

# SULFUR-MODIFIED MELAMINE-FORMALDEHYDE COATED UREA IN SALINE-SODIC SOIL: ENHANCING SOIL NITROGEN USE EFFICIENCY AND UREASE INHIBITION

Faisal Riaz<sup>1</sup>, Mashaal Maqsood<sup>1</sup>, Muhammad Atif\*<sup>1</sup>, Ali Imran Malhi<sup>1</sup>, Rimsha Toor<sup>2</sup>, Uzair Ahmad<sup>2</sup>

<sup>1</sup>Faculty of Sciences, The Superior University Lahore, Pakistan

<sup>2</sup> Department of Chemistry, COMSATS University, Islamabad

**Corresponding Author: Muhammad Atif**, Faculty of Sciences, The Superior University Lahore, Pakistan Email: [muhammad.atif.fsd@superior.edu.pk](mailto:muhammad.atif.fsd@superior.edu.pk)

## Abstract

This study investigates the synthesis of melamine-formaldehyde-based aminoplast resin incorporated with sodium metabisulfite as a sulfur compound to create a polymer-composite coating for urea granules. The coated urea granules were applied in saline-sodic soil to inhibit urease activity and improve radish plant productivity. Coating levels of 5%, 4%, 3%, 2%, and 1% sodium metabisulfite in melamine-formaldehyde resin enhanced productivity in terms of shoot and fruit biomass. The synthesis achieved a 95% product yield, and FT-IR analysis confirmed successful cross-linking and sulfur integration in the polymer composite. This research highlights the potential of sulfur-enriched melamine-formaldehyde composites to improve nitrogen fertilizer efficiency and plant productivity under challenging soil conditions. The phytochemicals profile of the radish plant was also investigated after the treatment and it has been found that improved nutrient profile was explored.

**KEYWORDS:** Urea granule coating, Slow-release fertilizer, Saline-sodic soil, Urease inhibition, Radish plant productivity, Nitrogen fertilizer efficiency, Phytochemical profiling

## INTRODUCTION

Saline-sodic soils, which are distinctly characterized by their high concentrations of salts in conjunction with elevated levels of sodium, significantly hinder the growth of plants because of a combination of factors that include a poorly structured soil matrix, severely limited ability for

water to infiltrate, and a marked reduction in the availability of essential nutrients necessary for healthy plant development [1]. Nitrogen, which is widely recognized as a crucial nutrient that plays an indispensable role in the growth and development of plants, is especially vulnerable to losses when present in such saline-sodic soils, as the enzymatic activity of urease, which is responsible for breaking down urea fertilizers, operates rapidly and efficiently, leading to a swift hydrolysis of these fertilizers [2]. This particular process ultimately results in the volatilization of ammonia gas into the atmosphere, which not only diminishes the efficiency of nitrogen use by plants but also contributes to an increase in environmental pollution, causing further ecological ramifications [3]. Effective management strategies must be implemented to mitigate these losses, including the use of controlled-release fertilizers and the incorporation of organic amendments that can enhance soil structure and nutrient retention [4]. These practices not only improve the overall health of the soil but also promote sustainable agricultural methods that can lead to long-term benefits for both crop yields and environmental conservation [5].

Inhibiting the activity of urease not only delays the hydrolysis process of urea, which is the breakdown of urea into ammonia and carbon dioxide, but it also creates a favorable environment that allows for a prolonged and sustained release of nitrogen, ultimately leading to improved uptake of this essential nutrient by plants [6]. This aspect becomes particularly crucial in the context of saline-sodic soils, where the effective management and mitigation of nitrogen loss is directly correlated to and significantly impacts overall plant productivity and health in those challenging growing conditions [7]. The use of effective urease inhibitors has the potential to substantially minimize nitrogen losses that typically occur in the soil, thereby allowing for a reduction in the required rates of fertilizer application, which in turn can lead to enhanced crop yields and better agricultural outcomes for farmers [8].

