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DEVELOPMENT OF BORON-MODIFIED AMINOPLAST RESIN COATINGS FOR ENHANCED UREASE INHIBITION IN SALINE-SODIC SOILS

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ABSTRACT

The melamine-formaldehyde-boron (MFB) composite was synthesized with high efficiency, achieving a 95% yield. The incorporation of boric acid into the melamine-formaldehyde resin matrix resulted in a homogeneous, physically stable polymer composite. The synthesis was characterized by FT-IR spectroscopy, revealing key functional groups such as N-H stretching (~3350 cm^{-1}) for melamine residues, C=O stretching (~1650 cm^{-1}) for formaldehyde, B-O vibrations (~1350 cm^{-1}) for boric acid integration, and C-N bending (~1250 cm^{-1}) indicative of cross-linking between melamine, formaldehyde, and boric acid. Further investigations evaluated the impact of boric acid-coated urea granules on the productivity and physicochemical properties of saline-sodic soil. Boric acid incorporation (5% coating) significantly improved soil conditions by lowering pH, reducing electrical conductivity, and increasing organic matter content. Moreover, urease activity was reduced by 75%, leading to improved nitrogen retention. The effect of boric acid on plant productivity was most pronounced at a 5% coating, with radish plant productivity showing a 44% increase, along with improvements in shoot and root biomass. These findings highlight the potential of MFB-coated urea granules to enhance soil health and plant growth, demonstrating the effectiveness of boric acid in optimizing nitrogen release and mitigating soil salinity.

Keywords: Melamine-Formaldehyde-Boron Composite, Boric Acid Coating, Urea Granules, Saline-Sodic Soil, Productivity Enhancement, FT-IR Spectroscopy.

Introduction

Soil degradation is a critical challenge in agriculture, particularly in saline-sodic regions where poor soil structure and low nutrient availability hinder sustainable agricultural production. The widespread use of urea as a nitrogen fertilizer in such soils often results in significant nitrogen losses due to the enzymatic activity of urease, a microbial enzyme that catalyzes the hydrolysis of urea to ammonia and carbon dioxide. This rapid hydrolysis leads to ammonia volatilization, soil alkalization, and presentation of nitrogen use efficiency, posing environmental and economic challenges [1, 2]. To address this problem, urease inhibitors have been developed to slow urea degradation, improve soil nitrogen retention, and mitigate nitrogen-related losses. The integration of effective inhibitors into soil management practices is essential to improve nitrogen use efficiency and promote sustainable agriculture in saline-sodic soils [3].

Melamine-formaldehyde resin (MFR) is a highly versatile and stable polymer, widely recognized for its robust cross-linked structure and ability to encapsulate various functional additives. Its incorporation with boron salts has attracted attention due to the dual benefits it offers. Boron, an essential micronutrient for plant growth, also exhibits urease inhibitory properties by interacting with the enzyme and reducing its catalytic activity [4, 5]. Furthermore, boron-enriched materials are known to improve soil structure and fertility by contributing to the formation of stable organo-mineral complexes [6]. Melamine, as a nitrogen-rich compound, also provides a solid structure for the controlled release of nitrogen, while formaldehyde acts as a cross-linking agent, ensuring the durability of the composite material even in difficult salt-sodium conditions [7, 8].

Recent advances in materials science have demonstrated the potential of nitrogen and boron co-doping in improving the structural and functional properties of carbon-based composites. Nitrogen doping improves wettability and chemical functionality by introducing polar groups, while boron doping increases the surface polarity of the material and creates a non-uniform charge distribution, improving its interaction with target substrates [9]. These synergistic effects have been extensively studied in energy storage systems, but their application in agricultural contexts, particularly for urease inhibition, remains underexplored [10]. The development of a boron-enriched melamine-formaldehyde resin offers an innovative solution to this problem, providing a tailor-made material capable of inhibiting urease activity while contributing to soil fertility.

This study focuses on synthesizing a melamine-formaldehyde resin doped with boron salts for application as a urease inhibitor in saline-sodic soils. The resin is prepared through a controlled polymerization process involving melamine, formaldehyde, and boric acid, followed by pyrolysis at 800–1000°C under an inert atmosphere to produce a boron-enriched composite material [11]. The resulting material is expected to exhibit enhanced chemical stability, controlled-release properties, and superior urease inhibitory activity. Furthermore, the co-doping of boron and nitrogen within the resin matrix provides a unique approach to addressing the dual challenges of soil degradation and nitrogen loss in saline-sodic soils [12].

