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SYNERGISTIC IMPACT OF IRON (III) OXIDE NANOPARTICLES AND ORGANIC WASTE ON GROWTH AND DEVELOPMENT OF *SOLANUM LYCOPERSICUM* PLANTS: NEW PARADIGM IN NANOBIOFERTILIZER

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Abstract

Nanoparticles have shown a significant effect in plant growth and crop production when used as fertilizers alone or in combination with other biofertilizers. The combination of Iron (III) oxide (Fe_2O_3) nanoparticles with flower waste and cow-dung showed significant enhancement in the growth of tomato plants compared to other fertilizers used. Student's t-test provided statistical significance under different combinations of fertilizers. After analyzing the growth of tomato plants over several weeks under these different fertilizers, it is concluded that Fe_2O_3 nanoparticles could be very useful as a component of new generation eco-friendly nanobiofertilizers, without having usual toxic and environmental risk factors that are associated with existing conventional chemical fertilizers.

Key words: Nanobiofertilizer, Iron (III) oxide (Fe_2O_3) Nanoparticles, biocompatibility, waste-derived fertilizer

Introduction

Over the last two decades, nanoparticles have found extensive application in diverse fields starting from electronics to energy, and medicine to life sciences (Giraldo *et al.,* 2014). Nanotechnology plies an expanding paradigm to specific research areas, such as reproducing biology, organic wastes converted into energy (Singh and Usha 2014; Zhang *et al.,* 2017) and other beneficial by-products through enzymatic Nano-bio-processing, chemical sensors, water treatment, prevention of diseases, and plant treatment by the use of various nanocides (Moraru *et al.,* 2003). A huge percentage of applied nutrients remain unavailable to plants due to the factors like leaching, photolytic breakdown, hydrolysis and decomposition (Bentley 1948). Hence, the current situation demands lessening in nutrient loss and increasing the crop yield by using fertilizers. One of the possible routes to surpass this problem is the use of novel bio-fertilizers having nanoparticles as one of the compositions. Nano-encapsulated nutrients and/or Nano-bio-fertilizers may have characteristics that can intensify crop yield in food crops mainly vegetable crops, timely release of nutrients by which plant growth is regulated, and targeted activity is enhanced (DeRosa *et al.,* 2010). Higher plants can acquire a mechanism to cope up with favorable and unfavorable conditions. Nowadays scientists/researchers are looking for new techniques that can enhance the native functions of plants. Nanoparticles with their unique physico-chemical properties can boost up the plant metabolism (Yuvakkumar *et al.,* 2011). Engineered nanoparticles have the potential to get inside plant cells and leaves by acting as chaperones for transporting genetic materials and chemicals (Galbraith 2007; Lin and Xing 2007). This area of research generates new possibilities in environmental sciences as well as in plant biotechnology (Siddiqui *et al.,* 2015). There are reports of enhancement of plant's capability to capture more light by targeted delivery of carbon nanotubes (C-nanotubes) into the chloroplast. The C-nanotubes can also aid as artificial antennae that allow chloroplast to harvest light of unusual wavelength like ultraviolet, green, and near-infrared

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(DeRosa *et al.,* 2010; Lahiani *et al.,* 2013). The engineered C-nanotubes are reported to enhance germination of seeds, and also ameliorate growth and development of plants (Smirnova *et al.,* 2012; Lahiani *et al.,* 2013). However, extensive exploration in the domain of nanotechnology is very much essential to discover their probable novel uses to target-specific transmission of chemicals (Bentley 1948), proteins and nucleotides for genetic modification of crops (Skoog 1937; Tripathi and Sarkar 2014). However, increasing application of nanotechnology also demands clarification of risk assessment of nanoparticles in organisms and related Nano-toxicity (Song *et al.,* 2012). However, very limited works have been reported till now on a study of the toxicity of NPs in higher plants compared to a bacterial system and animal models. Phytotoxicity studies reported both pros and cons of nanoparticles on various physiochemical and metabolic processes of higher plants such as germination of seed, elongation of root and also photosynthesis (Crosby *et al.,* 1960). However, the entire mechanism of uptake, aggregation, translocation of nanoparticles in the cells and tissues of plants are yet to be fully understood along with the impact of nanoparticles on plant development and genetics (Yuvakkumar *et al.,* 2011).

