Innovations

Synthesis of Manganese Nickel Ferrite Using Sol-Gel Method as Nano Fertilizer for Vigna Mungo Plant

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Abstract: *The present study investigates the synthesis of manganese nickel ferrite ($MnNiFe_2O_4$) nanoparticles using the sol-gel method and their usage as a nanofertilizer for the Vigna mungo (black gram) plant. Manganese, iron, and nickel are basic micronutrients for plant growth, and their delivery in nano-form can improve nutrient uptake and crop yield. The synthesized nanoparticles were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to validate their spinel structure and nanoscale morphology. The magnetic properties were also examined, indicating soft magnetic behavior suitable for agricultural applications. Pot culture experiments were conducted to assess the physiological effects of the nanofertilizer on Vigna mungo. Results demonstrated improved plant growth and development compared to traditional fertilizers, highlighting the potential of $MnNiFe_2O_4$ nanoparticles to increase agricultural productivity while minimizing environmental impact. This research suggests that nanotechnology-based fertilizers can play a significant role in sustainable agriculture by improving nutrient efficiency and supporting healthy crop growth.*

Key words: *Fertilizer, Vigna Munga, agriculture, XRD, VSM and SEM*

Introduction

Nanotechnology, the science of manipulating materials at atomic and molecular scales, typically in the 1-100 nm range, is revolutionizing various industries, including agriculture. In this domain, it is primarily used to develop efficient, sustainable, and high-precision farming practices [1-3]. Nanoparticles exhibit unique properties such as high surface-area-to-volume ratio, tunable surface charge, enhanced reactivity, and controlled release capabilities, making them ideal candidates for addressing key agricultural challenges [4,5].

With global food demand projected to increase by 70% by 2050 due to population growth, there is a pressing need for sustainable solutions in crop production. Traditional agriculture relies heavily on chemical fertilizers, a large portion of whichmore than 50% in most cases and up to 90% in somegets lost to the environment through leaching, volatilization, and runoff [6-8]. This not only represents a significant loss of nutrients but also causes soil degradation, water contamination, and contributes to greenhouse gas emissions. In contrast, nanofertilizers offer enhanced nutrient use efficiency (NUE) by releasing nutrients in a controlled and targeted manner [9-11].

The current focus in agricultural nanotechnology includes the development of nano fertilizers that provide essential nutrients such as nitrogen (N), phosphorus (P), potassium (K), and micronutrients like zinc (Zn), iron (Fe), manganese (Mn), and nickel (Ni) in nanoscale formulations. These nanofertilizers enable precise delivery and slow release of nutrients over extended periods (up to 40-50 days), reducing application frequency and mitigating environmental impact [12-15]. They also support the design of smart delivery systems responsive to soil pH, moisture, or enzymatic activity, optimizing nutrient availability when the plant needs it most [16-17].

In particular, nickel (Ni)long overlooked as a plant nutrientis now recognized as essential. It serves as a cofactor for urease, the enzyme responsible for hydrolysing urea into usable ammonia. Ni also plays roles in nitrogen fixation, seed germination, and supporting beneficial soil microbiota [18-20]. Though required only in trace amounts (typically 0.05 to 5 ppm), Ni deficiencies can impair nitrogen metabolism and overall plant health. In most soils, Ni is present in sufficient quantities, either naturally or as a contaminant in fertilizers and water. However, in Ni-deficient conditions, it is typically applied via foliar sprays in the form of nickel sulfate or nitrate [21].

Our investigation into $MnNiFe_2O_4$ nanoparticles merges the benefits of delivering three micronutrients Mn, Ni, and Fein a single, magnetically responsive nanostructure. Manganese contributes to photosynthesis, nitrogen metabolism, and resistance to pathogens; iron is crucial for chlorophyll synthesis and enzymatic functions; and nickel, as noted, enhances nitrogen metabolism. The integration of these into a ferrite nanoparticle not only improves bioavailability but also minimizes nutrient interactions that may otherwise reduce uptake when applied separately.

