GREEN SYNTHESIS OF NANO METAL OXIDES FOR AGRICULTURAL AND ENVIRONMENTAL APPLICATIONS

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Green Synthesis of Nano Metal Oxides for Agricultural and Environmental Applications

by

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Dedicated *to* My Grand Parents

Late (Shri) Ram Naresh & Shiv Baran Verma

The *reason* may be thy *light*….

CERTIFICATE

This is to certify that the thesis entitled **"Green synthesis of nano metal oxides for agricultural and environmental application",** being submitted by **Mr. Lahur Mani Verma** to the **Indian Institute of Technology Delhi** for the award of **"Doctor of Philosophy"** is a record of bonafide research work carried out by him. He has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis. To the best of our knowledge, the results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree or diploma.

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ABSTRACT

Recently, nanomaterial synthesis and application have entered a new realm of green synthesis and agricultural—environmental applications. The widespread problem of soil health, micronutrient deficiency and "low use efficiency" of conventional (bulk-regime) agrochemicals appears daunting in the face of increasing demand for food production in a climate-resilient and sustainable manner. Additionally, the global micronutrient deficiency in soil plant-continuum is translating into human population as "hidden hunger", which has drawn the public attention for its immediate solution.

This thesis, titled "Green synthesis of nano metal oxides for agricultural and environmental application", is centered around the utilization of sugar press mud (agro-industrial solid waste) for the green synthesis of nano metal oxides and extending its application toward the efficient and sustainable plant nutrition, as well as soil remediation.

The study starts by exploring the use of sugar press mud water extract in synthesizing wurtzite ZnO (P63mc), α-Fe2O3 and monoclinic CuO nanoparticles using base hydrolysis and in aqueous sol-gel process. The study evolves further into the screening of suitable metal precursor salts and comparison of PM water extract-based ligands with commercially available analytical grade surfactants. The study also attempted to identify the probable active chemical agent (capping agent) in PM extract.

Furthermore, the study about extending its application to agriculture and the environment includes experiments designed to study the interface of nano metal oxide with the biotic and abiotic components of the environment. First, the role of nano metal (Zn, Fe and Cu) oxides (MxOy) for sustainable and efficient crop nutrition was studied with randomised control block design (RCBD) pot trials using a soil matrix amended with 1.4% w/w dry sugar press mud and reinforced further with metal oxide NPs in the dose range of 10-100 mg/kg. Second, the nano

metal oxides were evaluated for their heterogenous photocatalytic potential in degrading the soil organic pollutant, i.e., RhB dye in aqueous medium using direct sunlight. Thirdly, these (MxOy) nanoparticles were also evaluated for their compatibility with agriculturally important fungi in a PDA-based food poison assay.

In summary, the green nano synthesis experiments confirmed the capping ability of the PM-based ligands and their anisotropic control by offering the nanoparticle of the smallest size of ~14 nm (ZnO) with the consistent morphology. The application of metal oxides (MxOy) as nano fertiliser has shown statistically significant ($p<0.05$) correlations with soil organic carbon (SOC) and various other agronomic parameters, as evidenced by the (~30-60%) increase in grain and biomass yield vis-a-vis significant mineral fortification. Also, the photocatalytic degradation of soil organic pollutant (RhB) by these nanoparticles has shown a rate constant (pseudo-first-order kinetics) of 0.03 to 0.7 min^{-1}. The interface studies of nanometal oxides (M_xO_y) with environmental biotic components targeted at the compatibility of nanomaterials with the fungi indicated no toxicity at the agriculturally operational dose (~0.2 mg/ml). However, findings suggested the possible exploration of ZnO and CuO NPs for their pesticidal value at (2.0 mg/ml) dose. Thus, this study offers a new pathway for the green synthesis of nanometal oxides (MxOy) by expanding the green nano synthesis to agri-waste utilization. In addition, this also provides crucial insights into the nano-regime agrochemicals with their environmental interface for sustainable crop nutrition and climate-resilient crop production.

सारांश

हाल ही में, नैनोमटेरियल संश्लेषण और अनुप्रयोग ने ग्रीन संश्लेषण और कृषि-पर्यावरणीय अनुप्रयोग के एक नए क्षेत्र में प्रवेश किया है। मृदा स्वास्थ्य, सूक्ष्म पोषक तत्वों की कमी और पारंपरिक (बृहद- प्रणाली) कृषि रसायनों की "कम उपयोग दक्षता" की व्यापक समस्या जलवायु-लचीले और धारणीय तरीके से खाद्य उत्पादन की बढ़ती मांग के सामने चुनौतीपूर्ण प्रतीत होती है। इसके अतिरिक्त, मिट्टी के पौधे-सातत्य में वैश्विक सूक्ष्म पोषक तत्वों की कमी मानव आबादी में "छिपी हुई भूख" के रूप में तब्दील हो जाती है, जिसने इसके तत्काल समाधान के लिए लोगो का ध्यान आकर्षित किया है।

