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Enhanced Efficiency Zn Coated Urea to Reduce the N_2O Emissions and Increasing the Crop Growth

The Thesis of the PhD dissertation

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INTRODUCTION AND OBJECTIVES

Nitrogen (N) is the most abundant and vital nutrient in plants. It is a central part of several compounds, such as proteins and nucleotides (Xie et al., 2022). Therefore, it plays a significant role in the growth and development of plants. Apart from the crops that can fix the N from the atmosphere, e.g., legumes, all other non-leguminous plants need N (20-50 g) to produce about 1 kg of biomass (Xu et al., 2012; Xie et al., 2021). External N application in the agroecosystem is necessary to sustain crop yield and production (Umar et al., 2020).

To meet the growing population's global food demand, a significantly higher amount of N is applied as chemical fertilizers in the agroecosystem (Wang et al., 2021c). During the green revolution period (1960-2009), synthetic N fertilizers were used extensively for producing maize, rice, and wheat (Yang et al., 2017). According to Galloway et al. (2008), the global utilization of N fertilizers is about 1.5×10^8 t annually. It is regrettable that currently, the nitrogen use efficiency (NUE) is very low (30-50%) in the agroecosystem (Umar et al., 2020; Wang et al., 2021c). In the modern agricultural system, about 50-70% of the applied N in the form of synthetic fertilizers is lost in the environment (Ladha et al., 2005; Umar et al., 2022), leading to substantial economic losses of about 81 million US dollar annually (Subbarao et al., 2012). Apart from the losses in the field, the production of chemical N fertilizers by the Haber-Bosch process consumes about 3-5% of global natural gas annually (Harindintwali et al., 2021). That natural gas consumption releases about 450 million tons of carbon dioxide (CO_2) every year, equivalent to the 1% emissions by humans (Service, 2019; Harindintwali et al., 2021).

Agriculture is one of the major contributors to N_2O emissions, a potent greenhouse gas playing a significant role in global warming and ultimately in climate change (Reay et al., 2012; Umar et al., 2022). It is reported that N_2O has 296 times higher global warming potential than CO_2 over 100 years (Xie et al., 2019). Nitrification and denitrification are the major processes in producing N_2O from agricultural soils. The production of N_2O increases when a higher amount of N fertilizer is applied compared to the crop requirement (Thangarajan et al., 2018; Machado et al., 2020). According to the Intergovernmental Panel on Climate Change (IPCC), nitrogen fertilizers are considered a source of N_2O emissions suggesting an emission factor (EF) of 1.6% as compared to 0.6% for crop residues under similar circumstances (IPCC, 2019). Over the last three decades, the concentration of N_2O is increased at the rate of 0.73 ppb yr^{-1} in the atmosphere (Stocker et al., 2013). More than 50% of the global N_2O is emitted from the agricultural fields receiving N fertilizers (Tian et al., 2020). Agricultural practices such as the amount of N applied, method of application and soil moisture contents significantly influence the N_2O emission (Liu et al., 2017). The response of N_2O emission is not always linear as it highly depends on the amount of fertilizer applied. Field studies reported that N_2O emission response was non-linear when a higher amount of N fertilizer was used compared to the crop needs (Song et al., 2018; Signor et al., 2013).

Adopting relevant management practices is necessary to overcome the above-mentioned fertilizer losses and environmental hazards. The 4R strategy needed to be adapted to reduce the loss of nutrients, increase plant utilization, and ultimately increase crop yield and production. From the 4R system, the “Right source/fertilizer” is one of the main components. It has been found that slow-release fertilizers (SRFs) and controlled-release fertilizers (CRFs) have already gained much attention from farmers and researchers (Rahman et al., 2021). The SRFs are known for the slow release of nutrients but the nutrient release factors such as period, pattern, and rate are uncontrollable and mostly depend on the soil conditions, weather, storage, and transportation (Rajan et al., 2021).

As we know, there are 18 essential nutrients for plants, and from them, some are required in higher quantities, known as a macronutrient (Umar et al., 2021). One of the macronutrients we discussed above is N, but some elements are required in minimal quantities and are known as micronutrients. Even though they are needed in smaller amounts, their deficiency can affect plant growth and development like a macronutrient deficiency. Of those micronutrients, Zinc (Zn) is one of the vital and essential nutrients in the soil-plant system as it contributes to several bio-physical roles (Nriagu, 2019; Castillo-Gonzalez et al., 2018). Zn is categorized in the elements required in trace amounts and is highly important to carry out normal metabolic functions (Sturikova et al., 2018). However, the higher concentration of Zn can be lethal to the living organism as it becomes toxic above optimal limits (Nriagu, 2019; Natasha et al., 2022, Niragu, 2007). Therefore, it is crucial to supply Zn at optimal concentration for sustainably carrying out the metabolic task without causing its toxicity and deficiency (Sturikova et al., 2018).

As an essential plant nutrient, Zn participates in several Physico-chemical and biological processes (Noman et al., 2019). Zn is necessary for activating more than 300 enzymes because it is one of the main structural components of all six classes of enzymes (McCall et al., 2000; Natasha et al., 2022). Because it is an integral part of the enzymes like superoxide dismutase (SOD), Zn plays a significant role in cellular defence mechanisms by tackling the free radicals (Castillo-Gonzalez et al., 2018). The other vital functions of Zn in plants include the synthesis of proteins, regulation of gene expressions, involvement in carbohydrate and phosphate metabolism, and along with that, it is the structural part of bio-membranes (Noman et al., 2019; Sturikova et al., 2018). Hence, the deficiency of Zn can hamper all these biological and physical processes in plants.

Nanoparticles (NPs) are materials that have particles size ranging from 1 to 100 nm (Reda et al., 2021; El-Saadony et al., 2021). The NPs possess properties different than the bulk materials. Previous studies reported that NPs have better Physico-chemical and biological properties as compared to bulk materials (Adhikari et al., 2020). The application of NPs as a fertilizer improved plant growth and development (Dimkpa and Bindraban, 2016).

In addition to the chemical nano-fertilizers, the use of naturally occurring clay materials such as zeolite and bentonite as a fertilizer/nutrient carrier is gaining importance. These clay materials are famous for their higher absorption capacity and CEC and slow-release properties (Umar et al., 2022). The major portion of bentonite consists of the clay mineral montmorillonite. Bentonite can be used for the improvement of the sandy soils, where it can increase the macro-micronutrients, CEC of the soil, and organic carbon (Semalulu et al., 2017; Czaban et al., 2014).