Beyond nutrient delivery, ferrite nanoparticles like $MnNiFe_2O_4$ have been explored for their magnetic, catalytic, and antimicrobial properties, which can indirectly benefit plant growth and soil health. Their magnetic properties aid in dispersal and retrieval from the environment, opening pathways for precision agriculture where minimal residues are desired.

In this work, the sol-gel synthesis method was chosen for its advantages in producing homogeneously mixed, high-purity nanomaterials at relatively low temperatures. Characterization using XRD confirmed phase purity and spinel formation, while SEM verified uniform particle distribution at the nanoscale. The soft magnetic properties revealed by VSM analysis suggested non-agglomerated behavior in soil matrices.

Finally, biological efficacy was assessed through controlled pot culture experiments using Vigna mungo. This model crop was selected for its agronomic importance and known sensitivity to micronutrient availability. The application of $MnNiFe_2O_4$ nanofertilizers led to improvements in plant height, root biomass, leaf chlorophyll content, and pod yield, underscoring their potential to replace or complement conventional fertilizers. The integration of manganese, nickel, and iron into a nanoscale ferrite structure offers a multifunctional, efficient, and sustainable alternative for crop fertilization. These findings support further exploration into the large-scale application of such nonmaterial's in agriculture and their role in addressing global food security.

Experimental Process Synthesis of $NiFe_2 O_4$ by Sol-Gel Method

NiFe2O4 sample were synthesized through sol-gel technique. Weighed amount of all required salts were dissolved properly in lowest quantity of deionized water required to get a clear solution. Citric acid is added to the solution. Ammonia solution is added to the solution to maintain pH. The solution was heat treated along with continuous stirring on the hot plate magnetic stirrer at 800˚C for 6 hours. During the heating process, the solution turns into viscous gel (figure a). The gel was heated at 2000˚C for 2 hour has allowed combustion to take place, it turns to brown resin (figure b). The dried gel is burned in the combustion process until the entire gel was burned out to form a powder sample (figure c). The obtained powder is grounded well using an agate mortar and pestle obtain the nano ferrite.

(a)Viscous gel (b) Dried gel (c) Powder sample

The prepared ferrite powder was annealed at 800^0C for 5 hours. The nano ferrite has been prepared at the 1000^0C for 6 hours and are used for further characterization.The systematic procedure for the synthesis of Fe_2O_4 nano ferrites by using sol-gel method $MnNiFe_2O_4$ was synthesised using simplistic and quick sol-gel auto combustion technique. The precursor solution of all required metal sulfate salts were prepared with minimum quantity of distilled water. Citric acid was added to solution. In addition to this Ammonia solution is added to maintain PH of the solution. The solution is heated with continuous stirring on the hot plate magnetic stirrer for 6 hours. During heating process, the solution turns into viscous gel then this gel was preheated at 1000^0C for 6 hours, results in the formation of fluffy product. The obtained powder is grounded well using an agate mortar and pestle to obtain the nano ferrite and are used for further characterization.

$Mn_{1-x}Ni_xFe_2O_4$(at x=0.5) nanoparticles has been synthesized using Sol-Gel technique at pH 10 and sintering temperatures of 200°C for 2 hours, 800°C for 5 hours and 1000°C for 6 hours. Ferric Sulphate Hydrate [Fe_2 (SO_4)$3H_2O$] and Manganese Sulphate Monohydrate [Mn(SO_4). H_2O] and Nickel Sulphate Monohydrate [Ni(SO_4).H_2O] were taken in desired stoichiometric quantities and dissolved separately to form homogenous solutions. Citric acid has been used as a binding agent. The three solutions were then mixed together homogenously with constant stirring and heated to 60°C and Ammonia was added drop wise to maintain the pH value as 10 and thick brown viscous gel was formed. The gel was then kept to dry in hot air oven at 200^0C for 2 hours. Later the obtained powder was crushed and sintered in muffle furnace at 800°C for 5 hours forms thick brown powder. The powder was later grounded well with mortar and pestle to obtain fine powders. The samples were made as pellet and sintered at 1000°C in a muffle furnace again.