"कृषि और पर्यावरण अनुप्रयोग के लिए "नैनो" धातु आक्साइड का हरित संश्लेषण" शीर्षक वाली यह थीसिस (शोध प्रबंध), नैनो धातु आक्साइड के हरित संश्लेषण के लिए सूगर प्रेस मड (कृषि-औद्योगिक ठोस अपशिष्ट) के उपयोग और पौधों के दक्षतापूर्वक तथा धारणीय पोषण, के साथ-साथ ही मिट्टी के उपचार की दिशा में इसके अनुप्रयोग विस्तार करने पर केंद्रित है। ।

अध्ययन क्षार हाइड्रोलिसिस का उपयोग करके और जलीय सोल-जेल प्रक्रिया में वर्टज़ाइट ZnO ($P63_{mc}$), α-(Fe_2O_3) और मोनोक्लिनिक (CuO) नैनोकणों को संश्लेषित करने में सूगर प्रेस मड के पानी के अर्क के उपयोग की खोज से शुरू होता है। अध्ययन उपयुक्त धातु अग्रदूत लवणों की स्क्रीनिंग और व्यावसायिक रूप से उपलब्ध विश्लेषणात्मक ग्रेड सर्फेक्टेंट के साथ पीएम जल अर्क-आधारित लिगैंड की तुलना करने में विकसित होता है। अध्ययन में पीएम अर्क में संभावित रासायनिक एजेंट (सक्रिय कैपिंग एजेंट) की पहचान करने का भी प्रयास किया गया।

इसके अलावा, कृषि और पर्यावरण में इसके अनुप्रयोग को विस्तारित करने के अध्ययन में पर्यावरण के जैविक और अजैविक घटकों के साथ नैनो मेटल ऑक्साइड के इंटरफेस का अध्ययन करने के लिए डिज़ाइन किए गए प्रयोग शामिल हैं। सबसे पहले, दक्षतापूर्वक तथा धारणीय फसल पोषण के लिए नैनो धातु (Zn, Fe और Cu) ऑक्साइड (MxOy) की भूमिका का अध्ययन 1.2% w/w सूखी सूगर प्रेस मड के साथ संशोधित मिट्टी मैट्रिक्स का उपयोग करके यादच्छिक नियंत्रण ब्लॉक डिजाइन (RCBD) पॉट परीक्षणों के साथ किया गया था। 10-100 मिलीग्राम/किग्रा की खुराक सीमा में मिट्टी और धातु ऑक्साइड नैनोकणों के साथ प्रबलित। दूसरा, नैनो धातु ऑक्साइड का मूल्यांकन मिट्टी के कार्बनिक प्रदूषक, यानी, सीधे सूर्य के प्रकाश का उपयोग करके जलीय माध्यम में आरएचबी डाई को कम करने में उनकी विषम फोटोकैटलिटिक क्षमता के लिए किया गया था। तीसरा, इन (एमएक्सओवाई) नैनोकणों का पीडीए-

आधारित खाद्य जहर परख में कृषि की दृष्टि से महत्वपूर्ण कवक के साथ उनकी अनुकूलता के लिए भी मूल्यांकन किया गया था।

संक्षेप में, हरित नैनो संश्लेषण ने सुसंगत आकारिकी के साथ ~14 एनएम (जेडएनओ) के सबसे छोटे आकार के नैनोकण की पेशकश करके पीएम-आधारित लिगैंड की कैपिंग क्षमता और उनके अनिसोट्रोपिक नियंत्रण की पुष्टि की। नैनो उर्वरक के रूप में धातु ऑक्साइड (एमएक्सओवाई) के अनुप्रयोग ने मिट्टी के कार्बनिक कार्बन (एसओसी) और विभिन्न अन्य कृषि संबंधी मापदंडों के साथ सांख्यिकीय रूप से महत्वपूर्ण (पी <0.05) सहसंबंध दिखाया है, जैसा कि अनाज और बायोमास में (~ 30-60%) वृद्धि से प्रमाणित है। महत्वपूर्ण खनिज सुदृढ़ीकरण की तुलना में उपज। इसके अलावा, मृदा कार्बनिक प्रदूषक (आरएचबी) के फोटोकैटलिटिक क्षरण ने 0.0345 से 0.7624 मिनट-1 की दर स्थिरांक (छद्म-प्रथम-क्रम बलगति विज्ञान) दिखाया है। कवक के साथ नैनोमटेरियल की अनुकूलता पर लक्षित पर्यावरणीय जैविक घटक के साथ नैनोमेटल ऑक्साइड (एमएक्सओवाई) के इंटरफ़ेस अध्ययन ने कृषि परिचालन खुराक (0.2 मिलीग्राम / मिलीलीटर) पर कोई विषाक्तता नहीं होने का संकेत दिया। हालाँकि, निष्कर्षों ने (2.0 ग्राम/मिलीलीटर) खुराक पर उनके कीटनाशक मूल्य के लिए ZnO और CuO NPs की संभावित खोज का सुझाव दिया। इस प्रकार, यह अध्ययन कृषि-अपशिष्ट उपयोग के लिए नैनो संश्लेषण का विस्तार करके नैनोमेटल ऑक्साइड (एमएक्सओवाई) के हरित संश्लेषण के लिए एक नया मार्ग प्रदान करता है। इसके अलावा, यह धारणीय फसल पोषण और जलवायु-लचीला फसल उत्पादन के लिए उनके पर्यावरणीय इंटरफेस के साथ नैनो-शासन कृषि रसायनों में महत्वपूर्ण अंतर्दृष्टि भी प्रदान करता है।

