engineering proceedings

MDPI

Proceeding Paper

Obtaining Environmentally Friendly Trace Element Preparations for Crop Production via the Electric Spark Treatment of Metals †

Konstantin Lopatko [1], Oksana Zazymko [1], Volodymyr Nazarenko [2,*], Kateryna Vynarchuk [1] and Mykola Tkachuk [1]

[1] Department of Technologies of Construction Materials and Materials Science, National University of Life and Environmental Sciences of Ukraine, 03041 Kyiv, Ukraine; lopatko_konst@hotmail.com (K.L.); zazymko_oks@nubip.edu.ua (O.Z.); Ukraine; vinarchuk-k@ukr.net (K.V.); btec1994@gmail.com (M.T.)
[2] Department of Computer Systems, Networks and Cybersecurity, National University of Life and Environmental Sciences of Ukraine, 03041 Kyiv, Ukraine
* Correspondence: volodnz@nubip.edu.ua
† Presented at the 3rd International Electronic Conference on Processes—Green and Sustainable Process Engineering and Process Systems Engineering (ECP 2024), 29–31 May 2024; Available online: https://sciforum.net/event/ECP2024.

Abstract: Traditional technological approaches used for the cultivation of field crops that involve many mineral fertilizers and chemical plant protection products are becoming costly, as well as environmentally and economically irrational. An alternative direction is the use of modern technological approaches, including those involving nanomaterials. This article presents a method of obtaining biologically acceptable and effective trace elements in the form of aqueous dispersions of metals. A complex compound was prepared, which includes metal nanoparticles in particular, such as iron (Fe)—1800 ppm; copper (Cu)—400 ppm; zinc (Zn)—1000 ppm; and manganese (Mn)—800 ppm. The compounds were tested in the field during the cultivation of winter wheat at different stages of organogenesis. The presented technology for growing grain crops is cost-effective and provides an increase in wheat cultivation profitability by 10–15%.

Keywords: electrospark synthesis; nanoparticles of biogenic metals; ecology of the agrosphere; biodegradation

Citation: Lopatko, K.; Zazymko, O.; Nazarenko, V.; Vynarchuk, K.; Tkachuk, M. Obtaining Environmentally Friendly Trace Element Preparations for Crop Production via the Electric Spark Treatment of Metals. *Eng. Proc.* **2024**, *67*, 62. https://doi.org/10.3390/engproc2024067062

Academic Editor: Juan Francisco García Martín

Published: 9 October 2024

1. Introduction

Over the past two decades, in connection with the search for new technological solutions to the problems of ecology and natural resources, a new scientific direction has begun to gain momentum all over the world, related to the integration of modern nanotechnological developments in various fields, such as instrumentation, micro- and optoelectronics, chemical technology, medicine, and biotechnology.

Currently, significant scientific potential has accumulated in various methods for obtaining nanomaterials from different metals and alloys, the purposeful creation of composite materials with special properties, and research on the physical and chemical properties of nanomaterials. Nanotechnology provides sustainable solutions by replacing traditional fertilizers with nanoparticles. These nanoparticles have unique properties that allow them to overcome bioavailability issues and enhance mineral uptake, increase yield, and reduce fertilizer losses, helping to protect the environment. Recent studies emphasize the effects of nanoparticles of basic and essential elements on plant growth, physiology, and development, taking into account their size, composition, concentration, and method of application. Key aspects of the research include evaluating the effectiveness of their methods of use and the impact of nanoparticles on the nutritional quality of crops. It should be noted that the concentration of metal nanoparticles significantly affects the yield, as this parameter determines the mass fraction of nanoparticles in the solution or on the soil surface, affecting their interaction with plants and the biological environment. Common features characteristic of the nanoscale state of matter make it possible to realize their useful properties and significantly reduce resource consumption. In recent years, there have been many publications on the use of nanomaterials in crop production, particularly regarding conditions where biogenic metals, which are considered as essential trace elements for the normal development of plant organisms, are undergoing shortages or are physiologically inaccessible.

The rational use of available resources can be demonstrated by solving the problems caused by the ecologization of modern production, especially in the field of agricultural production. Today, in the face of a global food crisis, there is a shortage of chemically uncontaminated agricultural products. Therefore, the physicochemical properties and reactivity of materials in the nanoscale state are of interest to researchers, since such materials can be used in various technological processes in the chemical, processing, and food industries.

The main prerequisites for the use of nanomaterials in agriculture [1–4] are based on such characteristics as the natural biogenicity of the metal, and the size and concentration of the nanoparticles. The general hypothesis of the biological functionality of metal nanoparticles is based on the idea that defects in the crystal structure of dispersed objects are a reflection of the physical processes that accompany the formation of a nanoparticle [4]. Comparison of the biological properties of nanomaterials obtained by different methods confirms the assumption that the effect of nanoparticles on biological organisms is not the same for each synthesis method. The main factor we take into account is the biogenicity of the metal, that is, the presence of biological functions.

Our research focus is to evaluate and present both the positive and negative aspects of nanoparticles, their impact on agricultural development, and their environmental sustainability. At the same time, emphasis is placed on the need for further research into the development of nanofertilizers aimed at improving food production and preserving the environment [5]. The key concept behind the use of nanomaterials is based on such considerations as the natural biogenicity of the metal, as well as the size and concentration of the nanoparticles. Meanwhile, it is proposed to consider one of the criteria of biological functionality to be the internal structure of a nanoparticle, which can consist of several elements and compounds, such as metal oxides, metals, and various organic substances. Short-term exposure to low concentrations of nanoparticles may have positive effects, while prolonged exposure to high concentrations may have negative effects. Specifically, silver, zinc, and copper in nanoparticle form may exhibit antimicrobial, antioxidant, and fungicidal properties.