Results and Discussion

The structural, morphological, compositional and magnetic properties of the samples were studied through XRD, SEM, EDS and VSM.

XRD Analysis

The XRD patterns for Mn_{1-x} $Ni_xFe_2O_4$ samples (x=0.5) prepared at pH 10 using solgel technique is shown in the Figure 3.1.A complete study of all the cell parameters is carried out from XRD analysis. The XRD peaks have been indexed with JCPDS PDF card No. 074-2082 (Kishore et al 2014). The samples all show single phase cubic spinel structure with Fd3m space group. The XRD showed all characteristic peaks (220), (311), (222), (400), (422), (511) and (440) with the most preferred orientation along (311). The samples show well-defined sharp peaks.

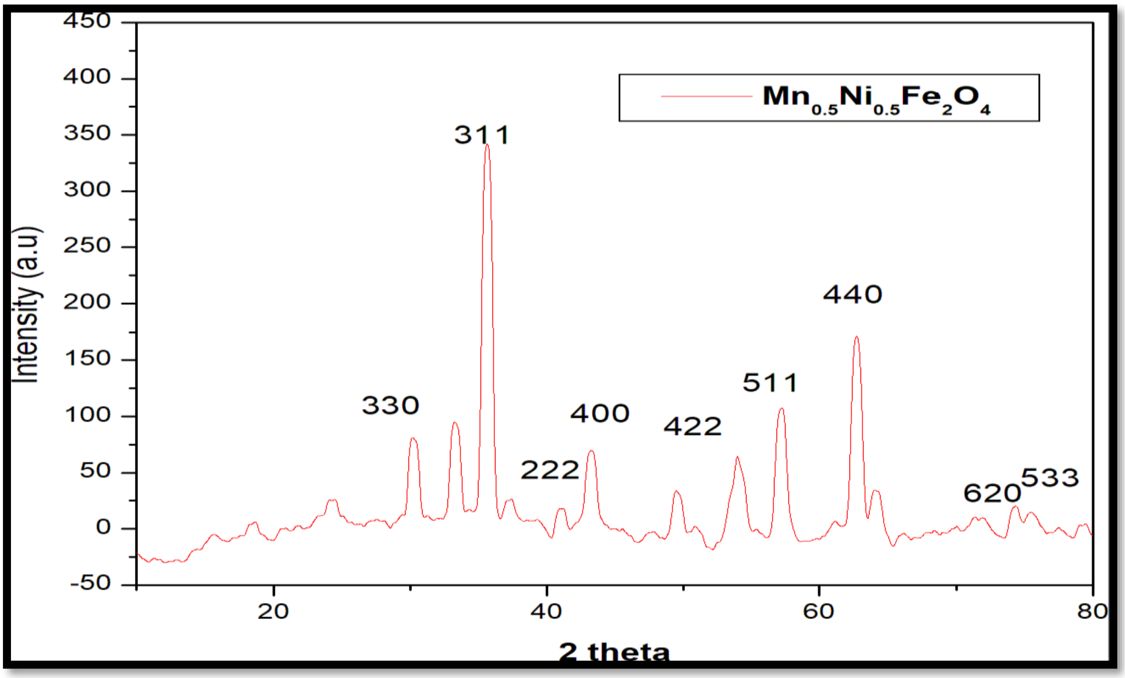

Figure 3.1 XRD peaks of Mn1-xNixFe2O4 samples for x=0.5

As the sintering temperature increases, manganese and nickel which have lower melting points than iron, diffuse into the iron oxide lattice leading to formation of cubic spinel structure. The crystallite particle size is calculated as 36 nmusing standard Debye Scherrer formula.

Further, $Mn_{1-x}Ni_xFe_2O_4$ samples it is seen that the single phase cubic spinel structure is more easily formed in presence of Ni substitution.