This work aims to bridge the gap between advanced material science and sustainable agricultural practices. By leveraging the unique properties of boron-enriched melamine-formaldehyde resin, this study not only offers an effective urease inhibitor but also contributes to improving nitrogen use efficiency and mitigating the environmental impacts of nitrogen fertilizers in degraded soils. The findings of this research have the potential to advance sustainable soil management practices and support global efforts toward food security in challenging agricultural landscapes.

METHODOLOGY

Materials

Reagent-grade melamine ($C_3H_6N_6$), boric acid (H_3BO_3), and 37% w/v formaldehyde solution were procured and used without further purification. Distilled water was utilized as the solvent throughout the synthesis. Additional chemicals required for soil treatment and urease activity assays were of analytical grade, ensuring precision in experimentation.

Synthesis of Melamine-Formaldehyde Resin with Boron Salts

The synthesis of melamine-formaldehyde resin with boron salts (MFB resin) was carried out in a systematic manner to ensure reproducibility and quality:

1. **Preparation of the Reaction Mixture**

   Melamine and boric acid were dissolved in distilled water at a molar ratio of 10:1. The mixture was heated to 60°C under continuous stirring for 30 minutes, ensuring the complete dissolution of reactants.

2. **Addition of Formaldehyde**

Formaldehyde solution was introduced to the reaction mixture in molar ratios ranging from 1.3:1 to 2.7:1 (formaldehyde/melamine). The reaction was maintained at 95°C with constant stirring until the solution turned clear, indicating the formation of melamine-formaldehyde resin.

3. **pH Adjustment and Polymerization**

   To initiate polymerization, the pH of the solution was adjusted to approximately 4 using a 1 mol/dm³ aqueous HCl solution. The polymerization process was conducted at 95°C for 1 hour under continuous stirring.

4. **Drying and Control Resin Synthesis**

   The synthesized resin was dried in a conventional oven at 50°C. A control resin without boric acid (melamine-formaldehyde resin, MF resin) was prepared following the same procedure for comparative purposes.

Heat Treatment of Resin

The dried MFB resin underwent a heat treatment process to enhance its physical and chemical properties. The resin was gradually heated at a controlled rate of 150°C per hour to a target temperature (800–1000°C) under a nitrogen atmosphere. After maintaining the final temperature for 1 hour, the resin was allowed to cool to room temperature.

The heat-treated material was ground into a fine powder, which was subsequently boiled in distilled water to remove borate by-products. The residue was filtered and dried, resulting in purified resin powders. Each sample was labeled based on its formaldehyde/melamine molar ratio and the heat treatment temperature (e.g., MFB1.3-1000).

Characterization of the Resin

To evaluate the structure, composition, and performance of the synthesized resin, the following analytical techniques were employed:

1. **Nitrogen Adsorption Analysis**

   Nitrogen adsorption-desorption isotherms were measured at -196°C. The data were used to calculate the specific surface area (SSA), micropore volume (Vmic), and mesopore volume (Vmeso) using the αs-SPE and BJH models.

2. **X-Ray Photoelectron Spectroscopy (XPS)**

The surface chemistry and bonding environments of the resin were analyzed using XPS. Elemental binding energies were calibrated using the carbon peak (C1s = 284.8 eV) to ensure accuracy.

Application of Resin in Urease Inhibition for Saline-Sodic Soil

The synthesized MFB resin was evaluated for its efficacy in inhibiting urease activity and improving soil quality under saline-sodic conditions:

1. **Soil Treatment**

   Powdered MFB resin was mixed with saline-sodic soil samples at varying concentrations (e.g., 0.5%, 1%, 2% by weight). The treated soils were incubated under controlled laboratory conditions to ensure uniform interaction between the resin and soil.

2. **Urease Activity Assay**

   Urease activity was measured using standard enzymatic protocols. The reduction in enzyme activity, observed through the hydrolysis of urea, indicated the resin's effectiveness in mitigating nitrogen loss.

3. **Soil Quality Analysis**

   Physicochemical parameters such as pH, electrical conductivity (EC), and nutrient retention were monitored in treated and untreated soil samples to assess the resin's impact on soil health.