Objectives

This study specifically embarks on the following objectives:

1. Synthesis and characterization of ZnO NPs and Zn fortified nano-bentonite
2. Development and characterization of Zn fortified nano-bentonite and ZnO NPs coated slow-release urea fertilizer using different binding materials (stearic acid and paraffin wax)
3. Evaluation of Zn and N release characteristics from slow-release macro-micronutrient fertilizer
4. Evaluation of the dissolution of ZnO NPs, and $ZnSO_4$ in two different soils
5. Evaluation of N_2O emission from coated and uncoated urea fertilizer under bare and planted soil conditions
6. Evaluating the comparative effect of coated and uncoated urea on plant growth and development

MATERIALS AND METHODS

Soil samples were collected from two sites. The first site was Atkár, located in the north of Hungary in the Gyöngyös district (47°42'24.5"N 19°54'35.6"E). The second sampling site was Gödöllő Szárítópuszta located in the central part of Hungary in Pest county (47°34'41.8"N 19°24'11.6"E). The Physico-chemical characteristics of the soils were as follows: Atkár soil (Texture: silty clay. Organic matter: 1.36%, EC: 0.0634 dSm^{-1}, pH: 7.10, Zn: 3.16 mg kg^{-1}); Gödöllő Szárítópuszta soil (Texture: sandy loam. Organic matter: 3.67%, EC: 0.095 dSm^{-1}, pH: 8.80, Zn: 2.85 mg kg^{-1}).

Preparation of ZnO NPs

A method presented by He et al. (2019) was adopted with modifications for the preparation of ZnO NPs (Figure 10). KOH and $ZnSO_4$ were used as a precipitating agent and Zn source respectively. Equal concentration (0.2 M) solutions were prepared of KOH and $ZnSO_4$ in 200 mL beakers. In the next step, the KOH solution was added to a 500 mL beaker and the beaker was placed on a magnetic stirrer. The solution of $ZnSO_4$ was added dropwise in KOH solution using a burette during vigorous stirring. The shaking was continued for 3 hours after the complete mixing of the $ZnSO_4$ solution in the KOH solution. After stirring the suspension was left for settling. The filtration was carried out using filter paper followed by washing of precipitates using distilled water and in the end with ethanol to remove all the impurities. The washed precipitates were then dried in an oven at 80 °C until the moisture was removed completely. The dried precipitates were ground into powder form using mortar and pastel. The ground powder was calcined in the furnace for 2 hours at 250 °C.

Zn adsorption potential of nano-bentonite

The batch adsorption method was used to evaluate the Zn sorption characteristics of nano-bentonite. $ZnSO_4.7H_2O$ was used to prepare Zn solutions of different concentrations (0-640 ppm with a difference of 40 ppm). Briefly, 1g of nano-bentonite was taken in 50 mL centrifuge tubes and 40 mL of Zn solution of different concentrations was added to the tubes. The tubes were then shaken on a rotary shaker for 2 hours followed by centrifugation at 5000 rpm for 20 minutes. The supernatant was then filtered using Whatman No.42 filter paper (0.25 µm). The filtrate was analyzed on atomic absorption spectrophotometer (AAS) (PERKIN-ELMER, 303, USA) at 213.9 nm wavelength with a slit width of 1.0 nm for Zn concentration. Standard reference material was used to calibrate the instrument. The Zn adsorption potential of nano-bentonite was evaluated by fitting different adsorption isotherms such as the Langmuir model, the Freundlich model, and the newly developed model for multilayer adsorption.

Adsorption models such as the ***Langmuir model***, ***Freundlich model,*** and ***New multi-layer adsorption models*** were to evaluate the maximum adsorption potential of nano-bentonite.

Preparation of Zn fortified nano-bentonite

For the fortification of nano-bentonite with Zn, a method presented by Yuvaraj and Subramanian (2018) was adopted with slight modifications (Figure 11). A Zn solution was prepared in a 250 mL beaker by dissolving 30 g $ZnSO_4.7H_2O$. In another 250 mL, beaker nano-bentonite was homogenized using distilled water. The Zn solution and the homogenized nano-bentonite were then transferred to a 500 mL beaker and the walls of the other two beakers were rinsed with distilled water. The material of both beakers was mixed in a 500 mL beaker and a 1-2 cm layer of distilled water was maintained on the surface. The sonication of the mixture was carried out for 3 hours in a sonication bath. After sonication, the extra solution was removed with the help of a vacuum pump. The remaining clay was dried in an oven at 35 °C until all the moisture was lost.

Preparation of Zn coated urea

Urea was coated with stearic acid, paraffin wax, and Zn fortified nano-bentonite (or) ZnO NPs (Figure12). The process was as follows, in the first step approximately 9 g of stearic acid was melted in a wide-mouth glass bottle and then the botel was let to cool down till ~50 °C, and then 50 g of urea and 3 g of Ca $(OH)_2$ was added and mixed until the free-flowing granules were obtained. The stearic acid-coated urea granules were left for 24 hours and then coated with paraffin wax. For paraffin wax coating 3g of wax was melted and mixed with urea along with Ca $(OH)_2$. In the last step Zn-fortified, nano-bentonite/ZnO NPs were coated on stearic acid+paraffin wax-coated urea granules by using paraffin oil as a binding material. Approximately 2 g of Zn fortified nano-bentonite or 1 g of ZnO NPs were used for the coating on 50 g of urea granules making it a coating of 4% Zn fortified nano-bentonite and 2% ZnO NPs.

Table 1: Chemical composition of prepared materials

Elements	**Zn fortified nano-bentonite**	**Zn fortified nano-bentonite-coated urea**	**ZnO NPs coated urea**
Zn	24.97%	1.03%	2.1%
S	17.09%	0.18%	0.57%
Si	12.67%	0.44%	0.75%
Al	4.05%	0.23%	0.27%
K	1.045%	---	0.05%
Fe	0.56%	0.05%	0.096%
P	190 ppm	---	---
Cu	70 ppm	---	---
Co	58 ppm	---	---
Mn	101 ppm	---	---
Ca	---	0.7%	0.82%
N	---	42.3%	41.8%

Characterization

X-ray powder diffraction technique was used to determine the size of the crystals of ZnO NPs and nano-bentonite. For this purpose, an X-ray diffractometer (Rigaku Ultima IV) was used which was equipped with Bragg-Brentano geometry, CuKα radiation, graphite monochromator, proportional counter, divergence, and detector slits of 2/3° were used to measure the samples. The specimens were scanned at 50 kV/40 mA from 3 to 80° 2θ with a goniometer step rate of 1°/min and data acquisition steps of 0.02°. Instrumental line broadening was determined by using an in-house silicon standard. The sharpest reflection measured for these bulk powder samples was 0.100° and the narrowest FWHM value measured on the silicon standard was 0.040°. Match! 3 software was used to evaluate the XRPD spectra.