EDS Analysis

Compositional analysis of the samples is done through EDS investigations and the presence of Mn, Ni, Fe and O is confirmed and represented in Figure 3.2.

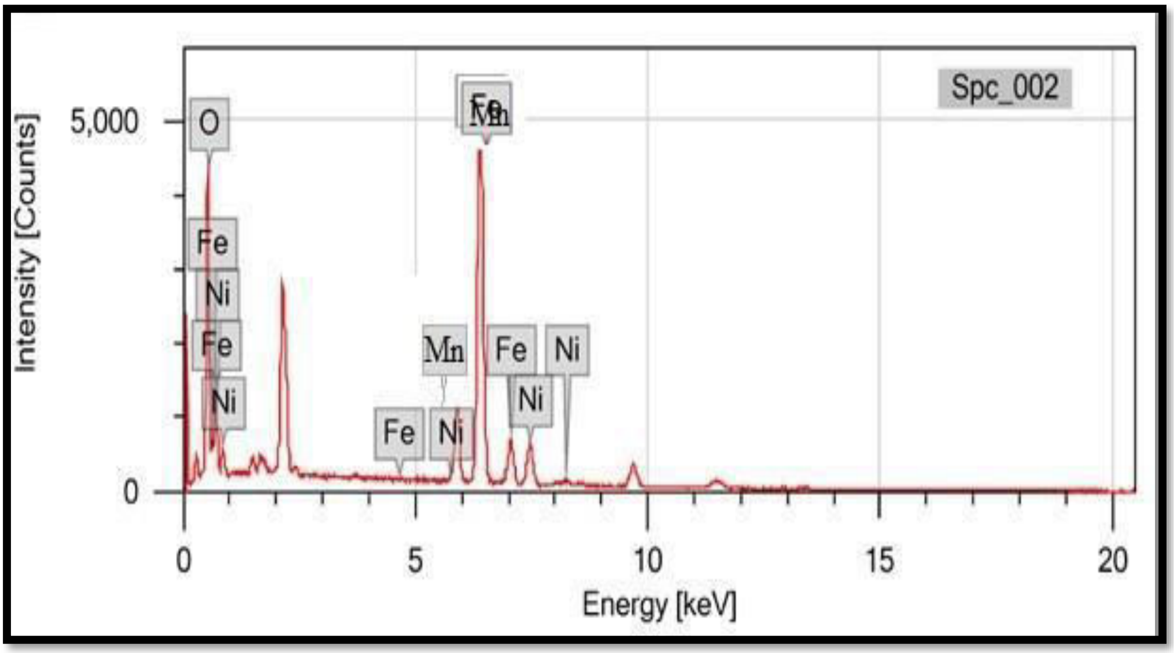

Figure 3.2 EDS peaks for $Mn_{1-0.5}Ni_{0.5}Fe_2O_4$

SEM Analysis

The SEM micrographs of $Mn_{0.5}Ni_{0.5}Fe_2O_4$ samples prepared is shown in Figure 3.3. The images clearly indicate all the particles are in nano size range. The figure shows remarkable changes in the microstructure, crystalline nature, particle size and porosity. The particles have round and hexagonal shapes with the crystalline edges. The particle size and well-defined crystalline edges are seen. All the figures show multigrain agglomeration due to magnetic nature of the particles seen as dark regions in the micrographs. The particle size is found using line-section method and confirmed to be in agreement with XRD results, the average particle size appears to be in the range of 40-70 nm, with some larger aggregated structures visible.

These sizes are consistent with the crystallite size (~36 nm) determined from the XRD analysis using the Debye-Scherrer method, suggesting that the particles are either mono crystalline or composed of a few crystallites.

