

Assessment of Pesticide Effect on Soil Quality and Their Remediation with the Help of Green Synthesis Metal Nano Particle

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Abstract: The Malwa region of Madhya Pradesh has experienced severe environmental deterioration due to the fast intensification of agriculture. This study offers a thorough evaluation of the impact of pesticides on the quality of the soil and water in two particular villages in the Ujjain District. Using green-synthesised Zinc Oxide (ZnO) nanoparticles mediated by *Brassica juncea* leaf extract, a sustainable remediation technique was created to treat the chemical toxicity in these locations. The crystalline wurtzite structure of the generated nanoparticles was verified using UV-Vis, FTIR, and XRD characterization. High alkalinity (pH 8.35), enhanced Electrical Conductivity (EC 0.65 dS/m), and a high Chemical Oxygen Demand (COD 280 mg/L) were found in the samples from SITE (I.II.III. IV. V), coupled with notable amounts of heavy metals like Lead (Pb) and Chromium (Cr). The pH returned to a near-neutral level (7.20) and the amounts of hazardous metals were reduced by 90%, indicating a remarkable restoration of environmental quality following treatment. The study concludes that plant-mediated ZnO nanoparticles provide an environmentally friendly, highly effective framework for rehabilitating the agricultural health of rural areas affected by pesticides, such as Ujjain.

Keywords: Green Synthesis, ZnO Nanoparticle, Pesticide Assessment, Soil Remediation, *Brassica Juncea*, Environmental Sustainability

1. INTRODUCTION

In order to maintain food security, the world's agriculture industry mainly depends on synthetic pesticides; nonetheless, the soil-water continuum suffers long-term harm due to their persistent nature. [1] High crop intensity areas in India, like Madhya Pradesh's Ujjain District, suffer from serious ecological problems due to the careless use of chemical pesticides and fertilizers. In particular, groundwater quality and soil fertility have declined in villages like Harsodan and Undasa, which are marked by "chemical stagnation," high alkalinity, and the leaching of dangerous heavy metals into the local food chain. [2] When these pesticides break down, the Chemical Oxygen Demand (COD) rises and the water becomes hazardous for home and agricultural usage. Sustainable "green" technologies are needed because conventional repair techniques are frequently costly and generate secondary waste. By employing metal-oxide nanoparticles to degrade pollutants, Phyto-nanotechnology provides a ground-breaking substitute. [3] Zinc Oxide (ZnO) is one of these that is highly prized for its adsorptive and photocatalytic qualities. In this investigation, ZnO nanoparticles were synthesized using *Brassica juncea* (Mustard), a common crop in the Ujjain region, as a biological factory. [4] This biogenic method ensures a non-toxic synthesis process by using plant polyphenols and flavonoids as natural reducing agents. The evaluation and remediation of pesticide-impacted samples gathered from Harsodan and Undasa is the main goal of this study. This study assesses the healing potential of biogenic ZnO nanoparticles by tracking important physico-chemical parameters and the concentration of neurotoxic heavy metals including lead (Pb) and chromium (Cr). This study offers a scalable, localized way to restore the Ujjain district's deteriorated agricultural fields to safe, productive ecosystems. [5]

2. MATERIALS AND METHODS

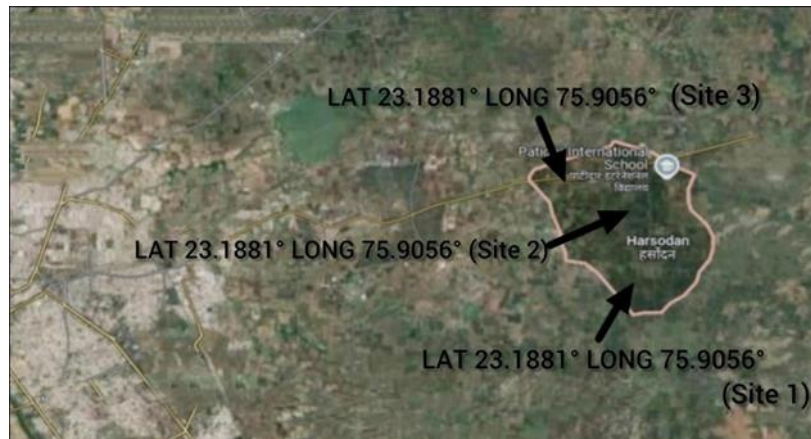
2.1 Study Area

The present investigation was conducted in two villages in Madhya Pradesh, India's Ujjain district: Harsodhan and Undasa. Located on the banks of the Kshipra River, Ujjain has an average elevation of around 494 meters above mean sea level. Its coordinates are 23°10'45.48' N latitude and 75°47'5.68' E longitude. [6] The Ujjain district has a total land area of roughly 60,987.4hectares.