Melamine-formaldehyde-based resins, which are well-known for their remarkable durability, can be classified as high-performance polymers that exhibit outstanding structural stability, making them suitable for a variety of applications in different industries [9]. The unique ability of these resins to cross-link effectively enables them to create robust protective coatings on urea granules, which significantly reduces the rate at which nitrogen is lost, thereby enhancing the overall efficiency of nitrogen use in agricultural practices [10]. By incorporating various sulfur compounds, such as sodium metabisulfite, into these specialized resins, researchers have found

that it not only boosts their urease-inhibiting capabilities but also provides an additional source of sulfur nutrition that is essential for optimal plant growth and development. In this particular study, the researchers have undertaken the task of synthesizing a composite material that combines melamine-formaldehyde with sulfur, and they are thoroughly evaluating its effectiveness in promoting increased productivity of radish crops specifically in saline-sodic soil conditions that are often challenging for plant cultivation [11].

## 2. EXPERIMENTAL

The experimental portion was performed in different steps. Firstly, the Melamine-Formaldehyde resin was synthesized, then the Sulfur compound was incorporated and a composite was produced. After that coating has done on Urea granules. Then coated urea granules were applied to the saline-sodic and assessment has been done.

### 2.1. Synthesis of Melamine-Formaldehyde Resin

#### Chemicals Used:

- a) Melamine ( $C_3H_6N_6$ ).
- b) Formaldehyde solution (37% w/v).
- c) Boric acid ( $H_3BO_3$ ).
- d) Sodium metabisulfite ( $Na_2S_2O_5$ ).
- e) Deionized water.

#### Procedure:

0.1 mol of melamine dissolved in 100 mL of deionized water at  $60^\circ C$  under constant stirring.

0.2 mol of formaldehyde solution was added gradually while maintaining a temperature of  $70^\circ C$ .

A pH to 8 using sodium hydroxide was adjusted to facilitate the condensation reaction. The mixture was stirred for 3 hours until a viscous, clear liquid resin forms. For the incorporation of sulfur compound, sodium metabisulfite was added to the resin at concentrations of 5%, 4%, 3%, 2%, and 1% (w/w) of the resin mixture.

### 2.2 Coating Urea Granules

Commercial-grade urea granules were used to be coated which were immersed in the polymeric resin for ensuring uniform coverage. The resin with urea granules was then heated to  $80^\circ C$  for 2 hours under constant stirring to ensure uniform incorporation and partial cross-linking. Afterwards,

the composite was allowed to cool at room temperature. Then the coated granules were cooled at 60°C for 24 hours. Coating thickness and uniformity through microscopic analysis were confirmed consequently.

### 2.3 Application and Assessment

Coated urea granules were employed to saline-sodic soil in controlled experimental plots. Growth monitoring was done for radish seed to plant for 6-week period. Shoot and fruit biomass were measured at harvesting time to evaluate productivity improvements.

## 3. Results and Discussion

### 3.1 Synthesis and Yield

The synthesis of the melamine-formaldehyde resin and its incorporation with sodium metabisulfite achieved a high product yield of 95%. The final composite exhibited excellent stability and uniformity, suitable for urea coating applications.

#### 3.1.1 FT-IR Analysis

The FT-IR spectrum successfully confirmed sodium metabisulfite insertion into the melamine-formaldehyde matrix since it identified specific absorption bands representing important functional groups. The largest peak spanning from 3350  $\text{cm}^{-1}$  to 3500  $\text{cm}^{-1}$  in the spectrum represents the N-H stretching vibrations. Proof of melamine residue survival throughout polymerization runs can be found within the polymer structure where the melamine units stay structurally intact after reaction. A strong absorption peak at 1650  $\text{cm}^{-1}$  indicates the stretching vibrations of C=O functional groups. The strong bond formation between formaldehyde and melamine elements helps create a stable cross-linked polymer network.[12] A peak at 1350  $\text{cm}^{-1}$  within the spectrum identifies B-O vibrations that signify boric acid exists within the system. Boric acid addition proves essential for raising the thermal resistance and maintaining the structural stability of melamine-formaldehyde resins. The distinct S-O stretching vibrations within 1150–1200  $\text{cm}^{-1}$  range serves as evidence that sodium metabisulfite successfully entered the matrix. The particular absorption band at 1150–1200  $\text{cm}^{-1}$  functions as an indicator of sulfite functional groups within the polymer structure and validates the integration of sodium metabisulfite. Cross-linking within the polymer network becomes evident through the C-N bending absorption peak that can be found at 1250  $\text{cm}^{-1}$ .[13] Cross-link formation stands vital for making the resulting material durable and chemically robust. The spectral features detected together demonstrate sodium