The infusion of metals, such as silver, zinc, and magnesium, has been observed to stimulate the growth of micromycetes and inhibit the synthesis of polysaccharides and flavonoids. These results demonstrated a more than twofold stimulation of melanin due to the influence of silver particles. For the development of cereal crops, zinc is considered an important component, but at high concentrations, it can be toxic. The size of nanoparticles significantly affects the expected result of their use, but this is far from the only important factor in their usage.

The authors' previous research work has centered around nanoparticles' usage in the cultivation of legumes; leguminous oily crops have shown positive results. Foliar treatment of plants during the growing season contributes not only to an increase in yield, but also to the quality of grain, beans, or sunflowers. Therefore, this led to the choice of employing electrospark techniques to obtain nanomaterials. This method has a proven track record of producing biologically favorable forms of drugs, namely through the production of colloidal solutions of metals, which ensures the bioavailability of the drug and the convenience of its dosage. The aim of this research work is to obtain metal nanoparticles for use in the cultivation of winter wheat.

2. Materials and Methods

The method of generating electrical discharges consists of creating electrical discharges between electrodes, which causes certain chemical and physical reactions in the environment around them. During electric discharges, processes of combustion, melting, evaporation, and condensation of material occur, which ultimately leads to the formation of nanoparticles. Parameters such as the amount of electric power, discharge modes, chemical composition of the medium, and material can be controlled to obtain nanoparticles with certain properties. The electrospark synthesis method is used to produce a variety of nanomaterials, including metals, oxides, carbides, nitrides, etc., and has the potential to produce nanoparticles with different structures and properties.

To predict the chemical and biological effects of the interactions of nanoparticles with biological structures (cells) at the appropriate atomic and molecular level, detailed study of the physical properties and the structural and phase compositions of nanomaterials, as well as the physicochemical properties of systems that are carriers of such particles, is necessary. The method of production, which is based on the intense thermal and force effect on the starting material, has corresponding advantages and prospects, since it provides the production of nanoparticles with a high level of free energy and a high ability to interact with the environment.

Chemically pure starting materials (99.95% of the content was the corresponding metal) were used to obtain metal colloids, namely iron (Fe), copper (Cu), zinc (Zn), magnesium (Mn), and deionized water with an electrical conductivity of no more than 20–30 microSiemens (μS). No other chemicals were used for the synthesis of metal nanoparticles or other chemicals.

TEM was conducted with Hitachi HF-3300, FEI Titan 80–300, and JEOL JEM-100SXII transmission electron microscopes, and SEM was conducted with a MIRA3 TESCAN.

The phase composition nanoparticles were studied by X-ray diffraction analysis on a diffractometer Ultima-IV (Rigaku, Japan), based on the angular dependences of the intensities of the diffraction peaks of scattered monochromatic CuKα radiation. XRD recording was performed in the 2 h range of 10–90 with a scanning step of 0.04 or 0.05, with a count time of 1 s per step.

To obtain the appropriate size and shape of the nanomaterials and ensure the long-term chemical and biological activity of the preparations, the following method of electrical discharge dispersion of conductive materials was used (Figure 1, 1—discharge chamber, 2—air sprayer, 3—compressor, 4–5—metal granules, 6—discharge (plasma) channel, 7—discharge pulse generator, 8—electrodes-anode and cathode) [6–10].

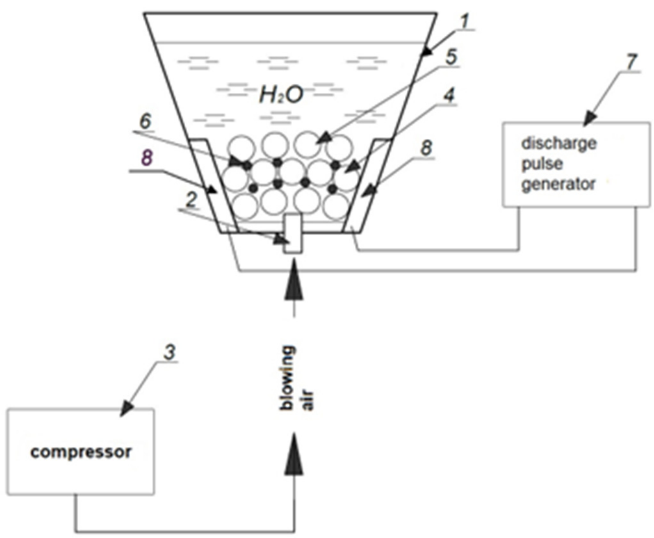

Figure 1. A scheme of the device for obtaining metal nanoparticles.

This method provides high temperatures in the local zones of plasma channel formation (from 8000 to 12,000 °C), which is sufficient for the melting and evaporation of any metal and alloy. To ensure the productivity of electrical discharge dispersion, a layer of conductive metal granules with maximum dimensions (5–10 mm) was used inside a discharge chamber made of dielectric material. With the help of a thyristor generator with capacitive energy storage, discharge pulses were formed, the amplitude of the voltage of which was regulated in the range of 40–220 V, and the current ranged from 30 to 150 A.