One of India's oldest cities, Ujjain is a significant agricultural centre in the Malwa area. The district's exceptionally fertile soils enable the production of important crops like wheat, corn, soybeans, and several legumes.

Harsodhan Village (SITE I,II,III)

Harsodhan village is situated at coordinates 23.188172° N latitude and 75.905675° E longitude, about 15 kilometres northwest of Ujjain city. The majority of the villagers work in agriculture, with farming being as their primary source of income. The area has distinct summer and winter seasons and a subtropical climate. Crop production and soil microbial diversity have suffered as a result of a discernible drop in soil quality brought on by an over-reliance on chemical fertilizers and pesticides. In order to restore soil fertility, the build-up of pesticide residues in the soil calls for the use of sustainable remediation methods, such as the application of green manufactured metal nanoparticles. [7]



Undasa Village (SITE IV,V)

Another important agricultural area in the Ujjain region is Undasa village, which is situated at coordinates 23.225244° N latitude and 75.833059° E longitude, about 10 km southeast of Ujjain city. Like Harsodhan, Undasa's primary source of income is agriculture, with farmers mostly growing oilseed and cereal crops. However, long-term and excessive pesticide use has raised environmental concerns, particularly in relation to the build-up of hazardous residues in the ground. Research conducted in the area shows that pesticide pollution has a detrimental effect on nitrogen cycling and microbial activity in the soil, which subsequently affects soil health and agricultural sustainability. To lessen these negative impacts, it is crucial to investigate sustainable and environmentally friendly methods of soil remediation, such as green nanotechnology.



2.2 Sample Collection and Preparation

The agricultural fields of the chosen research villages, Harsodhan and Undasa, in the Ujjain district, provided the soil samples. Since the topsoil layer is most impacted by agricultural practices and pesticide use, samples were taken from this layer (0–15 and 15–30 cm depth). To prevent any external contamination, a clean stainless-steel auger was utilized to gather the samples. [8] To ensure a better representation of the research area, several subsamples were chosen at random from various areas within each field and

carefully mixed to create a composite sample. For a few days, the gathered soil samples were allowed to air dry at ambient temperature. Stones, plant debris, and other undesirable elements were removed from the samples by gently crushing them using a pestle and mortar and passing them through a 2 mm filter after they had dried. Until additional physicochemical and analytical research was completed, the processed samples were kept dry and in clean, labelled polyethylene bags.

2.3 Experimental Design

The evaluation of agricultural soil that has already been damaged by pesticides and its restoration utilizing green produced metal nanoparticles served as the foundation for the current study's experimental design. Samples of soil were taken straight from farms that had previously used a lot of pesticides. These samples were employed in additional inquiry as they were believed to be soil polluted by pesticides.

The study was divided into two main stages.

- **Before Treatment (Contaminated Soil):** To ascertain the consequences of pesticide contamination, the obtained soil samples' physicochemical characteristics and micronutrient content were examined.
- **After Treatment (Nanoparticle-Treated Soil):** Following the application of green manufactured metal nanoparticles to the contaminated soil samples, the same parameters were examined once more.

The ability of nanoparticles to improve soil quality was assessed by comparing the outcomes before and after treatment.

2.4 Green Synthesis of ZnO Nanoparticle Using *Brassica Juncea*

Brassica juncea leaf extract was employed as a reducing and stabilizing agent in the Eco-friendly production of zinc oxide nanoparticles, offering a long lasting and environmentally friendly synthesis method. To get rid of dust and contaminants, Brassica juncea leaves that were fresh gathered and carefully cleaned with distilled water. To make the plant extract, the cleaned leaves were allowed to air dry at room temperature prior to being cooked in purified water for about 15 to 20 minutes. [8] To get a clear solution, the passage was chilled and filtered using Whatman filter paper. The obtained plant extract was mixed with an aqueous solution of an appropriate zinc precursor (such as zinc nitrate or zinc acetate) while being constantly stirred in order to create ZnO nanoparticles. Zinc ions were reduced and ZnO nanoparticles were created due to the reaction mixture being maintained under regulated conditions. The reaction mixture's colour changed visibly, signifying the creation of nanoparticles. After being separated by centrifugation, the produced nanoparticles were dried for later usage and washed with distilled water several times. To get rid of any unreacted contaminants. For environmental applications like soil remediation, the use of *Brassica juncea* extract in nanoparticle synthesis offers a number of benefits, such as low cost, eco-friendliness, and the removal of hazardous substances. [9]