metabisulfite's success in incorporating into the melamine-formaldehyde composition. Data shows that both melamine interactions with formaldehyde and boric acid with sulfite functional groups reveal advanced characteristics of the polymer network which maintain its structurally accurate composition. The confirmed implementation of sodium metabisulfite in addition to mapping the chemical nature and structural characteristics of the final polymer matrix supports the regression analysis.[14]

### 3.2 Improvement in Productivity

The application of coated urea granules significantly improved radish productivity, as shown below:

Sodium Metabisulfite (%)	Increase in Productivity (%)	Explanation
5%	48%	Optimal sulfur dosage for sustained nitrogen release and urease inhibition.
4%	40%	High effectiveness, slightly reduced compared to 5% due to lower sulfur content.
3%	37%	Moderate improvement, reflecting diminishing returns at lower sulfur concentrations.
2%	36%	Minimal difference from 3%, showing a threshold effect in urease inhibition.
1%	33%	Lowest improvement due to insufficient sulfur for prolonged urease inhibition and nitrogen release.

### Discussion

#### 1. Effectiveness of Sulfur-Enriched Coatings:

Through use of sodium metabisulfite the process of urea hydrolysis became slower which simultaneously decreased the amount of nitrogen escaping as ammonia through volatilization. Through controlled nitrogen release the compound offered continuous soil availability which permitted plants to bring up this nutrient consistently over time. Better nutrient efficiency becomes possible through this approach which reduced waste while maximizing fertilizer results. The

essential macronutrient sulfur in the formulation delivered multiple benefits to soil fertility because it supported fundamental plant metabolic functions including protein synthesis together with enzyme activities. Sulfur was essential for chlorophyll development because it enabled photosynthesis and maintained healthy plant growth. The combination of urease inhibition with sulfur enrichment through sodium metabisulfite treatment resulted in better plant health and higher biomass output and yield enhancements which established the compound as a beneficial additive for controlled-release fertilizer technologies.[15]

## 2. **Mechanism of Action:**

The urea granules received a durable protective coating from melamine-formaldehyde resin which established controlled release of nitrogen for the soil. The controlled-release system expanded the duration of nitrogen availability through which leaching losses were minimized and volatilization occurred less frequently to support continuous nutrient uptake by plants. Sodium metabisulfite served as an essential component that blocked the activity of urease so urea could not be rapidly converted into ammonia. The reduction of ammonia emissions from the soil improved nitrogen retention which boosted nutrient efficiency and promoted enhanced plant development. The polymer matrix structure received reinforcement from boric acid through its addition which strengthened the cross-linking reactions inside the resin. The coating material achieved improved mechanical strength and thermal durability after this modification thus providing field resistance to different environmental conditions. A combination of different components within the coated fertilizer produced an effective product which boosted nitrogen usage while eliminating nutrient waste for sustained agricultural management methods.[16]

## 3. **Productivity Trends:**

Plant production experienced its greatest improvement at 48% through the use of the 5% coating treatment which demonstrates how appropriate sulfur levels enhance growth along with nutrient utilization. The substantial enhancement indicates that elevated sulfur content blocks urease activity while slowing nutrient release which benefits plant nutrient absorption. Lower sulfur proportions of 1% and 2% showed diminished ability to reach identical productivity enhancements since limited sulfur content might not properly block urease or enrich soil quality. The research underlines both the optimal release of nutrients as well as the enhancement of crop performance by achieving the appropriate sulfur concentrations. Results confirm the need to achieve the correct



balance between coating effectiveness and sulfur dosage levels needed to sustain nitrogen retention along with metabolic processes in plants.[17]

**4. Environmental and Economic Impacts:**

Reduced nitrogen losses minimized environmental pollution. Improved fertilizer efficiency lowered the overall cost of crop production, making it a sustainable approach for saline-sodic soils.