The system of metal granules and plasma channels immersed in a dielectric liquid and the ohmic contacts between them is a complex electrical load that has a significant nonlinear nature and significant parametric dependencies on several technological factors: discharge pulse frequency, flow velocity, and working fluid temperature [3–6]. In addition, the physical nature of the occurrence of spark discharges in the layer of conductive granules determines the stochastic migration of plasma channels along their surface and the switching of current flow paths to adjacent pairs of granules. The instantaneous values of the equivalent electrical resistance of such a medium vary from 0.05 to 100 ohms [8,11].

Spark discharges in the liquid between the metal granules cause electrical explosions, resulting in significant hydrodynamic pressure (104–106 MPa), under the influence of which liquid and gaseous metal are evacuated from the interelectrode gap and the surface of the electrodes [12]. As a result of these processes, polydisperse colloidal systems of the corresponding metals are formed.

The parameters of the discharge circuit were changed within the following limits: the capacitance of the working capacitor C = 25 ÷ 200 µF, the charge voltage of the capacitor Uz = 50 ÷ 250 V, and the inductance of the discharge circuit L did not exceed 1 µH. The dispersion process was carried out in a discharge chamber filled with deionized water.

3. Results and Discussion

During the research process, we studied the regularities of the electrospark dispersion of metals, which determines the synthesis of nanoparticles of biogenic elements [9–13]. Electron microscopy (SEM and TEM) and X-ray diffraction analysis of the metal phase of colloidal solutions were used to research the composition, structure, and average size of the obtained nanoparticles of various metals. The obtained preparations of metal nanoparticles made from Zn, Fe, Mn, and Cu were studied by X-ray diffraction analysis, scanning electron microscopy, and transmission electron microscopy (Figure 2). The morphology of the synthesized metal nanoparticles was studied using scanning and transmission microscopy [14–17]. Physical methods were used to isolate the nanoparticles in the dispersed phase from the dispersion medium. This study considered the fact that the substance in the dispersed state is prone to consolidation. This does not allow nanoparticles to be in a strictly isolated state. High-resolution transmission electron microscopy indicated that the nanoparticles of almost all the metals studied had a predominantly spherical shape, with linear dimensions of 5–10 nm. All detected metal nanoparticles with a size of 5–100 nm acquired the characteristics of 3D nanomaterials, according to the international classification.

Copper nanoparticles with sizes in the longitudinal direction of 100 nm and 30–50 nm in the transverse direction were synthesized in the form of elongated grains with sharp ends (Figure 2d). This is due to the high thermal conductivity of copper, since the formation of column crystals of nanoparticles is realized as a mechanism for crystallization in the solid phase.

Nanoparticles of iron group metals, in particular iron, Fe, and manganese, Mn, have a similar morphology in the dispersed phase, with distinct size ranges and crystal-like particles of regular shape in the range of 20–50 nm (Figure 3b). Each of these metal nanoparticles has a unique size; therefore, the scales outlined in Figure 3 are individual to each particle type. TEM analysis was conducted using three different electron microscopes—Hitachi, FEI, and JEOL.

Nanosized copper with a particle size of 5 to 10 nm, like most other metals, approximates a regular spherical shape (Figure 3a,c). At the same time, the internal structures of nanosized particles obtained by electrospark dispersion under the condition of rapid condensation of the vaporous state of the metal can be radically different. The absence of continuous translational symmetry of the crystal lattice is characteristic only for metal particles whose size does not exceed 10–20 nm.