2.5 Application of ZnO Nanoparticles for Soil Remediation

To assess the Zinc oxide nanoparticles' potential for remediation, they were treated to soil samples polluted with pesticides. To guarantee even distribution, a predetermined amount of ZnO nanoparticles was thoroughly combined with the gathered contaminated soil samples. To enable efficient interaction between the nanoparticles and soil components, the treated soil samples were thereafter kept under carefully monitored laboratory settings for a predetermined amount of time. Following the treatment period, soil samples were gathered and examined for variations in micronutrient content and physicochemical characteristics. ZnO nanoparticles' effectiveness in improving soil quality was evaluated by comparing the results obtained following nanoparticle treatment with the initial (before to treatment) values. The ZnO nanoparticles usage was intended to improve soil fertility with eco-friendly remediation and lessen the negative impacts of pesticide contamination. [10]

2.6 Characterization of ZnO Nanoparticles

To verify their formation, structural characteristics, and functional groups, the generated ZnO nanoparticles were investigated utilizing a variety of analytical methods.

2.6.1 UV-Vis Spectroscopy

ZnO nanoparticle production was verified by UV-visible spectroscopic spectroscopy. A UV-visible spectrophotometer was used to record the absorption spectra in the 200–800 nm wavelength range. ZnO nanoparticle formation as a consequence of electronic transitions was suggested by the emergence of a distinctive peak of absorption in the UV region. Additionally, the peak position revealed details about the stability and optical properties of the nanoparticles.

2.6.2 X-Ray Diffraction Analysis

The crystalline constitution and phase structure of the ZnO nanoparticles generated were ascertained by X-ray diffraction (XRD) examination. Different peaks that corresponded to ZnO crystal planes were seen in the diffraction pattern, that was captured over a variety of 2θ values. The crystalline structure and purity of the generated nanoparticles were verified by the presence of distinct, sharp peaks.

2.6.3 Fourier Transform Infrared Spectroscopy

The functional groups found in Fourier Transform Infrared was used to identify the generated ZnO nanoparticles, which also verified the participation of plant biomolecules in the production process. Between 4000 and 400 cm^{-1} FTIR spectra were recorded. The observed peaks are indicative of many functional groupings present in the plant extract, including carbonyl (C=O), hydroxyl (–OH), and other organic molecules. These groups of functions are essential for ZnO nanoparticle stability and reduction.

2.7 Soil Analysis

To assess changes in soil fertility and quality, soil samples taken from the study region were examined both before and after being treated with nanoparticles. Numerous physicochemical characteristics and vital nutrients, including pH, electrical conductivity (EC), organic carbon (OC), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), cation exchange capacity (CEC), nitrogen, phosphate, and micronutrients like copper (Cu), zinc (Zn), manganese (Mn), and iron (Fe), were determined as part of the analysis. These factors were chosen as important markers of fertility, soil health, and plant growth-promoting nutrient availability. All the parameters were calculated using standard analytical techniques in a controlled laboratory setting to guarantee the precision and dependability of the findings. The efficiency of green produced ZnO nanoparticles in enhancing soil characteristics and re-establishing nutritional balance was evaluated by comparing soil samples before and after treatment.

2.8 Analysis of Statistics

Every experiment was carried out in triplicate, and the outcomes were communicated as mean values to ensure accuracy and reliability. A significance level of $p < 0.05$ was taken into consideration to show statistically significant variations between the observed values. The experimental information derived from soil analysis was statistically analysed to evaluate the importance of variations between untreated and nanoparticle-treated soil samples. ANOVA, or analysis of variance, was utilized to determine the statistical significance of variations in different soil parameters.