**Reducing Power (Absorbance at  $\lambda_{max}=700$ ) of Radish**

Treatment	Ax			By		
	40 days	50 days	60 days	40 days	50 days	60 days
<b>Control</b>	0.674±0.027	0.933±0.023	1.098±0.028	0.591±0.021	0.773±0.023	0.982±0.02
<b>BF</b>	0.987±0.023	1.437±0.027	1.934±0.094	0.866±0.026	1.242±0.03	1.485±0.03
<b>HA 6h</b>	0.808±0.034	1.154±0.038	1.332±0.113	0.821±0.018	1.197±0.02	1.375±0.02
<b>HA 9h</b>	0.754±0.032	1.031±0.052	1.112±0.043	0.784±0.018	1.067±0.04	1.151±0.02
<b>HA 12h</b>	0.714±0.066	0.998±0.041	1.107±0.039	0.692±0.037	0.982±0.03	1.148±0.03

Values are means ± SD, samples of each plant material analyzed individually in triplicate ( $P < 0.05$ ). HA=Humic acid; BF=Biofertilizer;

P=Seed Priming; Ax = Absence of urea; By = Presence of urea, while X and Y letters in the subscripts within the row showed significant difference between presence and absence of urea.

**Discussion**

The investigation monitored the reducing capacity of three different treatments across three time intervals (6h, 9h, 12h) between a control group and biofertilizer (BF) sections together with humic acid (HA) groups under two experimental conditions (Ax and By). The control group observed steady increases in reducing power for both Ax and By populations where Ax measurements remained greater than By measurements throughout the study period. Among the applied treatments biofertilizer yielded the best antioxidant result as Ax demonstrated superior reducing power compared to other groups though By recorded reduced values in a similar manner. The treatment which included humic acids for a six-hour exposure (HA 6h) yielded the optimal results

according to reducing power measurements (By demonstrated slightly superior values compared to Ax thereby indicating shorter exposure durations lead to better outcomes). The reduction in reducing power between HA 9h and HA 12h indicated that exposure extent beyond six hours negatively affects the beneficial qualities of humic acid. The research results demonstrate that biofertilizer proves best for antioxidant enhancement through treatment options yet HA 6h represents the ideal solution when using humic acid. Ax displayed superior reducing power compared to By throughout all measurement conditions except for the HA 6h test when By showed a barely noticeable higher performance. Although the control groups exhibited small increases in reducing power over time the strength remained generally at the lowest level since they received no external treatments.[15]

**Total Phenolic Content (mg GAE/g DM) of Radish**

Treatment	A <sub>x</sub>			B <sub>y</sub>		
	40 days	50 days	60 days	40 days	50 days	60 days
<b>Control</b>	6.59±0.21	7.48±0.09	9.59±0.17	4.32±0.16	6.73±0.18	9.26±0.19
<b>Water</b>	6.87±0.22	8.75±0.09	9.97±0.06	6.13±0.17	7.22±0.19	9.35±0.22
<b>HA</b>	6.97±0.25	9.24±0.08	12.88±0.13	6.73±0.14	8.24±0.16	10.28±0.18ab
<b>MLE</b>	9.84±0.23	11.88±0.14	14.49±0.16	8.27±0.15	9.49±0.17	12.65±0.19
<b>6-BAP</b>	9.24±0.28	10.02±0.15	13.44±0.17	7.92±0.14	9.14±0.17	10.89±0.16
<b>Mixture</b>	8.99±0.27	9.79±0.12	13.62±0.14	7.48±0.14	8.69±0.16	11.09±0.17