Evaluation of N and Zn release from coated urea

Nitrogen and Zn release characteristics from slow-release Zn coated urea was evaluated through an incubation experiment. The experiment was set up using sandy loam soil. The soil's Physico-chemical characteristics are given in the Table 3. Briefly, 50 g of soil was weighed in 150 mL plastic cups. The equal size (2 mm) urea granules (0.5 g) coated with Zn fortified nano-bentonite and ZnO NPs were placed in the cups below a 5 cm layer of soil. The urea granules without coating were used as a control treatment. Treatments were applied following a completely randomized design (CRD). The soil was moistened using distilled water and the moisture contents were maintained at 60% of the field capacity throughout the experiment. After applying the water, the weight of the cups was noted, and the moisture was maintained by weighing the pots every second day. To minimize the soil disturbance and to make the sampling process easy separate cups were used for each time sampling. The samples were collected every 5th day (0, 5, 10, 15, 20, 25, and 30 days). The soil samples were extracted for N by using 2M KCl and for Zn 0.05M EDTA.

Evaluation of the pore water solubility of ZnO NPs

Approximately, 200 g of air-dried soil was weighed in plastic pots. ZnO NPs of two sizes (small size and large size) were used. ZnO NPs were added in the form of suspension at a concentration of 500 mg L^{-1}. While the $ZnSO_4$ was added in the form of solution at the same concentration. 30 mL volume of suspension and solution was added to each pot. The experiment was replicated thrice. The CRD-factorial design was followed. The suspension of NPs was prepared by sonicating the required amount of ZnO NPs in distilled water for 10 min using a sonication bath. The added amount of suspension and solution were mixed completely with the soil using a spatula. After mixing the weight of every pot was noted and the moisture contents were maintained at 80% of the field capacity. The moisture loss was compensated every second day by adding distilled water. The aluminum foil was used to cover the samples with perforation to allow air exchange. The incubation was carried out for 7 days and 14 days. The soil samples without Zn spiking were used as a control treatment.

Leaching of incubated soil

To evaluate the solubility of ZnO NPs and $ZnSO_4$ in water, column leaching of the soil was carried out. For this purpose isocratic pump (ECOM, KAPPA 10, Czech Republic) attached to a steel, column was used. The specifications of the column were as follows: the volume of the column was 91 mL, the width was 2.2 cm and the length of the column was 24 cm. The eluent volume for leaching was pre-optimized. To perform the leaching the column was filled with Zn spiked soil and the upper and bottom caps were tightened. The upper cap of the column includes an inbuilt filter and both sides of the column also contain the spacer. The flow rate of the water was set at 1 mL per minute and the water was pumped from the bottom of the column to achieve the full saturation of the soil. The elute was collected from the upper part of the column and in each cycle, 5 mL of the volume was collected and around 40 mL of total elute was collected for each sample. The collected elute was centrifuged for 35 min at 5000 rpm at room temperature for the separation of leached ZnO NPs. The samples were filtered using 0.20 µm syringe filters and a few drops of concentrated HNO_3 were added to each sample. The samples were then analyzed for Zn concentration on AAS. Zn from the soil matrix was extracted using 0.05 M EDTA solution.

Evaluation of the nitrous oxide emission from bare soil

The nitrous oxide emission potential of uncoated and coated urea from unplanted soils was evaluated through a laboratory experiment. Two types of soil silty clay and sandy loam were used in this experiment. Open-ended plastic tubes were used to incubate the soil. The tubes contain the lids on both the lower and upper sides. The diameter, length, and volume of the tube were 10.2 cm, 15 cm, and 1225 cm^3 respectively. Approximately 2 kg of soil was used in each tube. The uncoated urea, Zn fortified nano-bentonite coated urea and ZnO NPs coated urea was applied at the rate 0.25 g N per tube. The fertilizer was completely mixed with the soil and the soil was then filled in the tubes. The soil without fertilizer was used as a control treatment. The tubes were arranged following a CRD-factorial design. The moisture contents in the soil were calculated. The added amount of water was calculated on a volumetric basis and the moisture contents already present in the soil were subtracted from the added amount of water. The water contents were calculated to achieve the 80% of the field capacity of the soils.

Evaluation of nitrous oxide emission from planted soil

The nitrous oxide emission potential of uncoated and coated urea from planted soils was evaluated through a laboratory experiment. Two types of soil silty clay and sandy loam were used in this experiment. Wheat was used as a test crop. The crop was planted in trapezoidal plastic pots. The dimensions of the pots were as follows: length 16 cm, width 15.5 cm, and volume 3968 cm^3. Around 6 kg of ground and sieved soil was added to each pot. A plastic tube chamber was placed in the center of the pot and two rows of the wheat crop were planted on both sides of the chamber. Nitrogen treatments were applied at the rate of 0.73 g N per pot in two split doses. The first dose was applied at the time of sowing and the second dose of N fertilizers was applied at the 5th leave stage of the crop. The potassium (MOP) and phosphorus (Superphosphate) were applied at the time of sowing at a recommended rate. The experiment was carried out following the Completely Randomized Design with factorial treatments. The soil moisture contents were maintained at 80% of the field capacity. The moisture loss was compensated by adding distilled water daily. Day and night conditions (12 hours) were maintained by using growing lamps (Mars Hydro, MH-150MA-41B, LG LED Solutions Ltd, China).

Flux measurement and calculation of cumulative N_2O emission

Nitrous oxide flux measurement was started right after adding water to the tubes. A nitrous oxide analyzer was used to measure the flux. The instrument worked on a principle of infrared correlation (NDIR). The flux measurement was carried out for 20 min for each sample. To calculate the flux the measurement data points were plotted using time on one axis and N_2O concentration on the other axis and a linear regression line were fitted to get the slope value. The N_2O emission flux (µg N m^{-2} hr^{-1}) was calculated using the following equation:

$$F = {\Delta N_2O \times 2 \times AN \times Vch \times f} \big/ {Vm \times Ach \times t}$$

Where F is the flux, ΔN_2O is the slope of the N_2O mixing ratio during sampling, AN is the atomic weight of N, Vch is the chamber volume (m^3), f is the factor, Vm is the molar volume (L), Ach is the soil surface covered by the chamber, t is sampling time.

The cumulative N_2O emission (kg N ha^{-1} yr^{-1}) was calculated using the following equation:

$$T = \frac{\sum_{i=1}^{n}(X_i + X_{i+1})}{2(t_{i+1} - t_i)} \times 24 \times 360 \times \frac{10000}{1000000000}$$

Where, T is the cumulative N_2O emission (kg N ha^{-1} yr^{-1}), X is daily average flux rate (µg N m^{-2} h^{-1}), i is the i^{th} measurement and $(t_{i+1}-t_i)$ is the days between two adjacent measurements.