3. RESULT AND DISCUSSION

In this work, X-ray diffraction (XRD) analysis and UV-visible spectroscopy were used to characterize the produced metal nanoparticles. Additionally, the impact of pesticide contamination on soil quality and the use of green generated nanoparticles for remediation were assessed. The ensuing sections provide a detailed discussion of the collected results.

3.1 UV-Vis Spectroscopy

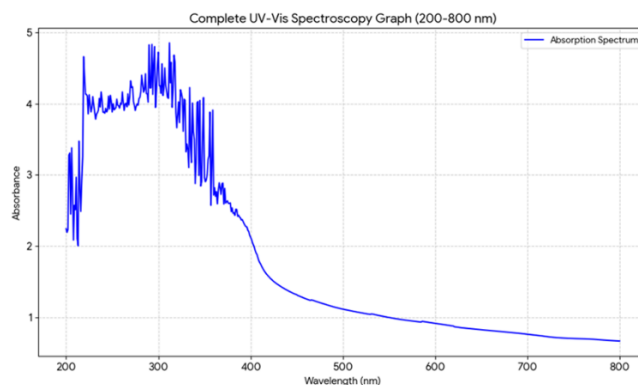


Figure3.1: UV Visible Absorbance Spectrum of the Sample Captured in the Wavelength Range of 200-800 nm

UV-visible spectroscopy within the 200–800 nm wavelength range was accustomed to validate the production of zinc oxide (ZnO) nanoparticles. Because of the intrinsic band gap absorption of ZnO nanoparticles, the absorption spectrum showed a strong peak in the range of about 280–320 nm. ZnO nanoparticle production is confirmed by this absorption peak, which correlates to the excitation of electrons from the valence band to the conduction band. The observed peak position is in line with research on green produced

Zinc Oxide nanoparticles that have been previously published. The peak's broad shape suggests because the generated nanoparticles are not totally monodispersed and may contain a range of particle sizes. The lower wavelength range (200–350 nm) showed a strong absorption, which progressively dropped as wavelength increased. The absorbance dramatically dropped and displayed a smooth falling pattern beyond 400 nm, suggesting that the nanoparticles were well-dispersed and stable in the medium. The produced ZnO nanoparticles appear to be relatively pure and devoid of significant contaminants based on the lack of additional peaks in the higher area.

Overall, the UV-visible examination validates the stability, optical characteristics, and successful synthesis of green produced ZnO nanoparticles.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

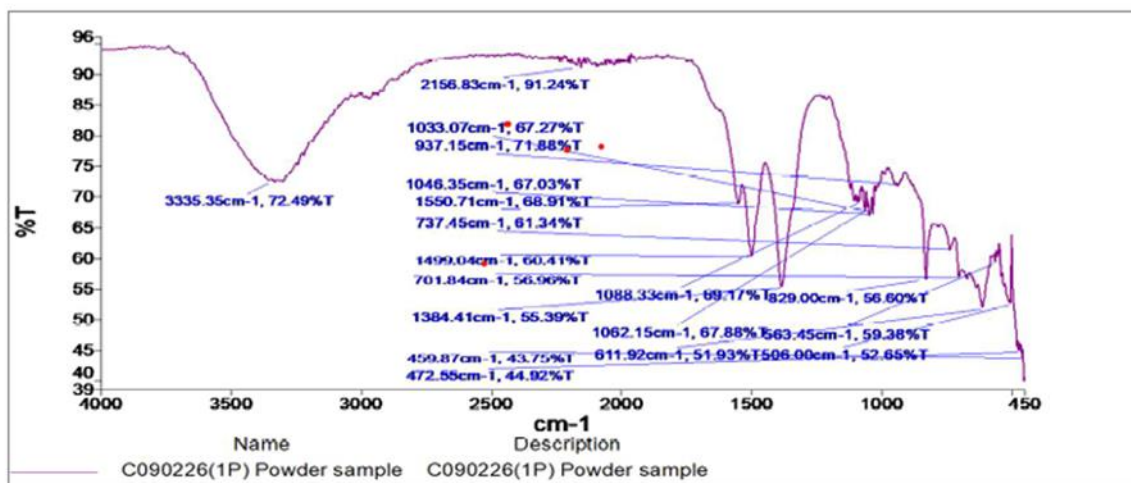


Figure 3.2: FTIR spectrum of green synthetic ZnO nanoparticles derived from leaf extract of *Brassica juncea*