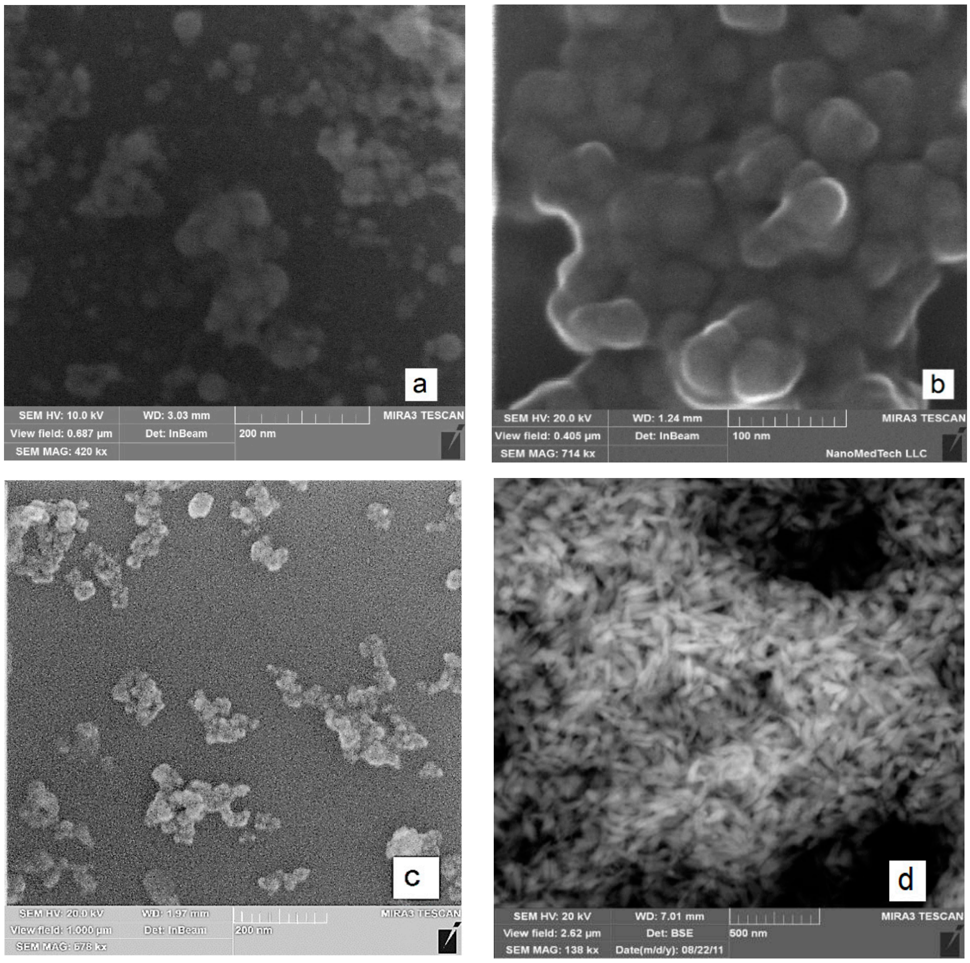

Figure 2. SEM of the nanoparticles of (**a**) zinc, Zn; (**b**) iron, Fe; (**c**) manganese, Mn; (**d**) copper, Cu.

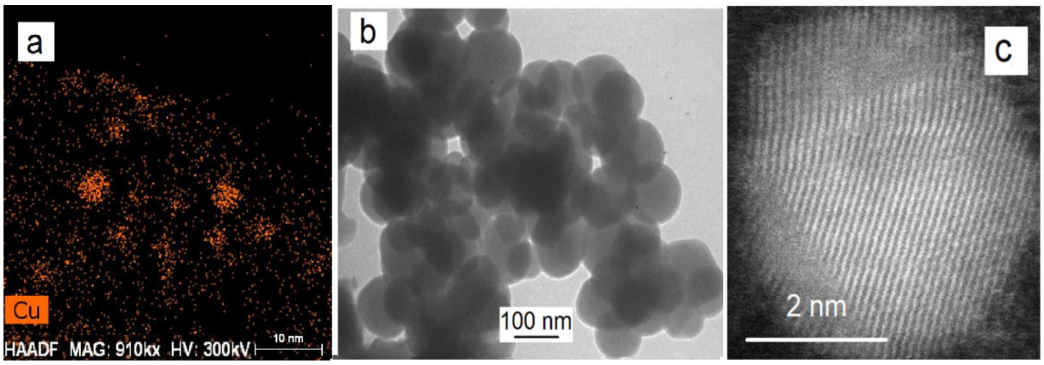

Figure 3. TEM of the particles of copper Cu from (**a**) Hitachi and (**c**) JEOL electron microscopes, and iron Fe from a (**b**) FEI electron microscope.

For metal nanoparticles with a size of 30–100 nm, such as iron, Fe, zinc, Zn, manganese, Mn, or copper, Cu, their internal structure is predominantly polycrystalline, and in some cases monocrystalline (Figure 2). The external morphological features of nanoparticles fit into the general regularities of the nanoscale fraction formed through spark erosion. Thus, on the surface of metal particles with dimensions of more than 30 nm, a swing film with a thickness of 5–10 nm is formed. At the same time, smaller particles, especially manganese and zinc, can be completely oxidized.

The results of X-ray diffraction analysis indicate the formation of a complex phase composition. The presence of an oxide phase is typical for all metals without exception, and can make up from 10 to 100% of the total volume of the nanoscale phase for different metals. For particles with a size of 5–20 nm, complete oxidation can occur, and their phase composition does not contain a metallic phase, only the corresponding oxides. An example is copper nanoparticles with an average size of no more than 20 nm. A metallic nucleus is not formed at all at such particle sizes, nor does oxidization occur during storage, given the colloidal state of nanoparticles produced by electrospark fusion in deionized water.

X-ray diffraction analysis has captured fragments of divalent oxide CuO and monovalent oxide Cu_2O. The absence of pronounced diffraction peaks, in the presence of the registration of individual fragments of oxide phases, may indicate a semi-amorphous state of the particles (Figure 4) that are formed during the process of electrospark synthesis. Analysis of the X-ray diffraction patterns of manganese particles shows that their phase composition corresponds to Mn3O4 oxide; the presence of other phases has not been detected. The metallic phase is also absent, which is due to the small sizes of the nanoparticles (20–30 nm) and crystallites (80 Å).