In this work, we have tried to assess the effect of Iron (III) Oxide (Fe_2O_3) nanoparticles alone and in an amalgam with biofertilizers derived from different flower waste and cow dung on the growth of tomato (*Solanum lycopersicum)* plants. Flower waste was proved to be a very excellent source of organic matter for plant growth (Sharma *et al.,* 2018). Moreover, compost, when incorporated with an additive, gives enhanced results (Manyapu *et al.,* 2017). The Fe_2O_3 nanoparticles act as an additive for the compost and can be reused again (Kim and Lee 2016). The aim of the current work is to ascertain the potential of the different organic waste materials as possible biofertilizers in combination with the nanoparticle.

Choice of the Fe_2O_3 nanoparticles as a model nanoparticle was due to its idiomatic physico-chemical characteristics. They have a large surface area and possess tremendous reactivity. Moreover, they have a tunable pore size and particle morphology.

Materials and methods

Synthesis and Characterization of Iron (III) oxide (Fe_2O_3) Nanoparticles

Aqueous precipitation method was adopted to synthesize Fe_2O_3 nanoparticles (Pandey *et al.,* 2016). 5.0g of Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) was used as the precursor salt, and liquid ammonia was used as the precipitating agent. After the entire precipitation reaction was carried out at 60°C - 70°C, the residual matter was subjected to repeated washing with the use of acetone. Then the residue was washed with distilled water. It was then subjected to drying at 100°C in a hot-air oven. Finally, calcination of the dried residue was done at 600°C for 3 hours in a muffle furnace.

Fe_2O_3 nanoparticles were characterized using X-ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR) Spectroscopy and Scanning Electron Microscopy (SEM) using similar methods as described by (Pandey *et al.,* 2016).

Collection and preparation of the sample

To prepare the different types of biofertilizers; flower waste, kitchen waste and cow dung were collected, and they were washed to remove the dirt and impurities, followed by chopping into finer pieces of about 1". These treatments lowered the total dissolved solids of initial raw material and increased the efficiency. The entire experimental set up was designed in such a way, where two treatment sets and one control set was used. The growth of tomato plants was observed under seven set of experimental soil conditions in different pots (fig. 1).

The soil of the first three experimental pots (Pot a, b, c) treated with flower waste fertilizer, kitchen waste fertilizer, and cow dung fertilizer respectively, these three pots served as the first treatment set, through which the comparative effect of these biofertilizers on tomato plant growth was assessed. The Pot 'd' of the experimental set up contained soil treated with Fe_2O_3 nanoparticles only which served as a control to evaluate the effect of Fe_2O_3 nanoparticles alone on tomato plant growth. Rest three pots of the experiment (Pot e, f, g) served as the second treatment set, these pots contained soil treated with a combination of flower waste and Fe_2O_3 nanoparticles, a combination of kitchen waste and Fe_2O_3 nanoparticles and the combination of cow dung and Fe_2O_3 nanoparticles respectively. In each of the experimental pots, the amount of soil was 1 kg and an amount of 300g of processed biofertilizer after decomposition was mixed with the soil. An optimal initial dose of 50mg of Fe_2O_3 nanoparticles was added to the soil of last four experimental pots to understand the effect of Fe_2O_3 nanoparticles on tomato (*Solanum lycopersicum*) plant growth. To maintain a constant supply of nanoparticles to the plants, 50 mg of Fe_2O_3 nanoparticles was added every 7 days throughout the entire experimental tenure. This optimized dose of Fe_2O_3 nanoparticles was standardized by several initial experiments. Each of the experimental pots was regularly watered on every