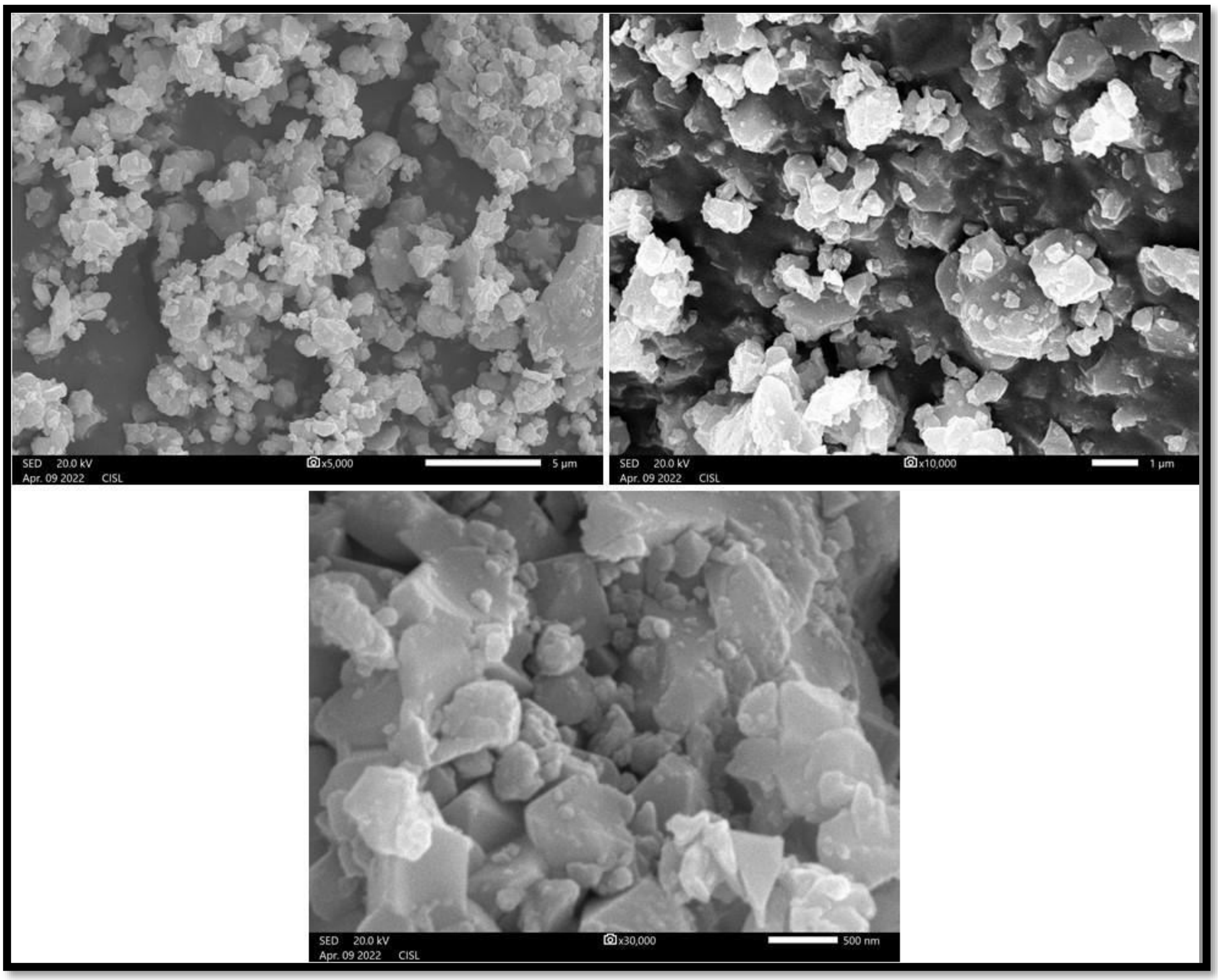

Figure 3.3 SEM micrographs of $Mn_{0.5}Ni_{0.5}Fe_2O_4$ sample

VSM Analysis

The hysteresis curves for $Mn_{1-0.5}Ni_{0.5}Fe_2O_4$ sample prepared is presented in Figure 3.4. The magnetic moment (Ms), remnant magnetization (Mr) and coercivity