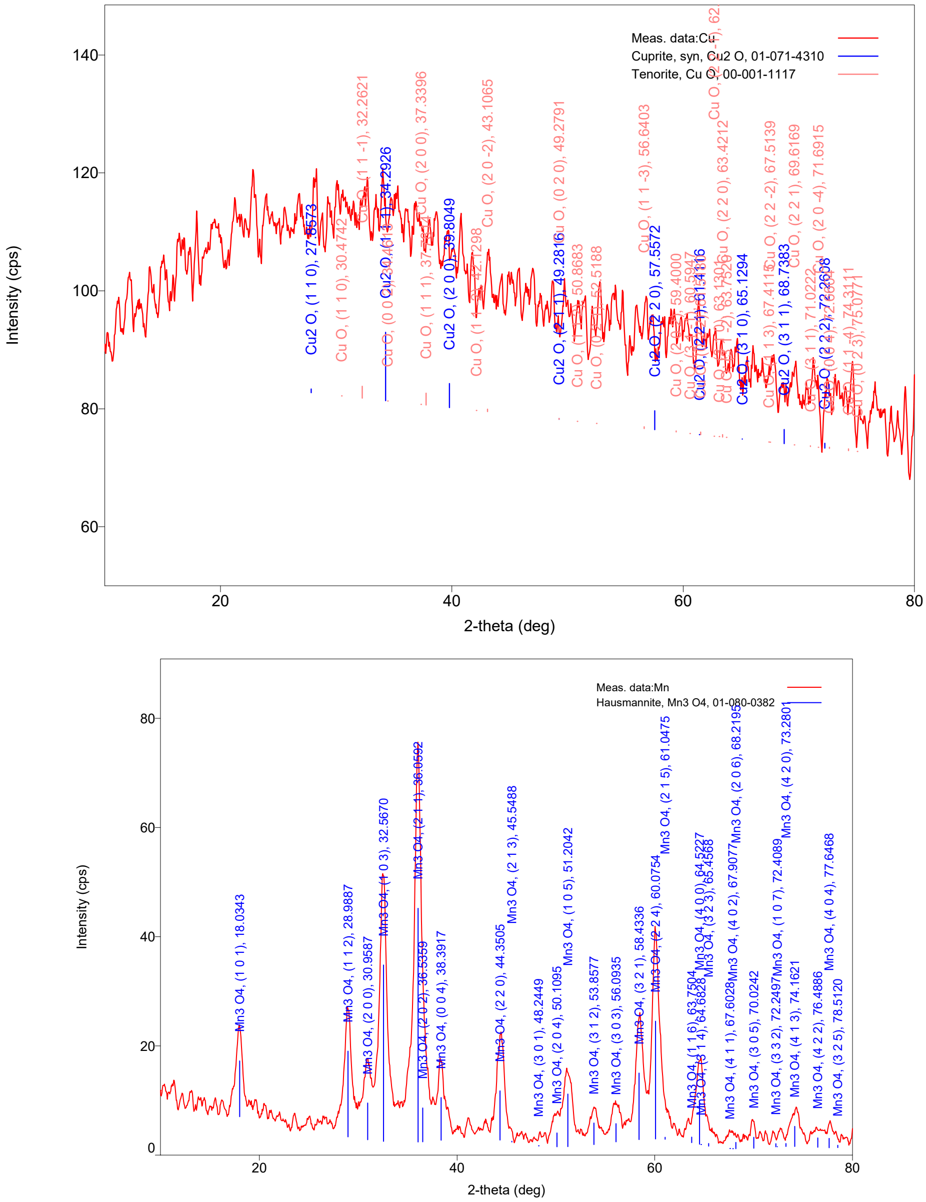

Figure 4. X-ray of copper (**top**) and manganese nanoparticles (**bottom**).

On radiographs of zinc and iron (Figure 5), in addition to the oxide phases, there are metallic phases for Zn (194: P63-mmc), Fe α (229: Im-3 m), and Fe γ (225: Fm-3 m). Separately, the presence of Fe γ as a metastable phase should be noted, as this significantly additionally affects the biological activity of iron nanoparticles (Table 1).