The emission factor of N_2O was also calculated using the following equation:

$$EF = \left\{\frac{(Cumulative\ N_2O - N_{fert} - Cumulative\ N_2O - N_{control})}{Total\ N\ added}\right\} \times 100$$

Where, *EF* is the emission factor for N_2O (% of added N), *Cumulative* $N_2O\text{-}N_{fert}$ is the cumulative N_2O emission from fertilized treatment, *Cumulative* $N_2O\text{-}N_{control}$ is the cumulative N_2O emission from unfertilized treatment.

Plant growth evaluation

For plant growth evaluation Fresh weight and dry weight of the plants were calculated. Fresh weight was calculated right after harvesting while the dry weight was calculated after drying plants completely in oven. The chlorophyll contents were evaluated by using spectrophotometric technique. The extracts were taken in pure acetone and the measurements were carried out on the following wavelengths 644.8 and 661.6 nm.

$$Chl\ a\ (\mathrm{µ}g/cm^2) = [11.24(A661.6) - 2.04(A644.8)] \times \frac{V}{W}$$

$$Chl\ b\ (\mu g/cm^2) = [20.13(A644.8) - 4.19(A661.6)] \times V/W$$

The nitrogen contents in plants were evaluated using CNS analyzer while the Zn contents were measured using AAS after digesting samples in microwave digester.

RESULTS

Characterization

The crystal size analysis of ZnO NPs by XRD is presented in Figure 14. Some strong peaks were noted in XRD spectra. The peaks at planes (201), (101), (100), (102), (002), (110), (112), and (103) confirmed the presence of ZnO in the NPs form. The size of NPs calculated by using the Scherrer equation ranged from 21-41 nm and the average size was noted as about 31 nm. The presence of quartz and montmorillonite was confirmed by the peaks at planes (005), (001), and (004). Based on the Scherrer equation the crystal size of nano-bentonite ranged from 6-50 nm and the mean crystal size was reported about 32 nm. The scanning electron microscope was used to carry out morphological analysis of ZnO NPs, nano-bentonite, and coated urea granules. The SEM images showed that the ZnO NPs appeared in the form of rectangles and the particles are a little bit aggregated. The SEM images of nano-bentonite showed a sheet-like structure. The sheet-like structure is the characteristic of montmorillonite.

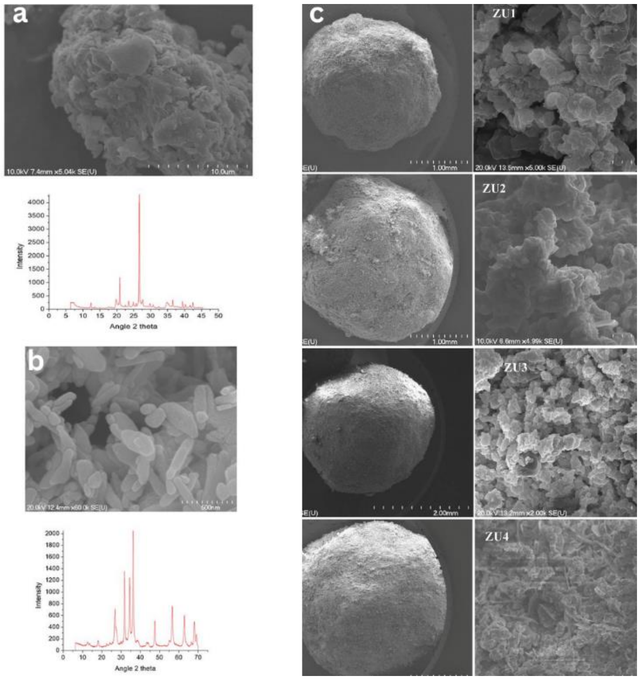

Figure 1: Characterization of nano-bentonite (a), ZnO NPs (b) and coated urea (c)

It was observed that urea granules appeared uniformly coated in all treatments except ZU2. The appearance of cracks can be seen in the SEM images of ZU2. It was also observed that the coating on ZU1 was also not uniform as compared to ZU3 and ZU4 treatment. The coating on ZU1 and ZU2 was carried out by using vegetable oil as a binder. The images showed that the ZU3 and ZU4 appeared uniformly coated. In the case of both ZU3 and ZU4, the coating was carried out by using stearic acid, paraffin oil, and paraffin wax as a binding material.

Zn adsorption potential of nano-bentonite

The Freundlich, Langmuir, and new multilayer adsorption models were used to evaluate the Zn adsorption potential of nano-bentonite. Results showed that the new multilayer adsorption model was the best fit model, that explained the Zn adsorption in a better way. The model fit indices $(R^2 = 0.992)$ showed that the new model is fitted to the data very well.

Table 2:Parameters of adsorption models used to evaluate the Zn adsorption potential of nano-bentonite

Constant values of adsorption Isotherm models									
Langmuir constants			Freundlich constants			New model constants			
q_e	Kl	R^2	Kfr	nfr	R^2	a_i	k	n	R^2
13.96	0.01	0.859	1.0	2.37	0.94	16.272	0.181	5.85	0.992

Release kinetics of Zn from ZnO NPs and Zn fortified nano-bentonite coated urea

Results showed that the amount of Zn released was significantly higher in the case of ZnO NPs coated urea (ZU2 and ZU4) as compared to the Zn fortified nano-bentonite coated urea (ZU1 and ZU3) (Figure 19). It was also observed that there was no significant difference among the treatments of ZnO NPs coated urea and Zn fortified nano-bentonite coated urea in terms of released amount of Zn. The release of Zn from ZU3 and ZU4 showed continuously increasing trend even on the 30th day of the experiment, while the maximum release of Zn from ZU1 and ZU2 was noted on the 15th day of the experiment and after that it become stagnant.