(Hc) derived from the study are listed in Table 3.1. The magnetization phenomenon in soft magnetic ferrites occurs due to domain wall motion or domain rotation (22). It is clear that all the samples show soft magnetic nature. The extremely reduced area of the hysteresis curves indicates minimal magnetostrictive loss. Particles of smaller size have reduced Ms values, due to pronounced surface effects of nano-particles. The surface of nano-particles consists of disordered or canted spins, which prevent the core spins from aligning along the direction of the applied field (Maaz et al 2009). This leads to decrease in Ms values at smaller sizes.

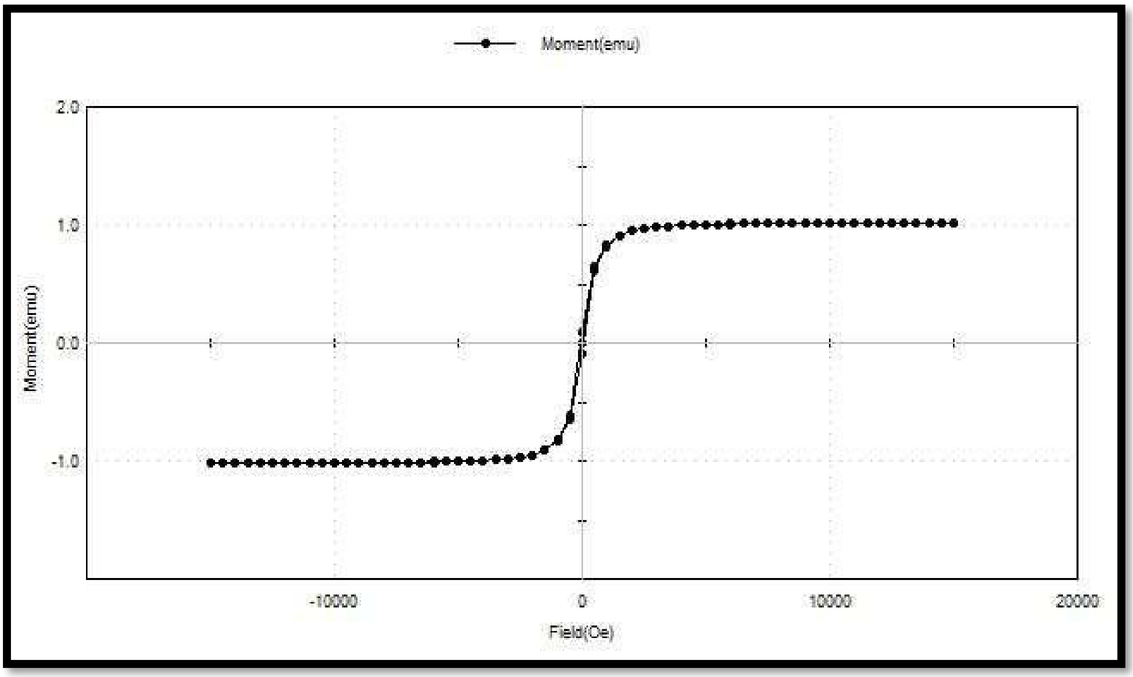

Figure 3.4 Hysteresis curves for $Mn_{1-0.5}Ni_{0.5}Fe_2O_4$ prepared

Table 3.1 Values of Ms, Mr and Hc for $Mn_{0.5}Ni_{0.5}Fe_2O_4$ prepared

Mass (g)	Sensitivity (emu)	HC (Oe)	MS (emu)	MR (emu)
28.000E-3	- 4.1000	65.701	1.0194	92.471E-3

Manganese Nickel ferrite as Nan fertilizer

The two sets of pot culture experiments were conducted to evaluate the response of vigna mungo (Black gram) plant to Manganese Nickel Ferrite nano fertilizer. The data from various experiments were statistically analyzed and also the results were compared with the commercially available Urea.