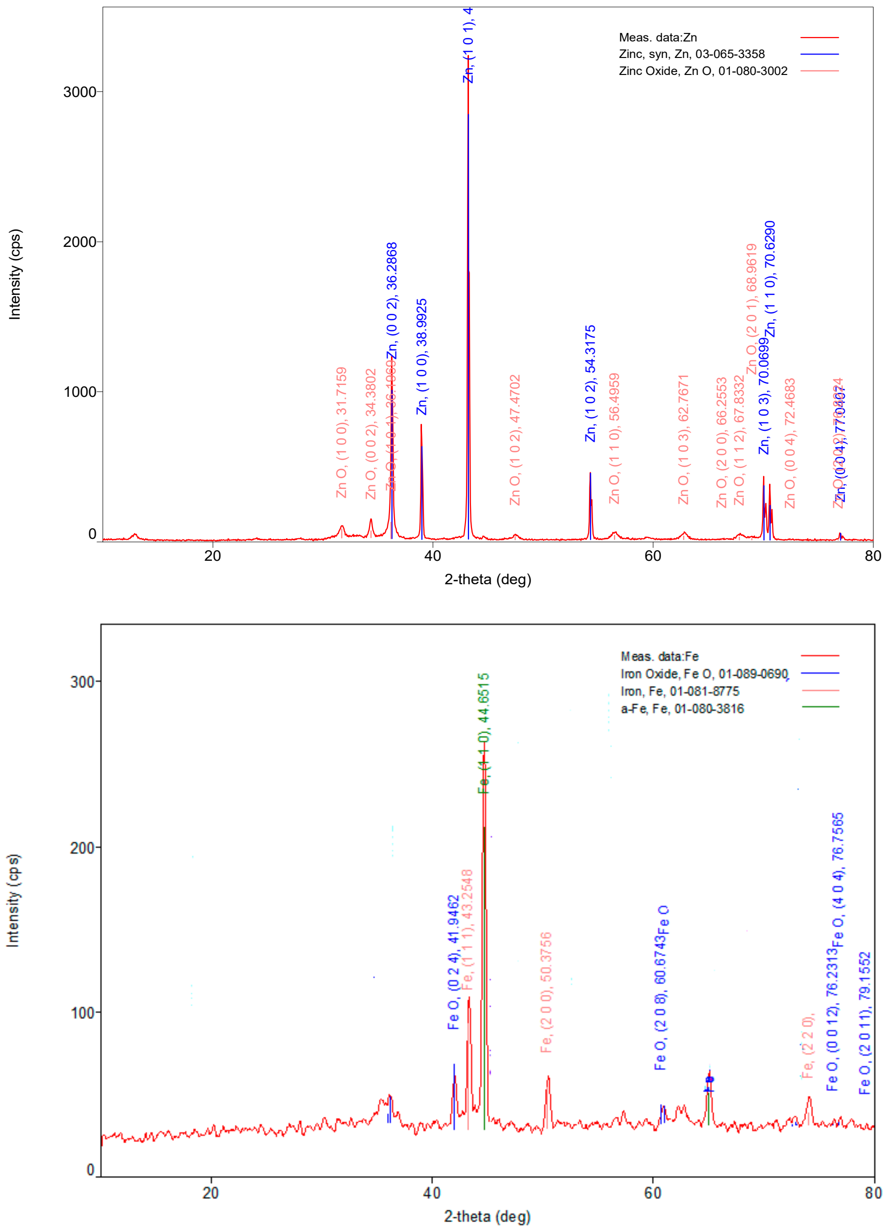

Figure 5. X-ray of zinc (**top**) and iron nanoparticles (**bottom**).

Table 1. Characterization of the formed phases of the metal nanoparticles.

Metal	Cu		Mn	Zn		Fe		
Phase	CuO	Cu_2O	Mn_3O_4	ZnO	Zn	FeO	Fe α	Fe γ
Space group	15: C12 /c1	224: Pn-3 m	141: I41 /amd	186: P63 mc	194: P63/mmc	148: R-3	229: Im-3 m	225: Fm-3 m
Crystallite size, Å	2.64	2.52	80	195	415	278	284	841
Content, %	80	20	100	24.1	75.9	34	46	20

Based on our own studies of the synthesis of nanosized metal particles by the method of electrospark dispersion in water, the following general structure of metal nanoparticles is proposed: the presence of a metal nucleus (under the conditions of a nanophase size greater than 30–40 nm and the chemical activity of the metal) and the formation of oxides in different oxidation states on the surface (Figure 6). The below diagram of the general structure of metal nanoparticles is novel and is based on the research work of the authors [18].

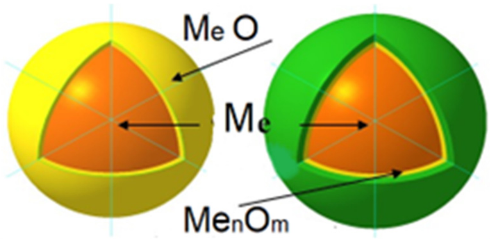

Figure 6. A diagram of the general structure of metal nanoparticles obtained by electrospark dispersion in an aqueous dispersion medium.

In our research, wheat was chosen as the primary agricultural crop, being one of the key crops determining food security [18–26]. As mentioned earlier, the main objective of using nanoforms of micronutrients such as iron, manganese, magnesium, copper, zinc, and other metals is to reduce the application rates of mineral components while preserving or increasing the agrotechnical effectiveness of their impact on plants compared to traditional forms of micronutrients, such as salt and chelate forms. The application rate of the prepared compound was 1–1.5 l/ha, and 1.0–1.5 L of the compound was diluted in 250 L of water. It has been established that the proposed technology increases grain yield and its quality indicators.

Using the treatment with metal nanoparticles at various stages of the organogenesis of winter wheat plants (Figure 7), we conducted a registration of the main morphological parameters of the plants. After the pre-treatment of the crops with working solutions and at an appropriate time (during changes in vegetation phase or organogenesis stage), the following morphological indicators were determined in the subsequent vegetation phase: root length, length, and leaf area.

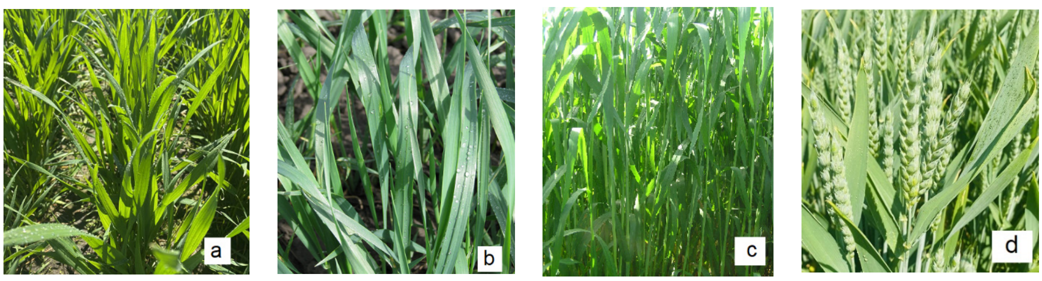

Figure 7. Vegetation phases during which morphological indicators were measured—(**a**) germination phase, (**b**) tillering phase, (**c**) phase of output to the tube, and (**d**) milk-wax ripeness phase.

Using laboratory biochemical methods, the total protein contents in the green mass and the grains were determined separately (at the milk-wax ripeness stage). At the stage of full maturity (Figure 7c,d), the content of gluten—a protein that essentially determines the nutritional value and variety (type) of wheat—was determined. The maturity state of each wheat sample was determined by visual assessment during each individual growth phase (germination, growth, and ripening of wheat grain).

At the same time, it is important to note changes in the quality indicators or nutritional value of the harvest grain—for example, an increase in gluten by more than two times, which can be considered a significant result of using metal nanoparticles in the cultivation of cereal crops, particularly winter wheat (Figure 8, Figure 8a depicts a vertical scale bar with 1 cm steps; the overall height of the plant sample in (a) equals 50 cm). Plant quality in each phase is determined visually, in comparison to a default sample.