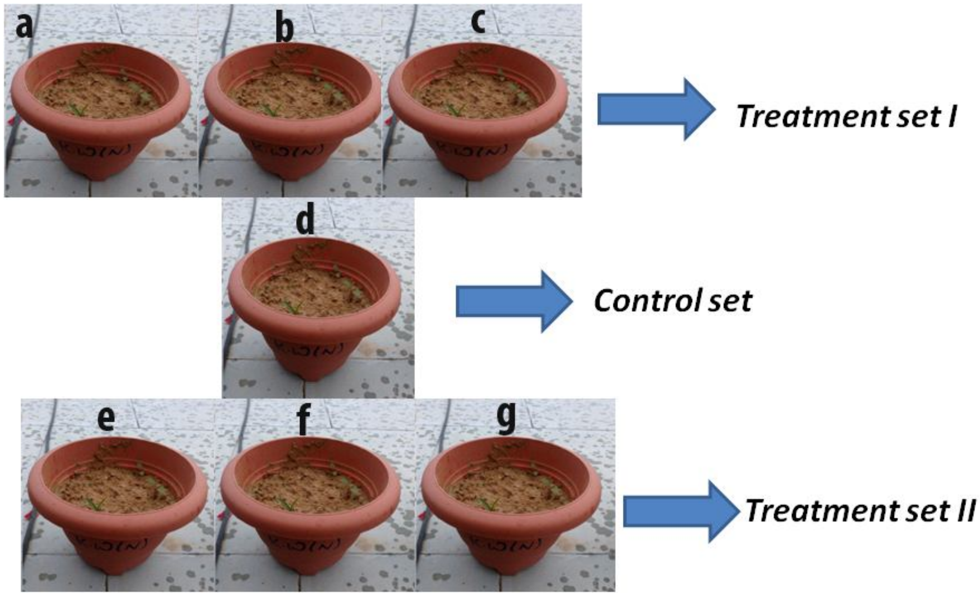

Fig. 1: Diagram showing the two treatment sets and control sets. Treatment set I comprising 'a,' 'b' and 'c' showing the pots where tomato seeds are planted under flower waste fertilizer, cow dung fertilizer, and kitchen waste fertilizer respectively, 'd' is the control set where tomato seed was planted under Iron (III) Oxide (Fe_2O_3) nanoparticles alone. Treatment set II comprises pots 'd', 'e' and 'f' where combination of flower waste and (Fe_2O_3) nanoparticles, cow-dung and (Fe_2O_3) nanoparticles and the combination of kitchen waste and (Fe_2O_3) nanoparticles were used as effective fertilizer respectively for the growth of tomato plants.

alternate day. pH of each of the experimental pots was measured to understand the initial acidity/alkalinity of the experimental soil after treatment with different conditions of biofertilizers and Fe_2O_3 nanoparticles (table 1).

Table 1: pH of the soil sample in the different treatment sets and control set

	Treatment Set I			Control Set	Treatment Set II		
	Flower Waste	Kitchen Waste	Cow Dung	Nano-particles	NPs + Flower Waste	NPs+ Kitchen Waste	NPs + Cow Dung
pH	8.0	8.4	8.27	8.25	8.21	8.3	8.13

For the seeding purpose, tomato seeds were cleaned using liquid soap solution and water (distilled) to remove contaminations. Clean and shade-dried seeds were used for planting. Then the seeds were sown in all seven pots.

During the study period, the growth of tomato plants in all of these experimental pots was analyzed weekly, and data were collected. All these experiments were repeated in triplicate, and the mean was taken for result analysis.

Statistical analysis

The arithmetic mean and standard deviation were calculated for all data. Statistical analysis was performed with Student's t-test. In all instances, $P < 0.05$ was taken as the minimum level of significance.

Results and discussion

Characterization Results of Nanoparticles

XRD data suggests the formation of crystalline Fe_2O_3 nanoparticles showing definite planes 012, 104, 110, 113, 024 very much concurrent with an existing database (JCPDS Card No85-0987). Crystalline size of individual nanoparticles was also formulated from XRD data using the Debye-Schrer equation $S = 0.9\lambda / \beta\cos\theta$. SEM results show an average size of 65 nm for individual nanoparticles, the slightly higher size of Fe_2O_3 nanoparticles found from SEM data compared to XRD results reflect the presence of partial amorphous phase present in the nanoparticles. FTIR spectra of Fe_2O_3 nanoparticles exhibit a broad peak at 3440 cm^{-1} suggestive of O-H stretching probably due to the adsorbed water. FTIR spectra show a sharp peak at 514 cm^{-1}, representative of Fe-O bond stretching, similar as reported by other researchers (Pandey *et al.,* 2016) (fig. 2).

Analysis of Plant Growth of S. lycopersicum:

Week-wise measurement and analysis of *S. lycopersicum* plants are shown in table 2 (Fig. 3).

