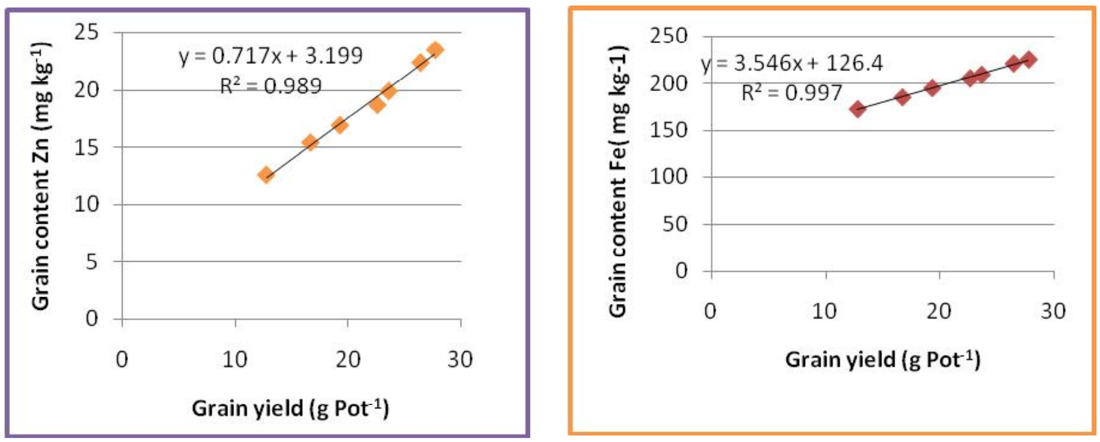


Fig. 3 and 4 Regression of Zn and Fe content in grain with grain yield

still being readily absorbed by plants. Zn concentration and grain yield have a very significant positive connection (r= 0.98**) as does Fe content (r= 0.99**). (Table-4). The current results are supported by regression of Zn and Fe levels in grain with grain yield (Fig. 3 and 4).

The result of the study proved the efficacious nature of NPK + Biochar based nano Zn and Fe composite @ 1g $kg^{-1}$ + Nano Foliar @ 500 ppm in significantly increasing the growth, yield attributes, and yield of rice.

**Conflict of interests :**

The author declared that there is no conflict of interest.

References :

1. Ali, S., M. Rizwan, S. Soureen, Sarwat Anwar., Basharat Ali and Muhammad Naveed (2019). *J. Environ Sci Pollut Res., 26:* 11288-11299.
2. Alireza Nezamzadeh-Ejhieh and Gholamhosein Raja. (2013). *J. Chem,* ID 685290.

3. Alloway, B.J. (2008). Zinc in soils and crop nutrition. 2nd Edition. Paris, France: IFA; and Brussels, Belgium: IZA.
4. Briat, JF., C. Curie and F. Gaymard (2007). *Curr. Opin. Plant Biol., 10:* 276-282.
5. El-Hassanin, A.S., M.R. Samak, S.R. Radwan, and G.A. El-Chaghaby, (2020). *Environ. Nat. Resour. J., 18*(3): 283-289.
6. Hansch, R. and R.R. Mendel, (2009) *Curr Opin in Plant Biol, 12:* 259-266.
7. Jackson, M.L. (1973). Soil chemical analysis. Prentice Hall of India Private Ltd., New Delhi, pp. 56-70.
8. Kotecha, P.V. (2008) *Indian J Community Med., 33:* 9-10.
9. Kumar, S.B., S.R. Arnipalli, P. Mehta, S. Carrau and O. Ziouzenkova (2022). *Nutrients., 14:* 2976.
10. Lin, Daohui and Xing, Baoshan. (2007). *J Environ. Pollut.,* (Barking, Essex : 1987). *150:* 243-50. 10.1016/*j.envpol*. 2007.01.016.
11. Mohanraj, J., K.S. Subramanian and A. Lakshmanan, (2019). *Madras Agric. J. 106:* 657-663.
12. Naik, S.K. and D. K. Das, (2007). *Arch. Agron. Soil sci., 53*(3): 305-313.
13. Pandey, A.C., S. Sharda, S.S. Sanjay and R.S. Yadav, (2010). *J. Exp. Nanosci., 5*(6): 488-497.
14. Peng, X., L. Wang Ye, C. Zhou, and H. Sun, (2011) *Soil Till. Res.,112:* 159–166.
15. Raliya and Tarafdar. (2013). *Agric Res., 2*(1): 48–57.
16. Reetu Bala, Anu Kalia & Salwinder Singh Dhaliwal (2019). *J. Soil Sci. & Pl. Nutri. 19:* 379-389.
17. Shaon Kumar Das, Goutam Kumar Ghosh, R. K. Avasthe and Manik Chandra Kundu, (2018). *J. Hill. Farming., 31*(1): 141-145.
18. Subramanian, K.S. and C.S. Rahale (2012). Nano-fertilizers—synthesis, characterization, and applications. In: *Proceedings of the application of nanotechnology in soil science & plant nutrition research*, September 18–27, IISS, Bhoopal, India, p 107.
19. Sun, H.J., H.C. Zhang, W.M. Shi, M.Y. Zhou and X.F. Ma (2019). *Plant Soil Environ., 65:* 83–89.
20. Yuvaraj, M. and K.S. Subramanian, (2014). *Trends in biosci., 7*(17): 2564-2565.