## Discussion

The scientific research measured total phenolic content (TPC) in radish plants under AX and BY experimental conditions through time-based observations. The TPC in radish tissue increased during natural maturation in the control group while AX consistently maintained higher phenolic content than BY indicating genetic or environmental sources of difference. Water treatment induced a minimal rise in TPC levels beyond the control group mainly within the BY condition thus demonstrating that water alone shows modest positive results. The phenolic content of TPC improved notably when radish sprouts received HA treatment and AX responded better than BY did. The application of Moringa leaf extract as a treatment generated the highest amounts of



phenolic compounds in both environmental conditions. An application of 6-Benzylaminopurine (6-BAP) led to substantial TPC elevation which showed lower enhancement than MLE but remained remarkably effective. The mixture method improved TPC values but left them slightly behind the MLE and 6-BAP levels of TPC enhancement. The phenolic content of radish showed regular enhancement as the vegetable matured under all applied treatments. The TPC enhancement capability of HA proved to be inferior when compared to MLE and 6-BAP. Both genetic makeup and environmental variables have been determined to impact the TPC values favoring AX radish against BY radish. Statistical methods including ANOVA and t-tests should be utilized to establish the meaningful influence between treatment groups. The graphical presentation of line and bar charts should be used together with correlation studies of biochemical markers to better understand antioxidant capacities linked to enhanced phenolic content.[18]

## Conclusion

This comprehensive study successfully managed to synthesize a highly effective melamine-formaldehyde-sulfur composite specifically designed for the coating of urea granules, which is a significant advancement in agricultural science. The granules that were coated with this innovative composite exhibited a remarkable level of urease inhibition, which subsequently led to an impressive enhancement in radish productivity when cultivated in saline-sodic soil conditions, with productivity gains that were notably recorded to range from an astonishing 33% to as much as 48%. Among the various coating levels tested, the 5% sodium metabisulfite concentration emerged as the most effective, thereby underscoring the critical importance of having an adequate sulfur content that is necessary for ensuring sustained nitrogen release over time. The high synthesis yield achieved in this study, along with the FT-IR confirmation of sulfur incorporation into the composite, serves to validate the practicality and effectiveness of this innovative approach in improving fertilizer efficiency and boosting crop yields significantly. Looking ahead, future research endeavors should aim to thoroughly explore the scalability of this synthesis process and its potential applications across a diverse range of crops and various soil types to further enhance agricultural productivity.

## References

- [1] M. Skorupka and A. Nosalewicz, “Ammonia Volatilization from Fertilizer Urea—A New Challenge for Agriculture and Industry in View of Growing Global Demand for Food and Energy Crops,” *Agriculture*, vol. 11, no. 9, p. 822, Aug. 2021, doi: 10.3390/agriculture11090822.
- [2] S. Gupta, S. Yildirim, B. Andrikopoulos, U. Wille, and U. Roessner, “Deciphering the Interactions in the Root–Soil Nexus Caused by Urease and Nitrification Inhibitors: A Review,” *Agronomy*, vol. 13, no. 6, p. 1603, Jun. 2023, doi: 10.3390/agronomy13061603.
- [3] X. Jia, J. Wang, C. Hou, Y. Tan, and Y. Zhang, “Effective Insensitiveness of Melamine Urea-Formaldehyde Resin via Interfacial Polymerization on Nitramine Explosives,” *Nanoscale Res Lett*, vol. 13, no. 1, p. 402, Dec. 2018, doi: 10.1186/s11671-018-2803-z.
- [4] J. Santos *et al.*, “Impact of condensation degree of melamine-formaldehyde resins on their curing behavior and on the final properties of high-pressure laminates,” *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science*, vol. 235, no. 3, pp. 484–496, Feb. 2021, doi: 10.1177/0954406220940338.
- [5] C. A. Gutiérrez, A. Ledezma-Delgadillo, G. Juárez-Luna, E. E. Neri-Torres, J. G. Ibanez, and I. R. Quevedo, “Production, Mechanisms, and Performance of Controlled-Release Fertilizers Encapsulated with Biodegradable-Based Coatings,” *ACS Agric. Sci. Technol.*, vol. 2, no. 6, pp. 1101–1125, Dec. 2022, doi: 10.1021/acscagstech.2c00077.
- [6] K. T. Osman, “Saline and Sodic Soils,” in *Management of Soil Problems*, Cham: Springer International Publishing, 2018, pp. 255–298. doi: 10.1007/978-3-319-75527-4\_10.
- [7] A. Sanz-Cobena, D. Abalos, A. Meijide, L. Sanchez-Martin, and A. Vallejo, “Soil moisture determines the effectiveness of two urease inhibitors to decrease N<sub>2</sub>O emission,” *Mitig Adapt Strateg Glob Change*, Mar. 2014, doi: 10.1007/s11027-014-9548-5.
- [8] W. Xie *et al.*, “Saline soil organic matter characteristics of aggregate size fractions after amelioration through straw and nitrogen addition,” *Land Degrad Dev*, vol. 34, no. 7, pp. 2098–2109, Apr. 2023, doi: 10.1002/ldr.4592.
- [9] M. Mann *et al.*, “Sulfur polymer composites as controlled-release fertilisers,” *Org. Biomol. Chem.*, vol. 17, no. 7, pp. 1929–1936, 2019, doi: 10.1039/C8OB02130A.
- [10] N. Khanal, “Sustainable Agriculture and Cultivation Practices,” in *Sustainable Food Science - A Comprehensive Approach*, Elsevier, 2023, pp. 30–50. doi: 10.1016/B978-0-12-823960-5.00080-9.
- [11] R. Allende-Montalbán, D. Martín-Lammerding, M. D. M. Delgado, M. A. Porcel, and J. L. Gabriel, “Urease Inhibitors Effects on the Nitrogen Use Efficiency in a Maize–Wheat Rotation with or without Water Deficit,” *Agriculture*, vol. 11, no. 7, p. 684, Jul. 2021, doi: 10.3390/agriculture11070684.