The flower waste nano bio-fertilizer plant is germinated fast then others as shown in the table. The seeds were sown on 23rd February 2016. The first growth was seen only in flower waste nano bio-fertilizer after the 10th day of sowing than others, as shown in, whereas the other plants germinated 14 days after sowing. On the

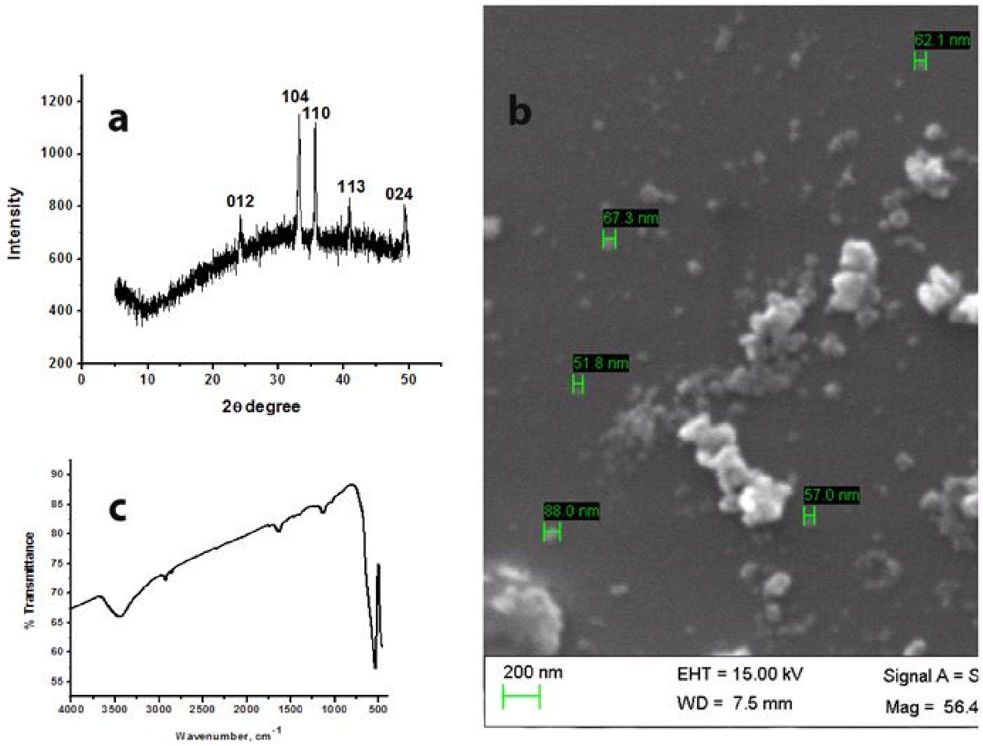

Fig. 2: Characterization data of Iron (III) Oxide (Fe_2O_3) nanoparticles 'a' shows the XRD pattern of Fe_2O_3, 'b' shows the SEM micrograph of Fe_2O_3 nanoparticles, 'c' shows the FTIR spectra of Fe_2O_3