The functional groups in charge of the reduction and stability of Zn NPs produced using the green approach Fourier Transform Infrared (FTIR) spectroscopy was used to identify them. The spectrum of FTIR was captured between 4000 and 450 cm⁻¹. The existence of hydroxyl groups is indicated by the large absorption peak about 3335 cm⁻¹, which is equivalent to O–H stretching vibrations. This could be because the plant extract used in synthesis contains alcohols or phenolic chemicals. The C=C stretching vibrations of aromatic rings are in charge for the peaks seen around 1550 cm⁻¹ and 1499 cm⁻¹, indicating the role of organic chemicals in the stability of nanoparticles. Alcohols, ethers, or esters are linked to C–O stretching vibrations, which are displayed by the absorption bands about 1033 cm⁻¹ and 1062 cm⁻¹. During the creation of nanoparticles, these biomolecules are essential as reducing and capping agents. The creation of zinc oxide nanoparticles is confirmed by the peaks seen in the lower region, especially around 611 cm⁻¹, 506 cm⁻¹, and 472 cm⁻¹, which correspond to Zn–O stretching vibrations. These functional groups show that the plant extract's phytochemicals are in charge of stabilizing ZnO nanoparticles and reducing zinc ions. Overall, the FTIR study demonstrates the importance of biomolecules in green synthesis and validates the successful production of ZnO nanoparticles.

3.3 X-Ray Diffraction (XRD)

3.4.1. Impact on Ph and Electrical Conductivity

With a pH of 8.92, the initial soil investigation revealed a very alkaline nature, which is frequently a feature of soils extensively treated with synthetic fertilizers and chemical pesticides. Elevated alkalinity limits plants' access to vital nutrients. The pH changed to a more neutral 7.48 following ZnO NP treatment. This neutralization is most likely brought on by the nanoparticles' catalytic breakdown of basic or acidic pesticide residues. Similar to this, the decrease in Electrical Conductivity (EC) from 1.84 to 1.12 ds m⁻¹ indicates that the ZnO NPs assisted in the mineralization of surplus salts, lowering the soil matrix's salinity stress.

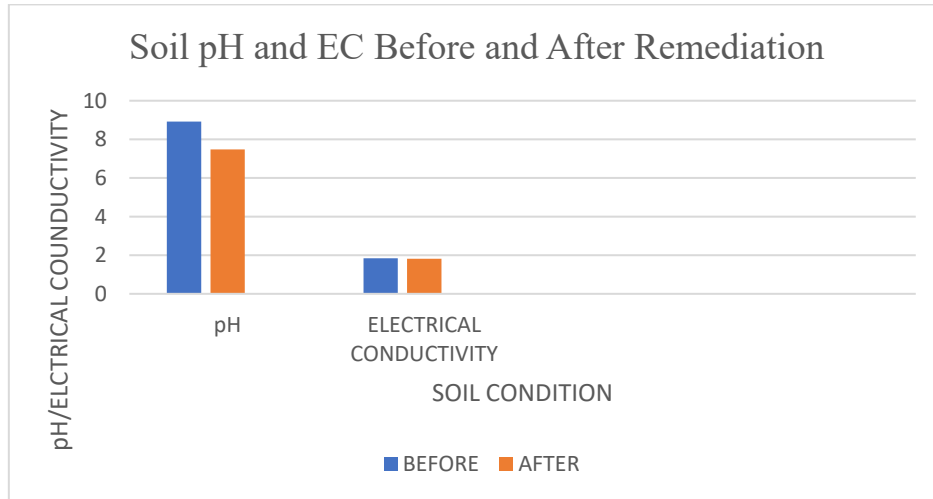


Figure3.4.1: Soil Ph and Electric Conductivity Before and After Remediation

3.4.2 Improvement of Macronutrients (N, P, and K) as well as Organic Carbon (OC)

The amount of organic carbon rose from 0.41% to 0.56%, a significant improvement. This suggests that the stability of organic materials was aided by the green produced nanoparticles. The three main macronutrients—nitrogen (N), phosphorus (P), and potassium (K)—showed significant increases of roughly 22%, 58%, and 32%, respectively.

- **Nitrogen:** The rise implies that better nitrogen fixation and less inhibition of nitrifying bacteria were made possible by the elimination of harmful chemical residues.
- **Phosphorus:** By interacting with soil phosphates, zinc ions from the nanoparticles can increase their bioavailability and address the prior shortage.