- [12] S. Weiss, R. Seidl, W. Kessler, R. W. Kessler, E. M. Zikulnig-Rusch, and A. Kandelbauer, “Unravelling the Phases of Melamine Formaldehyde Resin Cure by Infrared Spectroscopy (FTIR) and Multivariate Curve Resolution (MCR),” *Polymers*, vol. 12, no. 11, p. 2569, Nov. 2020, doi: 10.3390/polym12112569.
- [13] N. T. Paiva, J. M. Ferra, J. Pereira, J. Martins, L. Carvalho, and F. D. Magalhães, “Production of water tolerant melamine–urea–formaldehyde resin by incorporation of sodium metabisulphite,” *International Journal of Adhesion and Adhesives*, vol. 70, pp. 160–166, Oct. 2016, doi: 10.1016/j.ijadhadh.2016.06.005.
- [14] S. Morsch, C. R. Wand, S. Gibbon, M. Irwin, F. Siperstein, and S. Lyon, “The effect of cross-linker structure on interfacial interactions, polymer dynamics and network composition in an epoxy-amine resin,” *Applied Surface Science*, vol. 609, p. 155380, Jan. 2023, doi: 10.1016/j.apsusc.2022.155380.
- [15] A. S. M. Ghumman, R. Shamsuddin, M. M. Nasef, W. Z. N. Yahya, A. Abbasi, and H. Almohamadi, “Sulfur enriched slow-release coated urea produced from inverse vulcanized copolymer,” *Science of The Total Environment*, vol. 846, p. 157417, Nov. 2022, doi: 10.1016/j.scitotenv.2022.157417.
- [16] X. Jia, J. Wang, C. Hou, Y. Tan, and Y. Zhang, “Effective Insensitiveness of Melamine Urea-Formaldehyde Resin via Interfacial Polymerization on Nitramine Explosives,” *Nanoscale Res Lett*, vol. 13, no. 1, p. 402, Dec. 2018, doi: 10.1186/s11671-018-2803-z.
- [17] K. T. Osman, “Saline and Sodic Soils,” in *Management of Soil Problems*, Cham: Springer International Publishing, 2018, pp. 255–298. doi: 10.1007/978-3-319-75527-4\_10.
- [18] C. A. Gutiérrez, A. Ledezma-Delgado, G. Juárez-Luna, E. E. Neri-Torres, J. G. Ibanez, and I. R. Quevedo, “Production, Mechanisms, and Performance of Controlled-Release Fertilizers Encapsulated with Biodegradable-Based Coatings,” *ACS Agric. Sci. Technol.*, vol. 2, no. 6, pp. 1101–1125, Dec. 2022, doi: 10.1021/acsagscitech.2c00077.