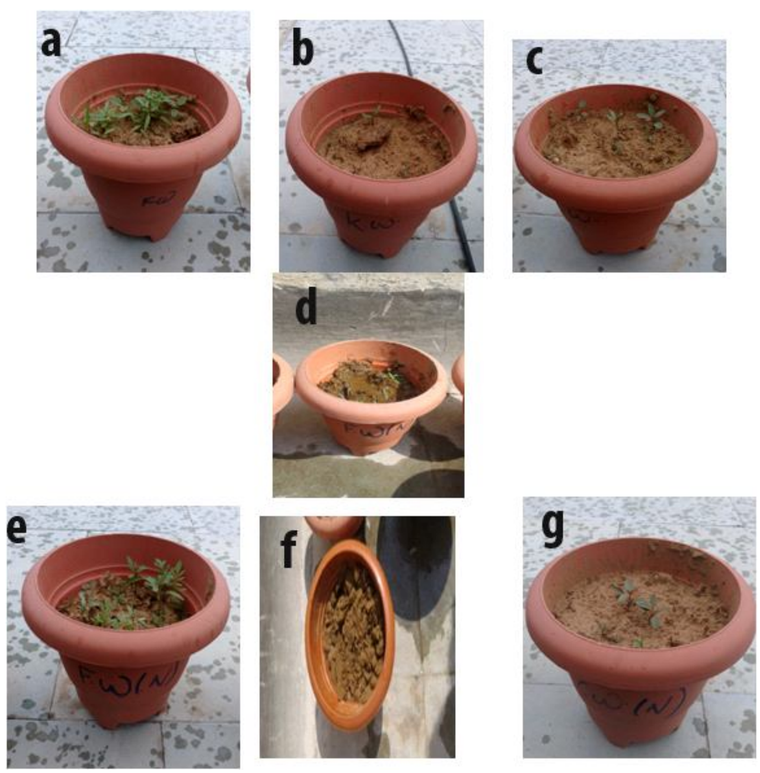

Fig. 3: Growth of tomato plants observed after 28 days of seeding under the different conditions in the treatment sets and control set comprising 'a', 'b' and 'c' showing the growth of tomato plants under flower waste fertilizer, cow dung fertilizer, and kitchen waste fertilizer respectively, 'd' is the control set where growth of tomato plant was monitored under Iron (III) Oxide (Fe_2O_3) nanoparticles alone. Treatment set II comprises d), e and f) where combination of flower waste and (Fe_2O_3) nanoparticles, cow-dung and (Fe_2O_3) nanoparticles and the combination of kitchen waste and (Fe_2O_3) nanoparticles were used as effective fertilizer respectively.

Table 2: Analysis of the growth regarding the height of tomato plants (*S. lycopersicum*) under different treatment condition

Date of Analysis	Control Pot I (Height in cm)			Control Pot II (Height in cm)	Treated Pot (Height in cm)		
	Flower Waste	Kitchen Waste	Cow Dung	Nanoparticles	NPs + Flower Waste	NPs + Kitchen Waste	NPs + Cow Dung
29/02/2016	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
07/03/2016	0.7±0.1	0.0±0.0	0.3±0.10	0.6±0.10	1.3±0.10	0.0±0.0	0.4±0.12
14/03/2016	1.8±0.15	0.5±0.01	1.5±0.10	2.0±0.12	2.9±0.15	0.0±0.0	1.7±0.15
21/03/2016	4.0±0.1	2.4±0.15	2.5±0.15	3.0±0.12	6.1±0.15	0.0±0.0	3.9±0.15
28/03/2016	6.0±0.1	4.0±0.10	3.0±0.20	3.3±0.10	8.1±0.12	0.0±0.0	4.6±0.20
04/04/2016	6.5±0.12	7.0±0.20	3.6±0.20	4.5±0.15	9.5±0.20	0.0±0.0	5.2±0.10
11/04/2016	7.1±0.12#	9.2±0.10	4.4±0.15##	5.6±0.15	11.3±0.20*	0.0±0.0	6.1±0.15**

Results are expressed as mean ± SD of three plants:
* P<0.0001 significantly different from flower waste
** P<0.001 significantly different from cow dung
** P<0.0001 significantly different from nanoflower waste
# P< 0.001 significantly different from iron oxide nanoparticles along
P< 0.05 significantly different from iron oxide nanoparticles along.

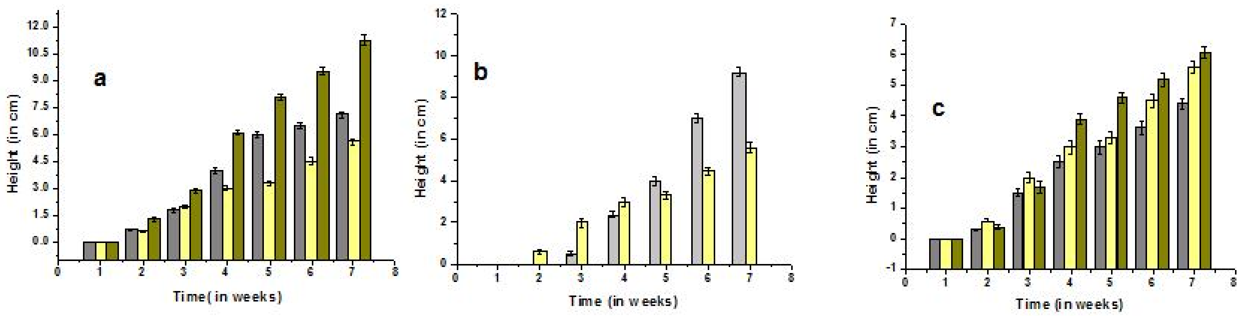

Fig. 4: Bar diagram showing Growth of Tomato plants measured in terms of height over time under different fertilizer composition , grey bars showing the growth of plants under flower waste fertilizer in 'a', under kitchen waste fertilizer in 'b' and under Cow dung fertilizer in 'c', light yellow bars shows the growth of plants under the treatment of only Iron(III) Oxide nanoparticles as fertilizer, olive bars showing the growth of plants under the combination of flower waste fertilizer and Iron(III) Oxide nanoparticles in 'a' and under the combination of Cow dung fertilizer and Iron(III) Oxide nanoparticles in 'c', absence of olive bars in 'b' showing total cessation of plant growth under the combination of kitchen waste fertilizer and Iron (III) Oxide Nanoparticles.