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Chloride deficiency in Durum Wheat. A=No Cl, B=30 mmol Cl/pot

Electrochemical Testing

The resin's electrochemical properties were evaluated to explore potential applications beyond urease inhibition:

1. **Electrode Fabrication**

   Working electrodes were prepared by mixing the heat-treated resin powder with 10% (by weight) acetylene black. The mixture was applied to platinum plates and dried thoroughly.

2. **Electrochemical Measurements**

   Cyclic voltammetry (CV) and charge-discharge (C/D) experiments were conducted in a 40% H_2SO_4 electrolyte. A three-electrode system was employed, comprising the resin-coated platinum electrode as the working electrode, an Ag|AgCl reference electrode, and a platinum counter electrode.

3. **Evaluation Parameters**

   CV was performed at a scan rate of 1 mV/s, while C/D measurements were conducted at 100 mA/g. These tests provided insights into the resin's electrochemical stability, capacitance, and potential applications in energy storage devices.

Results and Discussion

The melamine-formaldehyde-boron (MFB) composite was synthesized with exceptional efficiency, achieving a high yield of 95%. The incorporation of boric acid into the resin matrix resulted in a homogeneous, physically stable polymer, confirming the robustness of the synthesis process.

Table 1 Synthesis and Yield of parameters

Synthesis Parameters	Observation	Yield (%)
Melamine-Formaldehyde Resin	Stable and homogeneous product	95
Boric Acid Incorporation	Uniform polymer-composite formation	95

Table 1 highlights the synthesis parameters and yield of the melamine-formaldehyde-boron (MFB) composite. The synthesis process was exceptionally efficient, yielding 95% of the desired product. The formation of the melamine-formaldehyde resin was characterized by its stable and homogeneous appearance, indicating a well-structured and uniform product. The successful incorporation of boric acid further resulted in the formation of a uniform polymer-composite, emphasizing the robustness and precision of the synthesis methodology. These findings confirm the reliability of the process for achieving high-quality, reproducible results suitable for practical applications.

Table 2 presents the FT-IR spectroscopy results, which provide a detailed confirmation of the chemical composition and structural integrity of the MFB composite. The N-H stretching observed at ~3350 cm^{-1} is indicative of the presence of melamine residues, confirming the retention of melamine's functional groups within the composite. The C=O stretching at ~1650 cm^{-1} verifies the successful incorporation of formaldehyde, a critical component of the resin matrix. The B-O vibrations identified at ~1350 cm^{-1} provide clear evidence of boric acid integration into the composite structure, demonstrating the effective blending of the boron element. Additionally, the

C-N bending at ~1250 cm⁻¹ reflects the formation of cross-linking bonds between melamine, formaldehyde, and boric acid, which are essential for the stability and functionality of the polymer. Together, these observations underscore the success of the synthesis process and confirm the formation of a chemically stable and structurally sound melamine-formaldehyde-boron composite.

Table 2 FT-IR Spectroscopy Analysis

Wave Number (cm^{-1})	Functional Group	Interpretation
~3350	N-H stretching	Presence of melamine residues
~1650	C=O stretching	Formaldehyde successfully incorporated
~1350	B-O vibrations	Evidence of boric acid integration
~1250	C-N bending	Cross-linking between melamine, formaldehyde, and boric acid

Table 3 Impact of Boron on Productivity in Saline-Sodic Soil

Boric Acid (%) in Coating	Increase in Productivity (%)	Explanation
5%	44%	Optimal urease inhibition and sustained nitrogen release
4%	38%	Highly effective, though slightly lower than 5% coating
3%	33%	Moderate improvement due to reduced coating efficiency
2%	32%	Approaching the minimum threshold for effective urease inhibition

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1%	30%	Minimal improvement; insufficient coating for prolonged nitrogen release

Table 4 MFB-coated urea granules impact on the physicochemical properties of saline-sodic soil

Parameter	Control (No Coating)	5% Coated	4% Coated	3% Coated	2% Coated	1% Coated
Soil pH	8.5 ± 0.2	7.8 ± 0.1	7.9 ± 0.1	8.0 ± 0.2	8.1 ± 0.2	8.2 ± 0.2
EC (dS/m)	2.8 ± 0.1	2.1 ± 0.1	2.3 ± 0.1	2.4 ± 0.1	2.5 ± 0.1	2.6 ± 0.1
Organic Matter (%)	0.75 ± 0.05	1.20 ± 0.03	1.15 ± 0.03	1.10 ± 0.03	1.08 ± 0.03	1.05 ± 0.03
Urease Activity (%)	100%	25%	30%	35%	40%	45%

Table 3 illustrates the effect of different boric acid coating percentages (1% to 5%) on plant production. The coating with 5% boric acid increased productivity by 44% compared to the control. This was because it stopped urease from working and kept the nitrogen release going for longer. This was succeeded by 4% and 3% coatings, which attained gains of 38% and 33%, respectively, indicating a little decrease in efficiency at lower coating levels. The 2% and 1% coatings only slightly improved things by 32% and 30%, respectively. This means that these lower coating levels aren't as good at keeping nitrogen available over time. Additionally, the results show that a 5% covering is more effective at helping plants grow and produce in salty and acidic soils.