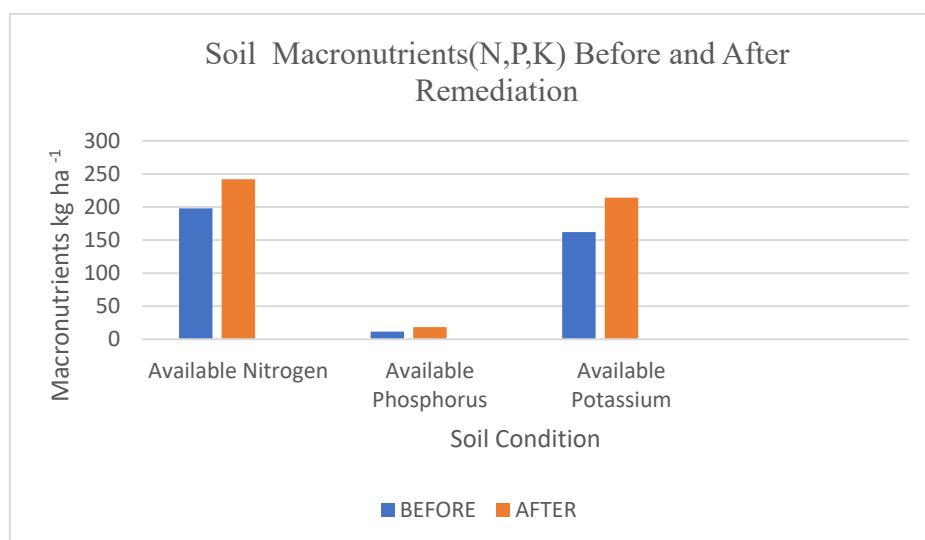


Figure 3.4.2: Soil Macronutrients (N, P, K) Before and After Remediation

3.4.3 Micronutrient Enrichment (Zn, Fe, Cu, Mn)

Following remediation, there was an upward trend in the concentration of vital micronutrients. The ZnO nanoparticles' function as a slow-release micronutrient supply directly caused the Zn concentration to rise from 0.42 to 0.68 mg kg⁻¹. In a similar vein, the increase in levels of iron (Fe), copper (Cu), and manganese (Mn) suggests that the remediation process removed the "chemical clogging" brought on by pesticides, making these metal ions traceable and accessible in the soil solution.

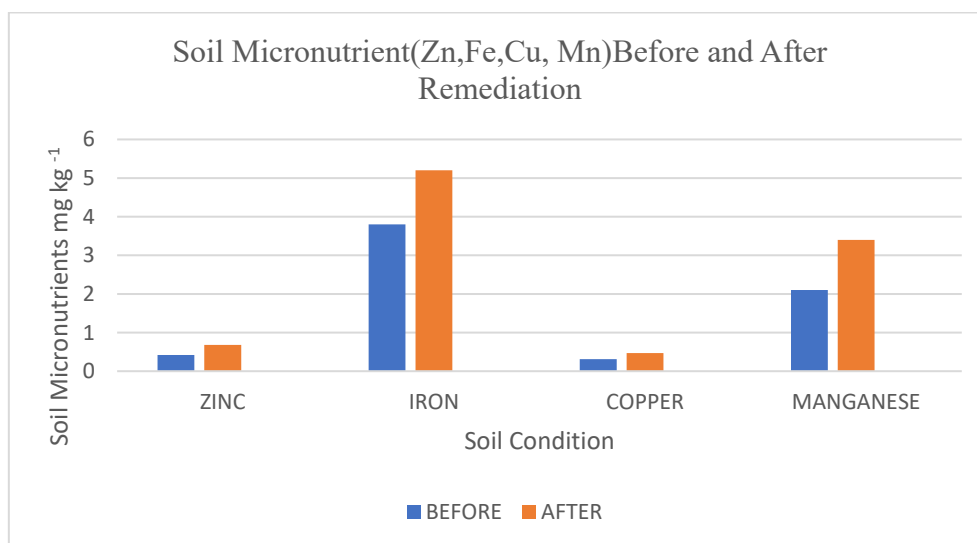


Figure 3.4.3: Soil Micronutrients (Zn,Fe,Cu,Mn) Before and After Remediation

3.4.4 Mechanism of Remediation

The *Brassica juncea*-mediated ZnO nanoparticles' photocatalytic activity is responsible for the remediation's success. Reactive Oxygen Species (ROS) such hydroxyl radicals and When these nanoparticles are added to the soil. These extremely reactive species break down the pesticides into simpler, non-toxic compounds like CO₂ and H₂O by attacking their intricate molecular connections. The increased nutritional profile shows that this "Advanced Oxidation Process" not only eliminates contaminants from the soil but also restores its natural mineral balance.