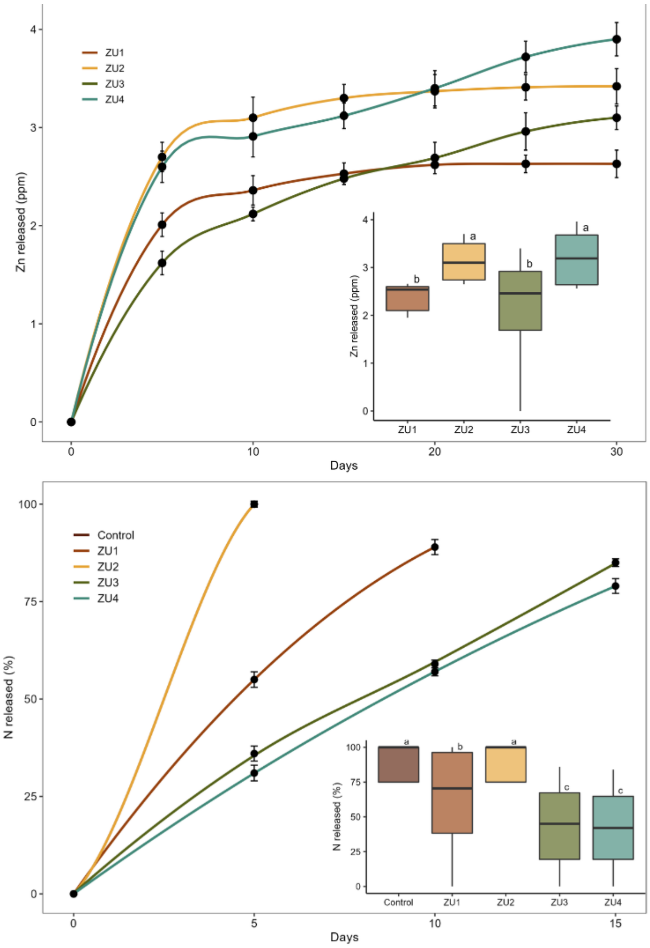

Figure 2: Zn and N release from the coated urea

Release kinetics of N from ZnO NPs and Zn fortified nano-bentonite coated urea

Results showed that the urea granules which were coated by using stearic acid and paraffin wax (ZU3 and ZU4) released N slowly as compared to the vegetable oil coated (ZU1 and ZU2) and uncoated urea granules (Figure 20). It was noted that the uncoated urea and ZU1 and ZU2 released complete N within 5 days of the experiment. While in the case of ZU4 and ZU3 only 28% and 35% of N were released in the first 5 days respectively. The 80% release of N from ZU3 and ZU4 was noted on the 15th day of the experiment. On the 15th day, both treatments were considered completely released. Kinetic models such as Korsmeyer-Peppas and Higuchi models were fitted very well to the data (Figures 41 & 42). Model fit indices for Korsmeyer-Peppas and Higuchi models were $R^2 = 0.96$ and $R^2 = 0.94$ respectively in the case of both ZU3 and ZU4 treatments. The dissolution constants of both models confirmed the slow release of N from ZU3 and ZU4 as compared to ZU1, ZU2, and uncoated urea.

Effect of NPs size, soil types, and incubation time on the solubility of ZnO NPs

It was also noted that maximum Zn in elute was observed when the soil was spiked with $ZnSO_4$ followed by NPs spiked soil. Minimum concentration of Zn was observed in control soil without Zn spiking. The results showed that the size of NPs significantly influences the dissolution of ZnO NPs ($p<0.05$). It was noted that pore water Zn concentration was significantly higher in both soils when soils were spiked with small size NPs as compared to large size NPs. Cumulatively, 21-23% of higher Zn concentration was noted in SL soil spiked with small size NPs, and about 10-13% higher Zn was observed in SC soil as compared to large size NPs. Along with the size of NPs, soil texture also influences the dissolution of ZnO NPs. In this study, the pore water Zn concentration was lower in SC soil as compared to SL soil. It was noted that 20.6%, 26.5%, and 14.5% higher pore water Zn were analyzed in SL soil as compared to SC soil when spiked with $ZnSO_4$, NPs (small size), and NPs (large size) respectively.

To evaluate the bioavailability potential of Zn retained on soil matrix EDTA (0.05 M) solution was used for the extraction. A significant amount of Zn was extracted from both soils using EDTA as an extractant. The extraction efficiency of EDTA was 54-57% in SC soil and 48-53% was noted in SL soil. All the Zn spiked soil treatments showed significantly higher Zn extraction as compared to control treatment without Zn spiking. It was noted that extracted Zn concentration from

SC soil was significantly higher (40.7 mg kg^{-1}) as compared to SL soil (34.3 mg kg^{-1}) when spiked with small size NPs.

Nitrous oxide emission potential of conventional and coated urea from unplanted soils

After continuous measurement of N_2O flux in the laboratory for 15 days, the flux was calculated and visualized. It was noted that the flux points were distributed in a wide range. Overall, the average flux during the 15 days measurement was highest for uncoated urea which was around 35% higher than nano-bentonite coated urea and ZnO NPs coated urea. The minimum flux was noted in the case of the control treatment (17.28±1.91 µg N m^{-2} h^{-1}).

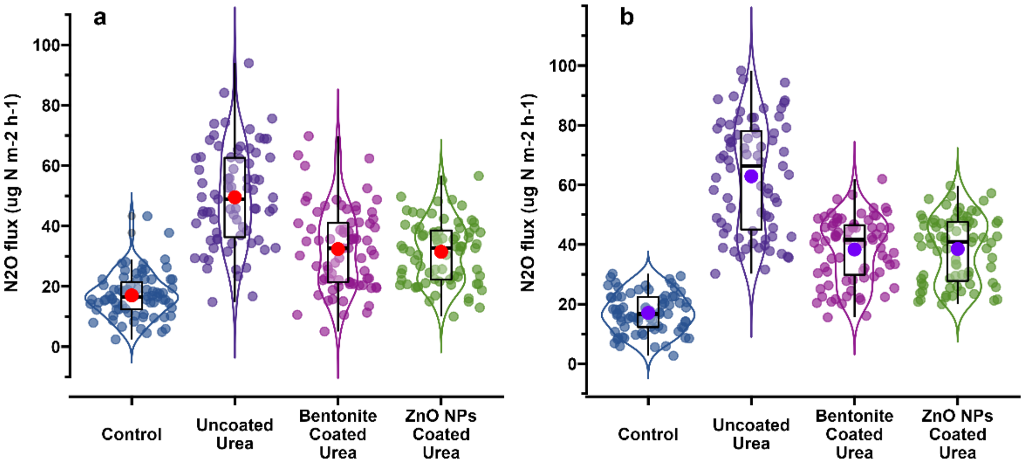

Figure 3: Flux points distribution in a) sandy loam, b) silty clay soils under bare soil condition

Flux points for silty clay soil were distributed in a wide range. In the case of control treatment majority of the points are lied close to zero, while for uncoated urea the maximum points are measured between 20-40 µg N m^{-2} h^{-1}. The points distribution for nano-bentonite coated and ZnO NPs coated urea are distributed in a range of 10-20 µg N m^{-2} h^{-1}.

The overall, average flux during the period of 15 days was recorder maximum for uncoated urea which was approximately 40% higher than nano-bentonite coated urea and ZnO NPs coated urea. The minimum was recorded for control treatment (17.35±1.96 µg N m^{-2} h^{-1}).