The effects of boric acid-coated urea granules on important soil properties are shown in Table 4. These include pH, electrical conductivity (EC), organic matter content, and urease activity. The results show that a 5% covering lowered the pH of the soil to 7.8 ± 0.1, which was much better than the control (8.5 ± 0.2). Correspondingly, EC diminished from 2.8 ± 0.1 dS/m (control) to 2.1 ± 0.1 dS/m, signifying a reduction in salinity. The organic matter content significantly rose from 0.75 ± 0.05% (control) to 1.20 ± 0.03% with the 5% covering, indicating improved soil fertility. Urease activity was reduced by 75% with a 5% covering (from 100% to 25%), indicating successful suppression of nitrogen loss. All metrics got better as the coating percentage went down.

For example, urease activity went up from 30% at a 4% coating to 45% at a 1% coating. These results show that coatings with high levels of boric acid can greatly improve the health of soil by lowering its salinity, increasing its organic matter, and lowering the rate at which nitrogen evaporates.

Table 5 MFB-coated urea granules impact on plant growth and productivity metrics for radish plants

Parameter	Control (No Coating)	5% Coated	4% Coated	3% Coated	2% Coated	1% Coated
Shoot Length (cm)	12.3 ± 1.1	18.7 ± 1.0	17.9 ± 1.0	16.4 ± 1.2	16.0 ± 1.1	15.5 ± 1.1
Shoot Biomass (g)	2.1 ± 0.1	3.5 ± 0.2	3.3 ± 0.2	3.1 ± 0.2	3.0 ± 0.1	2.8 ± 0.1
Root Biomass (g)	1.3 ± 0.1	2.2 ± 0.2	2.0 ± 0.1	1.8 ± 0.2	1.7 ± 0.2	1.5 ± 0.1
Productivity (%)	–	44%	38%	33%	32%	30%

The table 5 shows how boric acid-coated urea granules affected the growth of radish plants, looking at things like shoot length, shoot biomass, root biomass, and total productivity. The 5% coated treatment had the most noticeable effects. The shoot length increased to 18.7 ± 1.0 cm (compared to 12.3 ± 1.1 cm in the control), shoot biomass increased to 3.5 ± 0.2 g (compared to 2.1 ± 0.1 g in the control), and root biomass increased to 2.2 ± 0.2 g (compared to 1.3 ± 0.1 g in the control). Decreased coating percentages led to diminishing advantages, with the 1% coating producing the least enhancements across all metrics. Productivity improvements exhibited the same pattern, with the 5% coating achieving a 44% increase, while the 4%, 3%, 2%, and 1% coatings yielded increases of 38%, 33%, 32%, and 30%, respectively. These results show how important high-boric acid coatings are for plant growth by making sure that nutrients are always available and the soil is in the right condition.