Figure 8. Plants in the tillering phase—(**a**) experiment, (**b**) control, and plants in the full maturity phase of wheat—(**c**) control, (**d**) experiment.

The positive results of the study conducted by the authors are that the substance made based on nanomaterials that were obtained using the electric spark method provides positive results for all stages of plant growth and maturation, as well as their total protein content yield (Figures 7 and 8—comparisons of control samples with experimental ones are presented). The scientific novelty of this work lies in the study of the regularities of the electrospark synthesis of biogenic metal nanoparticles, and the optimization of the modes of obtaining the colloidal form of trace elements based on nanoparticles.

4. Conclusions

The presented technology—the electric spark method—can be considered ecologically and environmentally safe. It does not pose a threat to the environment, the agricultural sphere, or humans due to the probable biodegradation of the resulting products. Using the method of electron microscopy, it was established that the nanoparticles obtained by the electrospark method have a predominantly polycrystalline structure. At the same time, there are also particles with a single crystal structure and amorphous ones.

Laboratory studies and field tests have proven that this form of trace element is effective and provides economically valuable results, namely an increase in grain quality indicators in winter wheat. This research program included three treatments of winter wheat crops, and at the main stages of organogenesis, phenological studies were carried out, with comparisons between the vegetative organs of the plants from the experimental plots and those of the control plants. An increase in vegetative mass of 10–15% was established in the initial phases of vegetation, and at the time of full maturity, the difference in vegetative mass was at least 30% compared to the control.

Laboratory screening of the final harvest indicated increases in the main quality indicators of the winter wheat grain—namely, a total increase in protein in the green mass of 7.5%, an increase in gluten in the grain of 2.5 times, and an increase in yield of 33%—due to treatment with a complex compound (Fe—1800 ppm; Cu—400 ppm; Zn—1000 ppm; Mn—800 ppm) through nanoparticles containing the substances of the compound.

Considering the importance of the results obtained, especially in the context of food security, further research should be aimed at studying the mechanisms of exposure to nanoparticles in colloidal form, studying the threshold of their toxicity, and determining dose-dependent effects. The study of these issues will contribute to the development of an interesting and effective method of obtaining trace elements for crop production to ensure food security and the sustainable development of the agricultural sector.

Author Contributions: Conceptualization, K.L. and O.Z.; methodology, K.V.; software, V.N.; validation, K.L. and M.T.; formal analysis, O.Z.; investigation, K.V.; resources, V.N.; data curation, V.N.; writing—original draft preparation, K.L.; writing—review and editing, O.Z.; visualization, V.N.; supervision, O.Z.; project administration, V.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: These research results have been obtained thanks to the director of the "Basic scientific institute of materials science and research. E.O. Paton", and thanks to Igor Vladimirsky and Evgeniy Biba, who performed the X-ray structural analysis of the metal nanopowders.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Usman, M.; Farooq, M.; Wakeel, A.; Nawaz, A.; Alam Cheema, S.A.; Rehman, H.U.; Ashraf, I.; Sanaullah, M. Nanotechnology in agriculture: Current status, challenges and future opportunities. *Sci. Total Environ.* **2020**, *721*, 137778. [CrossRef] [PubMed]
2. Kobraee, S. Effect of foliar fertilization with zinc and manganese sulfate on yield, dry matter accumulation, and zinc and manganese contents in leaf and seed of chickpea (*Cicer arietinum*). *J. Appl. Biol. Biotechnol.* **2019**, *7*, 20–28. [CrossRef]
3. Joudeh, N.; Linke, D. Nanoparticle classification, physicochemical properties, characterization, and applications: A comprehensive review for biologists. *J. Nanobiotechnol.* **2022**, *20*, 262. [CrossRef] [PubMed]
4. Lopatko, S.; Chayka, V. The main ways for metal nanoparticles degradation. *Biol. Syst. Theory Innov.* **2022**, *13*, 87–95. [CrossRef]
5. Achari, G.A.; Kowshik, M. Recent Developments on Nanotechnology in Agriculture: Plant Mineral Nutrition, Health, and Interactions with Soil Microflora Developments on Nanotechnology in Agriculture: Plant Mineral Nutrition, Health, and Interactions with Soil Microflora. *J. Agric. Food Chem.* **2018**, *66*, 8647–8661. [CrossRef]
6. Meuller, B.O.; Messing, M.E.; Engberg, D.L.J.; Jansson, A.M.; Johansson, L.I.M.; Norlén, S.M.; Tureson, N.; Deppert, K. Review of spark discharge generators for production of nanoparticle aerosols. *Aerosol Sci. Technol.* **2012**, *46*, 1256–1270. [CrossRef]
7. Pichahchy, A.E.; Cremers, D.A.; Ferris, M.J. Elemental analysis of metals under water using laser-induced breakdown spectroscopy. *Spectrochim. Acta Part B At. Spectrosc.* **1997**, *52*, 25–39. [CrossRef]
8. Veklich, A.; Tmenova, T.; Zazimko, O.; Trach, V.; Lopatko, K.; Titova, L.; Boretskij, V.; Aftandiliants, Y.; Lopatko, S.; Rogovskiy, I. Regulation of biological processes with complexions of metals produced by underwater spark discharge. In *Nanooptics and Photonics, Nanochemistry and Nanobiotechnology, and Their Applications: Selected Proceedings of the 7th International Conference Nanotechnology and Nanomaterials (NANO2019), Lviv, Ukraine, 27–30 August 2019*; Springer International Publishing: Berlin, Germany, 2020; pp. 283–306. [CrossRef]
9. Tseng, K.H.; Chang, C.Y.; Chung, M.Y.; Cheng, T.S. Fabricating TiO_2 nanocolloids by electric spark discharge method at normal temperature and pressure. *Nanotechnology* **2017**, *28*, 465701. [CrossRef]
10. Vons, V.A.; de Smet, L.C.; Munao, D.; Evirgen, A.; Kelder, E.M.; Schmidt-Ott, A. Silicon nanoparticles produced by spark discharge. *J. Nanoparticle Res.* **2011**, *13*, 4867–4879. [CrossRef]
11. Sergiienko, R.A.; Ilkiv, B.I.; Petrovska, S.S.; Lopatko, K.G.; Lopatko, S.K.; Vinarchuk, K.V.; Hayasaka, Y.; Tomai, T.; Verkhovliuk, A.M.; Zaulychnyy, Y.V. Structure and properties of silicon nano-and microparticles obtained by electric-spark dispersion method. *Mol. Cryst. Liq. Cryst.* **2023**, *752*, 112–127. [CrossRef]
12. Han, K.N.; Kim, N.S. Challenges and opportunities in direct write technology using nano-metal particles. *KONA Powder Part. J.* **2009**, *27*, 73–83. [CrossRef]
13. Jamkhande, P.G.; Ghule, N.W.; Bamer, A.H.; Kalaskar, M.G. Metal nanoparticles synthesis: An overview on methods of preparation, advantages and disadvantages, and applications. *J. Drug Deliv. Sci. Technol.* **2019**, *53*, 101174. [CrossRef]
14. Tseng, K.H.; Lin, Y.S.; Lin, Y.C.; Tien, D.C.; Stobinski, L. Deriving optimized PID parameters of nano-Ag colloid prepared by electrical spark discharge method. *Nanomaterials* **2020**, *10*, 1091. [CrossRef] [PubMed]
15. Hammer, K.A.; Carson, C.F. Antibacterial and antifungal activities of essential oils. In *Lipids and Essential Oils as Antimicrobial Agents*; Wiley: Hoboken, NJ, USA, 2011; pp. 255–306. [CrossRef]
16. Zakharchenko, S.; Shydlovska, N.; Perekos, A.; Lopatko, K.; Savluk, O. Features of Obtaining of Plasma-Erosion Nanodispersed Silver Hydrosols and Their Bactericidal and Fungicidal Properties. *Metallofiz. I Noveishie Tekhnol.* **2020**, *42*, 829–851. [CrossRef]