Initial characteristics of soil and Water

The initial soil of experiments was characterized for various soil physicochemical and the soil quality assessment indicates that the site is environmentally safe, with all tested volatile organic compounds (VOCs), heavy metals, and industrial/agricultural chemicals falling well within the permissible limits set by Indian soil standards. The soil exhibits a slightly alkaline pH (7.85), moderate organic matter (1.62%), and a sandy loam texture, which supports good drainage and aeration. Physicochemical parameters such as electrical conductivity, moisture content, and dry density are within acceptable ranges, indicating stable soil structure and non-saline conditions. However, the nutrient analysis reveals deficiencies in nitrogen (254 kg/ha), phosphorus (8.68 kg/ha), and potassium (96 kg/ha), categorizing the soil fertility as low. While the levels of calcium, magnesium, and other secondary nutrients are adequate, the primary macronutrient shortfall suggests limited agricultural productivity unless amended. To improve fertility, the soil would benefit from organic compost applications and the use of nitrogenous, phosphatic, and potassic fertilizers, along with sustainable practices like crop rotation and green manuring. Overall, the soil is structurally sound and uncontaminated, but requires nutrient enrichment to support optimal agricultural use.

The initial assessment of the water sample reveals that the water is of excellent quality, both chemically and microbiologically. The pH of the water is 6.52, falling within the acceptable Indian Standard IS 10500:2012 range of 6.5-8.5. The colour, odour, taste, and turbidity are within the prescribed acceptable limits, indicating good physical characteristics. The Total Dissolved Solids (TDS) level is low at 42 mg/l, well below the 500 mg/l acceptable limit, confirming the water is soft and not mineral-laden. Major anions like sulphate (6 mg/l), chloride (10 mg/l), and fluoride (<0.1 mg/l) are significantly below threshold limits, while cations like calcium (4 mg/l), magnesium (1 mg/l), and alkalinity (8 mg/l) also remain very low, indicating low mineral content and negligible hardness (14 mg/l as $CaCO_3$).

The levels of heavy metals and toxic substances including arsenic, lead, mercury, cadmium, selenium, chromium, iron, copper, and zinc were all below detection limits or trace (<0.001 mg/l), ensuring compliance with IS limits and suggesting no contamination. Organic pollutants such as phenolic compounds, cyanide, nitrate, ammonia, and volatile organics (e.g., chloroform, bromodichloromethane, etc.) were all non-detectable, meeting the most stringent standards. A comprehensive panel of persistent organic pollutants (POPs), including pesticides (e.g., DDTs, HCH isomers, aldrin, chlorpyrifos, etc.) and PCBs, were all found below 0.01 μg/l, indicating no trace of agricultural or industrial contamination.

The microbiological profile is entirely cleanno total coliforms, E. coli, Salmonella, Vibrio, or any other pathogens were detected. The total bacterial count, yeast, mould, and anaerobic bacteria were also absent, making the water safe from a public health perspective. Radioactivity levels, including both alpha and beta emitters, were absent, ensuring no nuclear contamination. Hence, the water is chemically non-polluted, microbiologically sterile, and safe for potable use. It complies with both acceptable and permissible limits of IS 10500:2012 across all parameters. The absence of hazardous substances, pathogens, and radiological residues indicates that the water source is pristine and suitable for human consumption without the need for treatment.