Cumulative N_2O emission

The results showed that the uncoated urea emitted maximum cumulative N_2O in both soils (Silty clay and Sandy loam) at 82.6 and 64.14 kg N ha^{-1} yr^{-1} respectively followed by nano-bentonite coated urea (50.4 and 41.94 kg N ha^{-1} yr^{-1}) and ZnO NPs coated urea (50.6 and 40.88 kg N ha^{-1} yr^{-1}) (Figure 25). The minimum cumulative emission was noted in the case of control treatment (22.4 and 22.02 kg N ha^{-1} yr^{-1}) in silty clay and sandy loam soils respectively.

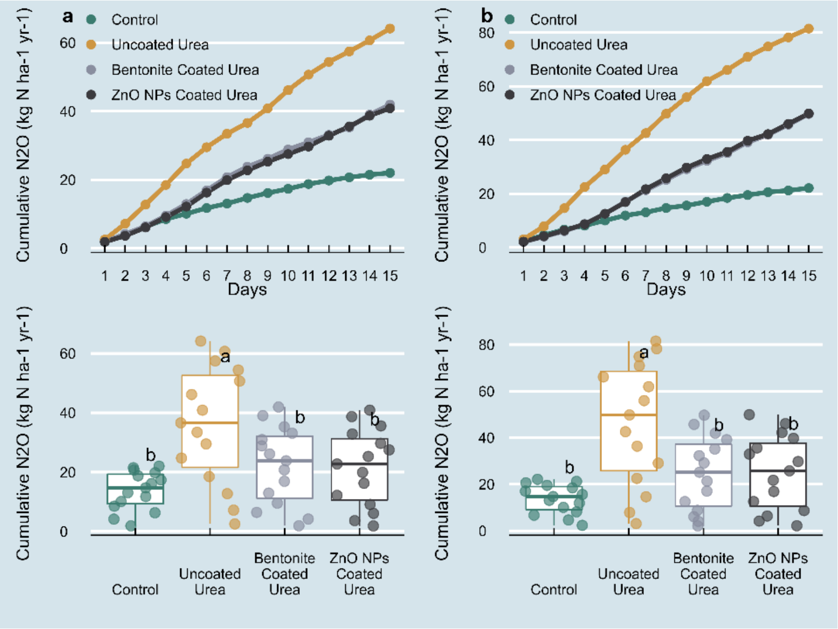

Figure 4: Cumulative N2O emission from a) sandy loam, b) silty clay soil under bare soil conditions

Nitrous oxide emission potential of conventional and coated urea from planted soils

After data analysis, it was observed that the daily flux intensity was higher in silty clay soil as compared to sandy loam soil. The maximum average daily flux from silty cay soil was 77.3 µg N m^{-2} h^{-1} recorded from the treatment where conventional urea was applied on 4th day after the application of first dose of fertilizer. While the maximum daily average flux value from sandy loam soil was 66.4 µg N m^{-2} h^{-1} from conventional urea on the 10th day of the first dose of fertilizer. It was observed that the flux was higher during first 15 days in both soils and after the application of second dose of fertilizer on 20th day the flux values were not as much higher as recorded during first 15 days. The coated urea significantly delayed the N_2O emission and overall, the emission of N_2O from coated urea was lower ($p \leq 0.05$) as compared to the conventional urea. The comparison of fertilizer application method showed that the surface or deep placement of fertilizer have no significant effect ($p \geq 0.05$) on N_2O emission in sandy loam soil, while it was noted that the deep placement of the fertilizer significantly reduced the emission of the N_2O from silty clay soil.

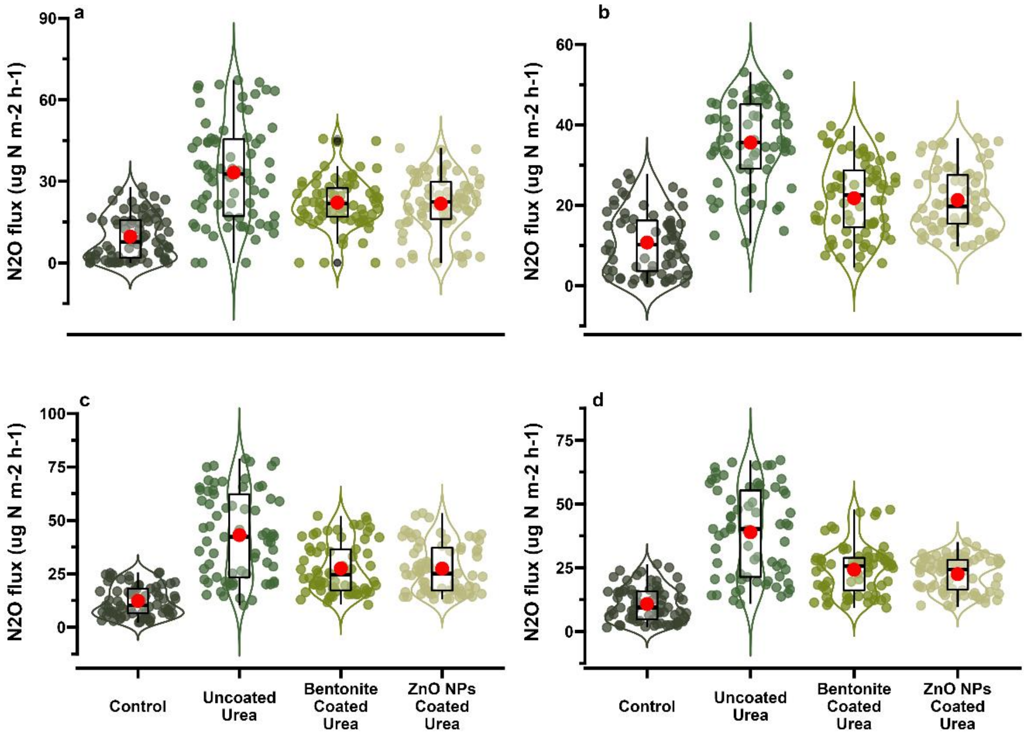

Figure 5:Flux points distribution in sandy loam a) surface placement b) deep placement and silty clay c) surface placement d) deep placement under planted conditions

Cumulative N_2O emission

After the calculation of cumulative N_2O emission, it was noted that the cumulative emission of N_2O was significantly higher ($p \leq 0.0001$) in both soils where conventional urea was applied. While it was observed that there was no significant difference in cumulative N_2O emission between ZnO NPs coated urea and Zn-fortified nano-bentonite-coated urea. The cumulative N_2O emission in silty clay soil under conventional urea application was 14.3% higher as compared to sandy loam soil. The minimum cumulative N_2O emission was measured in control treatments where no fertilizer was applied. Even though the emission of N_2O from silty clay was higher as compared to sandy loam soil but the difference was statistically not significant ($p \geq 0.06$).