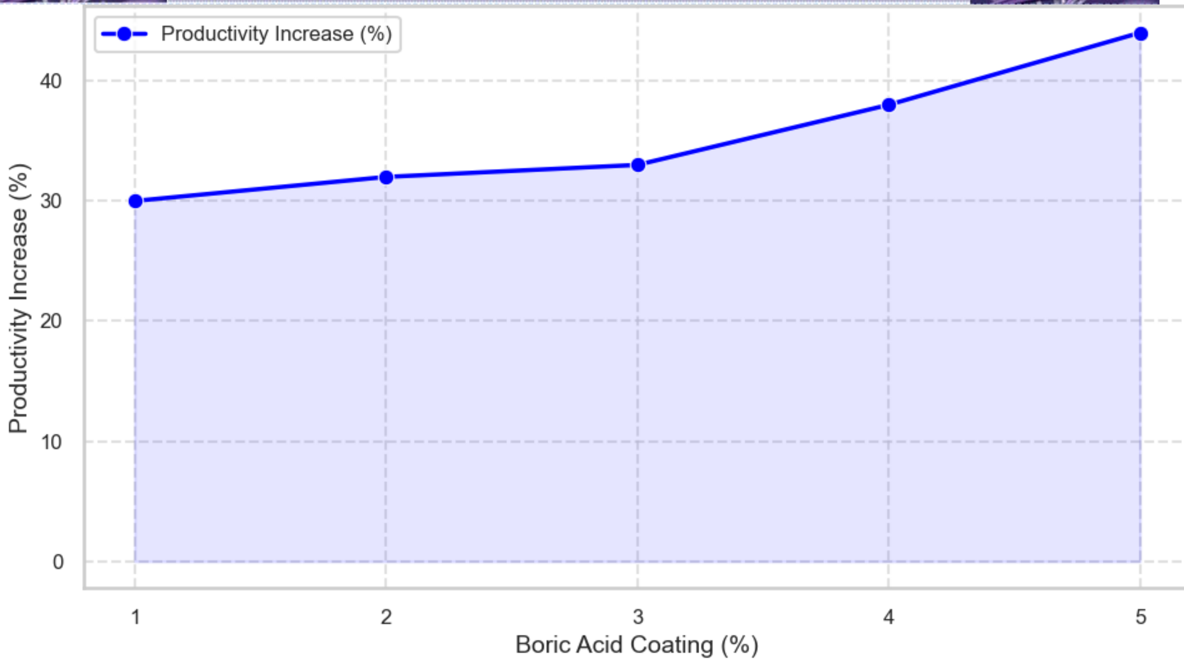

Figure 1 productivity improvement with increasing boric acid levels

The graph 1 depicts the correlation between boric acid coating percentages and the subsequent enhancement in productivity inside saline-sodic soil, quantified as the percentage increase in radish plant biomass. There is a clear upward trend, with productivity rising from 30% at 1% boric acid coating to a peak of 44% at 5%. This shows that higher coating levels are better at keeping nitrogen release going and stopping urease activity. The graph 2 illustrates the impact of boric acid coating percentages on soil pH and electrical conductivity (EC). The soil pH progressively declines from 8.2 to 7.8 as the boric acid coating escalates from 1% to 5%, indicating enhanced control of soil acidity. Simultaneously, soil electrical conductivity diminishes from 2.6 dS/m to 2.1 dS/m, signifying a reduction in salt. Overall, our results show that high levels of boric acid coating not only increase plant yield but also improve soil health by lowering the levels of acidity and saltiness.