other hand, kitchen waste nano bio-fertilizer did not show any growth. Kitchen waste fertilizer showed very good growth; this is due to the deactivation of nanoparticles due to the varied chemical composition and high pH. In the case of cow-dung nano bio-fertilizer and cow-dung fertilizer, little difference in growth was observed. Cow-dung nano bio-fertilizer gave better growth of tomato plant than cow-dung fertilizer. One simple nano bio-fertilizer was also planted which gave good result as compared to cow-dung nano bio-fertilizer.

The fastest growth was observed only in the pot treated with flower waste nano-bio-fertilizer on the 10th day after seeding. Pot with kitchen waste fertilizer showed maximum growth in plant height after 49 days. The least growth was observed in the pot treated with cow dung fertilizer. However, in the control pot where the soil was treated with the Fe_2O_3 nanoparticles only, significant growth in plant height was observed after 49 days (fig.3). A significant increase ($p < 0.0001$) in plant height was observed in the pot treated with the combination of floral waste nanofertillizer and Fe_2O_3 nanoparticles, as compared to the floral waste fertilizer alone. Cowdung and Fe_2O_3 nanoparticles combination also showed a significant increase in plant height ($p < 0.001$) as compared to the cow dung fertilizer alone. Maximum growth in plant height was observed in the flower waste and Fe_2O_3 nanoparticles combination group which was significantly different ($p < 0.0001$) from the cow dung and Fe_2O_3 nanoparticles combination group. On the other hand, no germination was observed with kitchen waste and Fe_2O_3 nanoparticles even after 49 days, the growth of plants under these various conditions are also shown in the bar diagram (table 2; fig. 4).

The growth of plant under treatment of flower waste and Fe_2O_3 nanoparticles combination as fertilizer is much better than the flower waste fertilizer alone. The difference in their growth is around 4.2 cm, and this significant difference indicates that Fe_2O_3 nanoparticles combination with the flower waste is very efficient and this may be due to the NPK ratio of flower waste which is good for plant growth and the further combination of the Fe_2O_3 nanoparticles with it enhances the fertilizer effect. In case of kitchen waste Nano-fertilizer, the seeds are not germinated, and the probable reason may be that the combination of Fe_2O_3 nanoparticles with kitchen waste is somehow decreasing the soil fertility which is inhibiting the germination, it might be possible that higher alkaline pH of kitchen waste fertilizer is partially reducing the trivalent Iron of Fe_2O_3 nanoparticles and therefore diminishing its activity. The NPK ratio of kitchen waste being better than the flower waste might be responsible for the better growth with the kitchen waste fertilizer alone than the flower waste fertilizer. The cow-dung and Fe_2O_3 nanoparticles combination as fertilizer showed better growth than the cow-dung fertilizer suggesting a combination of the Fe_2O_3 nanoparticles with the cow-dung enhances the activity of the fertilizer. Hence, the results show that the combination of flower waste and Fe_2O_3 nanoparticles as nano bio-fertilizer and the combination of cow-dung and Fe_2O_3 nanoparticles as nano bio-fertilizer are more effective for tomato plant growth than simple fertilizers.

Conclusion

Fe_2O_3 nanoparticles co-digested with cow dung, kitchen waste, and flower waste found to improve the quality of fertility of the soil. The effect was quite pronounced as the combination of flower waste, and Fe_2O_3 nanoparticles showed excellent results in the growth of tomato plant. According to our data, the flower waste + Fe_2O_3 nanoparticles combination and cow dung + Fe_2O_3 nanoparticles were effective for inducing plant growth.

Improvised nano biofertilizers can be useful in future agricultural applications. However, a detailed study regarding proper formulation, risk assessment, and quality control needs to be done before implementing this for holistic uses.

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