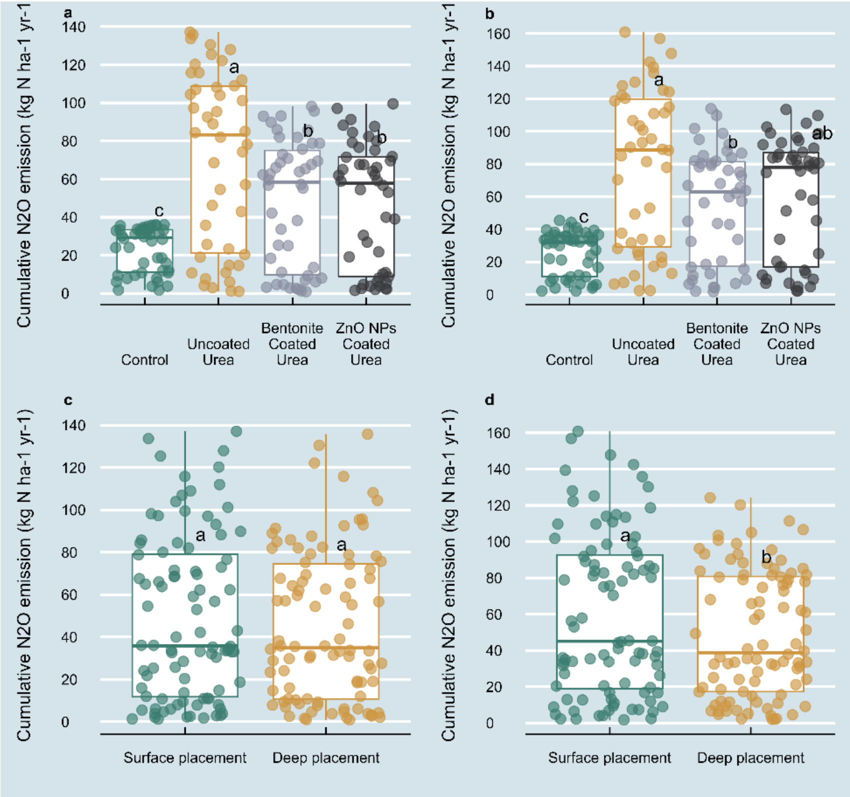

Figure 6: Cumulative N2O emission from a) sandy loam b) silty clay soils under planted conditions

Emission factors

The results showed that the N_2O emission factors for coated and uncoated fertilizers were significantly ($p \leq 0.03$) higher in silty clay soil as compared to sandy loam soil. The N_2O emission factor values for uncoated urea, nano-bentonite coated urea, and ZnO NPs coated urea in silty clay soil were as 1.0, 0.46 and 0.46 respectively. While the emission factor values in sandy loam soil were as follows 0.7, 0.33 and 0.31 for uncoated urea, nano-bentonite coated urea and ZnO NPs coated urea respectively.

Table 3:Nitrous oxide emission factors from conventional and Zn coated urea applied in bare and planted soil conditions

			Sandy loam soil			Silty clay soil		
			Uncoated Urea	Bentonite coated	ZnO NPs coated	Uncoated Urea	Bentonite coated	ZnO NPs coated
Emission factors (% of applied N lost in the form of N_2O)	Planted soil	Surface Placement	5.3	3.3	3.4	6.1	3.65	3.62
		Deep Placement	5.33	3.2	2.95	4.44	2.7	3.6
	Bare soil		0.7	0.33	0.31	1.0	0.46	0.46

After cumulative N_2O emission the emission factors were calculated for applied treatments in both soils (Table 7). Results showed that the EF for conventional urea in sandy loam soil was 5.3% in both surface placement and deep placement methods. The EFs for both coated urea (Bentonite coated and ZnO NPs coated) were significantly lower sandy loam and silty clay soil (3.3% and 3.4%) and (3.2% and 2.95%) respectively. Similarly, the EF for conventional urea in silty clay soil was 6.1% when applied on the surface, while a significant reduction in EF (4.4%) was noted when applied deeper in the soil. The EFs for bentonite coated urea in sandy loam, silty clay soil was (3.3%, 3.65% and 3.2%, 2.7%) when applied at surface and deep in the soil respectively. Similarly, the EFs for

ZnO NPs coated urea in sandy loam, silty clay soil was (3.4%, 3.62% and 2.95%, 3.6%) when applied at surface and deep in the soil respectively.

Effect of Coated urea fertilizer on plant growth

To evaluate the effect of slow-release coated urea on plant growth, shoot fresh weight (FW), dry weight (DW), and chlorophyll contents were measured. Maximum FW was recorded from the pots where coated urea was applied followed by conventional urea and the minimum FW was recorded in control treatment. Both coated urea treatments have no significant effect ($p \geq 0.05$) with respect to each other but showed significantly higher ($p \leq 0.001$) FW as compared to conventional urea and control. Apart from the treatments soil type also affect the FW significantly. It was observed that the silty clay soil significantly ($p \leq 0.001$) showed higher FW as compared to sandy loam soil. The interaction effect of treatments and soil type on FW was also significant. Results depicted that the application method of fertilizer had no significant ($p \geq 0.05$) effect on FW.

Similar trend was also observed in case of DW, where the coated urea application showed significant increase ($p \leq 0.001$) in DW as compared to conventional urea and control treatment. Like FW, soil type also effects the DW significantly ($p \leq 0.001$), while the method of application has no significant ($p \geq 0.05$) effect on DW. It was observed that in sandy loam soil the conventional urea application has no significant effect ($p \geq 0.05$) as compared to control treatment.

Chlorophyll *a* contents were significantly affected by the treatments ($p \leq 0.001$) and soil type ($p \leq 0.0035$). Maximum chlorophyll *a* was observed under coated urea application (~42.5 µg cm^{-2}) in both soil types followed by conventional urea 38.1 µg cm^{-2} in silty clay soil and 34.3 µg cm^{-2} in sandy loam soil. Minimum chlorophyll *a* was detected in control treatment 31 and 27.6 µg cm^{-2} in silty clay and sandy loam soil respectively. It was observed that method of application has no significant effect on chlorophyll *a*.

Like chlorophyll *a*, similar trend was also observed in chlorophyll where coated urea application improved the chlorophyll *b* contents as compared to conventional urea. In case of soil type, higher chlorophyll *b* was observed in plant leaves grown in silty clay soil as compared to sandy loam soil. The method of application has no significant effect on chlorophyll *b*.

Zn and nitrogen contents in plants

Analysis of the digested plant samples showed that the application of Zn coated urea significantly ($p \leq 0.0001$) affect the plant Zn contents. Highest Zn concentration in plants was reported with the application of ZnO NPs coated urea (53.76 mg kg^{-1}) and (60 mg kg^{-1}) in both sandy loam and silty clay soils respectively. The maximum Zn concentration with the application of Zn fortified nano-bentonite coated urea was reported 48.5 and 55.2 mg kg^{-1} in sandy loam and silty clay soil respectively.