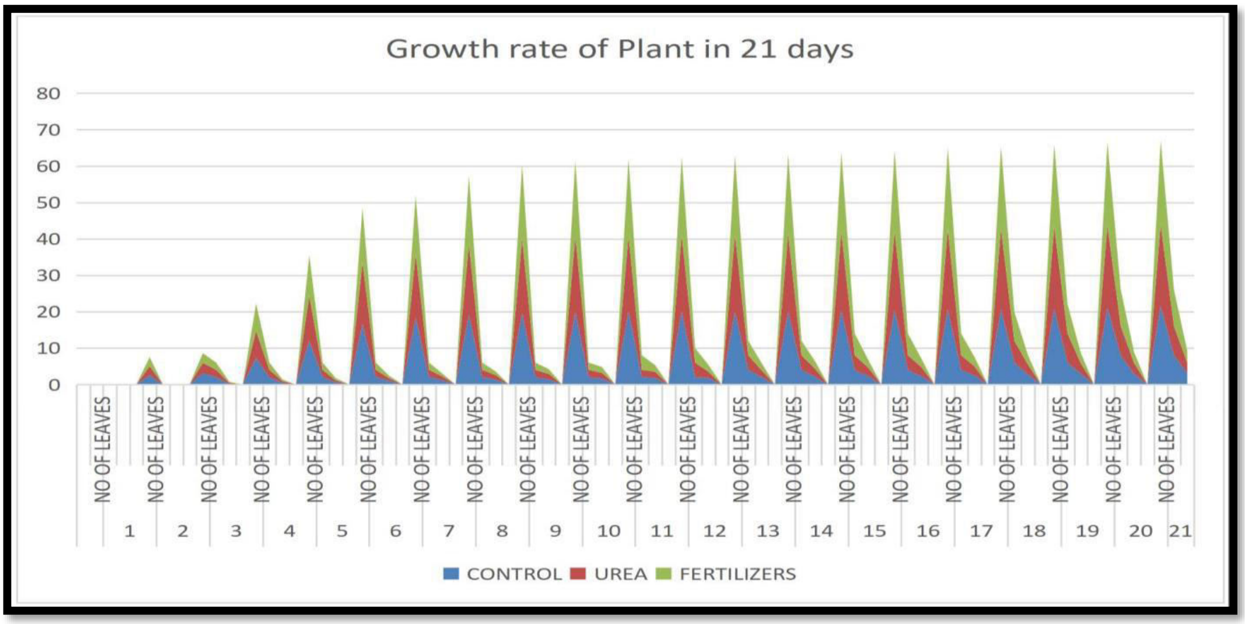

Figure 3.5. Growth Rate of Plant without fertilizer, with urea as fertilizer, with MNF as nanofertilizer

Our results suggest that MNF is a potential substrate for the development of nanofertilizer with higher efficiency of fertilization by approximately 20%. Despite the results being convincing to use nanotechnological approaches to evolve nano fertilizers, more extensive research need to be done in open field conditions in order to gain insight of emerging technologies and improve the productivity of crops at the farm gate.

Growth Rate of Plant without fertilizer, with urea as nanofertilizer, with MNF as nanofertilizer.

Week-1

Fig-1 Control

Fig-2 Urea

Fig-3 Fertilizer

Week-2

Fig-4 Control

Fig-5 Urea

Fig-6 Fertilizer

Week-3

Fig-7 Control

Fig-8 Urea

Fig-9 Fertilizer

The figures-1, 4, 7 represent the growth of the vigna mungo plant under control
The figures-2,5,8 represent the growth of the vigna mungo plant with urea as fertilizer
The figures-3,6,9 represent the growth of the vigna mungo plant with MNF fertilizer

Conclusion:

In summary the MnNiFe2 O4 nanoparticles have been synthesized by solgel technique. The compound was successfully synthesized and have been analysed using x-ray diffraction (XRD), scanning electron microscope (SEM) and vibrating sample magnetometer (VSM). The synthesized sample exhibits a single phase cubic spinel structure in x-ray diffraction. The SEM image shows that the sample is in distorted spherical shape that are agglomerated together. The average size of the prepared sample were calculated from SEM instrument is in the range 45nm. The magnetization Ms of the prepared sample were calculated from VSM instrument as 1.0194emu and coercivity He is found to be 65.701 Oe and retentivity

Mr as 92.471 E- 3emu. The synthesized MnNiFe2O4 has been used as a nanofertilizer in vigna mungo planet, it is seen that, the prepared MnNiFe2O4 has high capacity to act as a nanofertilizer.

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