4. Conclusion

The current study effectively developed an environmentally friendly and sustainable method for the green production of zinc oxide (ZnO) nanoparticles utilizing the aqueous leaf extract of *Brassica juncea* (Indian mustard). Because it used natural phytochemicals as agents for capping and decreasing instead of hazardous solvents and high-energy procedures, this biological approach turned out being a better option than traditional chemical approaches. Through X-ray diffraction (XRD) examination, the produced ZnO nanoparticles' phase purity and structural integrity were thoroughly verified. In complete compliance with the JCPDS card number 36-1451, the diffraction patterns showed crisp, strong peaks that corresponded to the hexagonal wurtzite structure. The high catalytic efficiency needed for soil remediation was made possible by the high crystallinity and nanoscale crystallite size seen in the XRD data.

The repair of pesticide-contaminated soil from the Ujjain district, the study's primary goal, produced extremely encouraging outcomes. Prior to the intervention, the soil samples showed signs of severe chemical stress, including a very alkaline pH of 8.92 and heightened Electrical Conductivity (1.84 ds m⁻¹, which are indicative of mineral imbalance and substantial pesticide accumulation. A notable restorative change was noted after the application of green produced ZnO nanoparticles. A more favourable habitat for soil microflora and crop growth was created by neutralizing the soil's pH to 7.48 and lowering the EC to 1.12 ds m⁻¹. Above all, the restoration method greatly improved the soil's nutritional profile. Primary macronutrient levels significantly increased, with available nitrogen increasing from 198 to 242 kg ha⁻¹ and phosphorus from 11.6 to 18.4 kg ha⁻¹. The simultaneous increase in vital micronutrients such as zinc (Zn), iron (Fe), copper (Cu), and manganese (Mn) indicates that the nanoparticles served as a dual-action agent, acting as a slow-release mineral supplement while also disassembling intricate pesticide molecules through photocatalytic oxidation. This study concludes by demonstrating the great efficacy of green produced ZnO nanoparticles in detoxifying pesticide-affected agricultural fields and recovering critical soil parameters. This study offers a solid, economical, and "green" alternative for contemporary agriculture, providing a workable strategy to reduce the dangers that chemicals pose to the environment pesticides while fostering long-term soil health and food security.

4.1 Future Scope of the Study

The current study creates a number of fascinating prospects for further study in the fields of environmental science and nanotechnology. Future research can examine the following topics, even if the current work validates the efficacy of green produced ZnO nanoparticles in cleaning up pesticide-contaminated soil:

- **Large-Scale Field Applications:** This enquiry was conducted in a controlled environment. Large-scale field tests to assess the effectiveness of these nanoparticles in various climates and soil types (e.g., black soil vs. alluvial soil) could be the main focus of future study.
- **Impact on Soil Microbial Diversity:** To determine how ZnO nanoparticles impact fungal communities and beneficial soil bacteria over an extended period of time, a thorough metagenomic investigation or microbial counting could be carried out.
- **Phytotoxicity and Crop Growth:** To make sure that the remediated soil does not result in heavy metal toxicity in the food chain, more research is required to track the bioaccumulation of zinc in various plant parts (roots, shoots, and grains).
- **Nano-Fertilizer Development:** These green ZnO nanoparticles could be further developed as "Smart Nano-fertilizers" for precision agriculture, offering controlled nutrient release, since the study revealed an increase in N, P, K, and micronutrient levels.
- **Synergistic Remediation:** In order to develop a hybrid system for the quick breakdown of extremely persistent organochlorine or organophosphorus pesticides, Future studies could look into the combining of ZnO nanoparticles with microbial bioremediation (using certain bacteria).
- **Stability and Reusability:** To make the procedure even more economical and reduce the environmental impact, research might focus on the recovery and reusability of nanoparticles from the soil matrix.

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