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ABBREVIATIONS

°C	Degree centigrade
µg	Microgram
µL	Microlitre
µM	Micro molar
ANOVA	Analysis of variance
Cm	Centimetre
M	Molar
DMRT	Duncan's new multiple range test
USDA	United State Department of Agriculture
ESI	Electron spray ionization
DW	Dry weight
FAO	Food and Agriculture Organization
Fig.	Figure
FT-IR	Fourier transform infrared spectroscopy
PM	Sugar press mud
T	Temperature
LC-MS	Liquid chromatography mass spectrophometer
h or hr	Hour
NPS	Nanoparticles
HR-LCMS	High-resolution liquid chromatograph mass spectroscopy
ICAR	Indian Council of Agricultural Research
UNDP	United Nations Development Program
ITCC	Indian type culture collection
Kg	Kilogram
L	Liters
PMWE	Press mud water extract
SDG	Sustainable Development Goal
ML	Milli litre
Mg	Milligram
WHO	World Health Organisation
Min	Minutes
Mm	Millimetre
Nm	Nanometers
UN	United Nations
CN	Carbon Nitrogen
PDA	Potato dextrose agar
INR	Indian Rupee

PO	Peroxidase
SOM	Soil organic matter
SOC	Soil organic carbon
RMSD	Root-mean-square deviation
RPM	Revolutions per minute
s /sec	Seconds
SD	Standard deviation
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
HR-TEM	High Resolution Transmission Electron Microscopy
UV	Ultraviolet
DRS	Diffuse reflectance spectroscopy
XPS	X-ray photoelectron spectroscopy
DLS	Dynamic light scattering
NTA	Nanoparticle tracking analyzer
CT	cetyltrimethylammonium bromide
MC	Methyl cellulose
ZNAH	ZnO nanoparticles using simple acid hydrolysis
ZNBH	ZnO nanoparticles using simple base hydrolysis
ZNMC	ZnO nanoparticles with methylcellulose as capping agent
ZNCT	ZnO nanoparticles with cetyltrimethylammonium bromide as capping agent
ZNPM	ZnO nanoparticles with sugar press mud water extract as capping agent
FEAH	Iron oxide nanoparticles using simple acid hydrolysis
FEBH	Iron oxide nanoparticles using simple base hydrolysis
FEMC	Iron oxide nanoparticles with methylcellulose as capping agent
FECT	Iron oxide nanoparticles with cetyltrimethylammonium bromide as capping agent
FEPM	Iron oxide nanoparticles with sugar press mud water extract as capping agent
CUAH	CuO nanoparticles using simple acid hydrolysis
CUBH	CuO nanoparticles using simple base hydrolysis
CUMC	CuO nanoparticles with methylcellulose as capping agent
CUCT	CuO nanoparticles with cetyltrimethylammonium bromide as capping agent
CUPM	CuO nanoparticles with sugar press mud water extract as capping agent
NPS	Nanoparticles
MXOY	Metal oxides
EC	Electrical conductivity,
DTA	Diethylenetriaminepentaacetic Acid,

HDD	Hydrodynamic diameter
NMR	Nuclear magnetic resonance
EDTA	Ethylenediaminetetraacetic acid
DTPA	Diethylenetriamine pentaacetate
λ	Lambda (wavelength)
ν	Nu (frequency)
h	Planck constant
θ	Theta (angle)
β	Beta (full width at half maxima)
α	Alpha
Δ	Delta (heat)
ζ	Zeta (surface charge on NPs)
eV	Electron volt
γ	Gamma