The dried and ground plant samples were analyzed on CNS analyzer for total N contents in plant body. The results showed that the maximum N contents in plants were measured in the treatments where coated urea was applied (> 40 g N kg^{-1}) in both soils, followed by uncoated urea and control. It was observed that the N contents were higher in case of silty clay soil as compared to sandy loam soil, but the difference was not significant statistically ($p \geq 0.05$) between coated urea treatments. On the other hand, N contents in plants were significantly ($p \leq 0.001$) higher in silty clay soil with the control treatments and where conventional urea was applied. The effect of application methods on the plant N contents was also compared using Wilcoxon t-test and it was concluded that the application method of fertilizers has no significant ($p \geq 0.05$) effect on plant N contents.

CONCLUSION AND RECOMMENDATIONS

For the fulfillment of the aims of this study the following objectives were undertaken 1) Synthesis and characterization of ZnO NPs and Zn fortified nano-bentonite. 2) Development and characterization of Zn fortified nano-bentonite and ZnO NPs coated slow-release urea fertilizer using different binding materials (stearic acid and paraffin wax). 3) Evaluation of Zn and N release characteristics from slow-release macro-micronutrient fertilizer. 4) Evaluation of the dissolution of ZnO NPs, and $ZnSO_4$ in two different soils. 5) Evaluation of N_2O emission from coated and uncoated urea fertilizer under bare and planted soil conditions. 6) Evaluating the comparative effect of coated and uncoated urea on plant growth and development.

The first specific objective was to evaluate the synthesis and characterization of ZnO NPs and Zn-fortified nano-bentonite. The precipitation method for the synthesis of ZnO NPs proved an effective method to synthesize ZnO NPs with a size range of less than 100 nm. The shape of the NPs was round to rectangular. Nano-bentonite was proved an effective adsorbent for the cations based on the previous studies conducted for the removal heavy metals from the liquid media. We used nano-bentonite to evaluate its adsorption potential specifically for Zn. It was proved that a significant amount of Zn was adsorbed on nano-bentonite based on the multilayer adsorption phenomenon.

The second specific objective was to prepare a slow-release Zn coated urea. To reduce the dissolution of urea hydrophobic materials were used such as stearic acid, paraffin wax and paraffin oil, vegetable oil and the final coating of Zn containing materials such as ZnO NPs and Zn-fortified nano-bentonite was used. Based on the characterization it was concluded that the coating was even and fine when paraffin oil was used as a final binder as compared to vegetable oil.

The third objective was to evaluate the release of N and Zn from the coated slow-release urea. It was concluded that coating of urea with stearic acid, paraffin wax and paraffin oil significantly delayed the solubility of urea as compared to uncoated urea. It was also concluded that both ZnO NPs and Zn-fortified nano-bentonite can act as an effective Zn carrier and could be used as a coating material on to the macronutrient fertilizers.

The fourth objective was to evaluate the dissolution of ZnO NPs in different soils. Based on the results it was concluded that the ZnO NPs significantly reduced the release of Zn as compared to conventional $ZnSO_4$ because the pore water Zn concentration was higher in case of $ZnSO_4$. It was also hypothesized that the fixation of ZnO NPs was less in both soils because the extraction of Zn using 0.05M EDTA was significantly higher in case of ZnO NPs.

The fifth objective was to evaluate the N_2O emission from coated and uncoated urea under bare and planted soil conditions. It was concluded that the coated urea delayed the N_2O emissions and reduced the daily flux intensity in both soils under planted and bare soil conditions. It was also proved that after the establishment of the crop cover the emission of N_2O was significantly reduced. In general, it was concluded that the use of coated slow-release urea can reduce the environmental impact of applied nitrogen in agroecosystems.

The sixth specific objective was to evaluate the effect of coated fertilizer on plant growth. It was concluded that slow-release coated urea significantly increased the biomass production of wheat. The chlorophyll contents of the wheat plants were also increased with the application of slow-release urea.

Future Research Recommendations

Based on the findings this study proposes the following recommendations for the future research:

- This study proved the general effectiveness of stearic acid and paraffin wax in reducing the solubility of urea. It is suggested for the future research that the different concentrations of the coating materials such as stearic acid and paraffin wax should be tried to further improve the effectiveness of the coating in reducing the solubility of urea.

- The dissolution of ZnO NPs should be tested on a long-term basis and different factors such as pH, ionic strength, and the speciation of ZnO NPs in soil solution should be evaluated in the future research.
- In this study the N_2O emission from coated and uncoated urea was evaluated under laboratory conditions. In future research it is recommended to evaluate the efficiency of coated urea under field conditions.
- It is also recommended that the variable rates of coated fertilizer application should be used to evaluate the effective amount of coated fertilizer for a specific crop.

NEW SCIENTIFIC RESULTS

1. In this study, nano-bentonite was tested as a Zn carrier and from the results it was proved that nano-bentonite can adsorb a significant amount of Zn and can release it slowly courtesy of cation exchange phenomenon. Previous studies only reporting the use of bentonite and nano-bentonite as an adsorbent for the removal pollutants from liquids. Our study is first of its kind which is evaluating its role as an environmentally friendly nutrient carrier for crop production.
2. Coating of urea with hydrophobic materials and Zn carriers proved an effective strategy to supply both macro and micronutrients together to the crops. Even though, ZnO NPs used widely as a coating material, but this study is first of its kind where Zn fortified nano-bentonite was used as a Zn carrier on urea granules. So, this study provides an insight for the further utilization of nano-bentonite as an environmentally friendly nutrient carrier.
3. Complete release of N from coated urea was delayed up to 15 days as compared to uncoated urea which completely released the N within first 5 days. The release of Zn from coated urea was reduced and the upward trend in Zn release was noted even on the 30th day of the experiment.
4. The coating of urea proved an effective strategy in reducing the N_2O emission as compared to conventional urea. Results showed a significantly higher cumulative N_2O emission from conventional urea as compared to coated urea. The emission factor of coated urea was lower than the conventional urea.

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Conference abstracts/posters

1. N Workshop Madrid (Halving the N Waste by 2030) Madrid, Spain (23/10/2022-28/10/2022). Link: https://nworkshop.org/
   Poster presentation: *Comparative impact of coated urea and conventional urea on* N_2O *emission in different soils under crop plantation and bare soil conditions.*
2. 55th Croatian and 15th International Symposium on Agriculture, February 16-21, Vodice, Croatia 2020.
   Poster presentation: *Use of ZnO nanoparticles and other conventional Zn sources to increase grain yield, grain Zn content and water use efficiency in hybrid maize (Zea mays L.)*