17. Pradhan, A.; Seena, S.; Pascoal, C.; Cássio, F. Can metal nanoparticles be a threat to microbial decomposers of plant litter in streams? *Microb. Ecol.* **2011**, *62*, 58–68. [CrossRef]
18. Vynarchuk, K.; Lopatko, K.G. Effect of nanoparticles on morphological parameters of wheat. *Mol. Cryst. Liq. Cryst.* **2024**, *768*, 701–717. [CrossRef]
19. Thakur, S.; Thakur, S.; Kumar, R. Bio-nanotechnology and its role in agriculture and food industry. *J. Mol. Genet. Med.* **2018**, *12*, 1000324.
20. Mishra, S.; Singh, H.B. Biosynthesized silver nanoparticles as a nanoweapon against phytopathogens: Exploring their scope and potential in agriculture. *Appl. Microbiol. Biotechnol.* **2015**, *99*, 1097–1107. [CrossRef]
21. Chhipa, H. Applications of nanotechnology in agriculture. In *Methods in Microbiology*; Academic Press: Cambridge, MA, USA, 2019; Volume 46, pp. 115–142. [CrossRef]
22. Kale, S.K.; Parishwad, G.V.; Patil, A.S.H.A.S. Emerging agriculture applications of silver nanoparticles. *ES Food Agrofor.* **2021**, *3*, 17–22. [CrossRef]
23. Miazek, K.; Iwanek, W.; Remacle, C.; Richel, A.; Goffin, D. Effect of metals, metalloids and metallic nanoparticles on microalgae growth and industrial product biosynthesis: A review. *Int. J. Mol. Sci.* **2015**, *16*, 23929–23969. [CrossRef]
24. Cruz-Luna, A.R.; Cruz-Martínez, H.; Vásquez-López, A.; Medina, D.I. Metal nanoparticles as novel antifungal agents for sustainable agriculture: Current advances and future directions. *J. Fungi* **2021**, *7*, 1033. [CrossRef] [PubMed]
25. Maity, D.; Gupta, U.; Saha, S. Biosynthesized metal oxide nanoparticles for sustainable agriculture: Next-generation nanotechnology for crop production, protection and management. *Nanoscale* **2022**, *14*, 13950–13989. [CrossRef] [PubMed]
26. Fouda, M.M.; Abdelsalam, N.R.; El-Naggar, M.E.; Zaitoun, A.F.; Salim, B.M.; Bin-Jumah, M.; Allam, A.A.; Abo-Marzoka, S.A.; Kandil, E.E. Impact of high throughput green synthesized silver nanoparticles on agronomic traits of onion. *Int. J. Biol. Macromol.* **2020**, *149*, 1304–1317. [CrossRef] [PubMed]