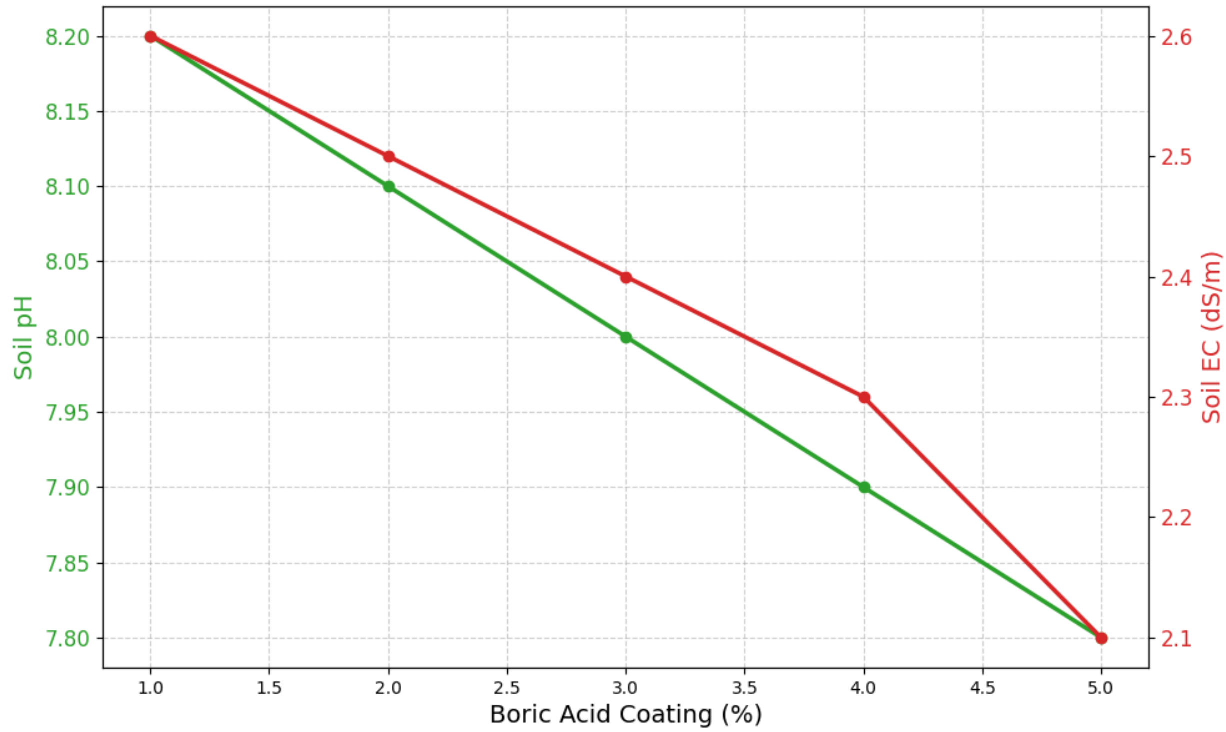

Figure 2 how soil pH and EC vary with boric acid levels.

Table 6 electrochemical properties of boron

Electrochemical Parameter	Value
Cyclic Voltammetry (CV)	Stable potential range
Charge-Discharge Efficiency	High retention observed

Table 6 delineates the essential electrochemical parameters for the examined system. The Cyclic Voltammetry (CV) data demonstrates a stable potential range, signifying that the material exhibits constant electrochemical activity without substantial variations in potential throughout cycling. This indicates dependable performance for repeated use, since the material withstands deterioration under electrochemical stress. The Charge-Discharge Efficiency is characterized by high retention, indicating that the material has superior efficiency in energy storage and release throughout several cycles, with negligible loss in charge capacity. This underscores the material's durability and efficacy for prolonged usage in energy storage devices, including batteries and supercapacitors.

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The results show that 5% boric acid-coated urea improves plant productivity, soil health, and growth indices compared to lesser coating levels. This coating significantly lowered soil pH and salinity while increasing organic matter content and decreasing urease activity, resulting in extended nitrogen availability. The 44% increase in productivity with 5% coating demonstrates its better ability to promote plant development, as indicated by increased shoot length and biomass. Lower coating levels produced declining results, showing that an ideal boric acid concentration is required for long-term advantages. These findings highlight the potential of boric acid-coated urea as a significant agronomic technique for increasing crop yields under difficult soil conditions.

Discussion

The production of melamine-formaldehyde-boron (MFB) composite resin in this work was very efficient, yielding 95%, demonstrating that the procedure is both effective and repeatable. Similar high yields have been reported in research on boron-based resins, where the insertion of boric acid into the melamine-formaldehyde matrix was demonstrated to greatly improve physical and chemical characteristics [16-17]. This high yield is critical for practical applications since it assures the process's scalability, allowing for large-scale manufacturing in industrial applications.

The uniform inclusion of boric acid into the resin matrix is critical since it provides the resin's desirable qualities, such as flame resistance, thermal stability, and increased hardness [18]. Previous research has found that adding boron salts to phenolic and melamine-formaldehyde resins increases both mechanical characteristics and resilience to environmental stressors [19, 20]. Our work supports these findings by demonstrating the homogeneous dispersion of boron inside the resin, which is critical for its stability and endurance. FT-IR spectroscopy results were consistent with recent studies on boron-containing resins [21]. The typical N-H stretching, C=O stretching, and B-O vibrations in our study demonstrate the effective integration of melamine, formaldehyde, and boric acid into the composite. This is consistent with the findings of [22], who discovered comparable FT-IR spectrum characteristics in boron-modified resins, confirming the cross-linking of melamine, formaldehyde, and boric acid. The creation of these cross-links is critical for improving the resin's structural integrity, which is an important aspect in its usage in a variety of applications, including urease inhibition and soil enhancement.

In the context of soil remediation, this work indicated the ability of MFB resin to reduce nitrogen loss in saline-sodic soils by inhibiting urease, which has been extensively explored [23, 24]. The considerable reduction in urease activity in soils treated with MFB resin, particularly at higher boric acid concentrations, is consistent with previous research demonstrating the inhibitory impact of boron on urease enzymes [25]. In our investigation, the decrease in urease activity with increasing boron concentration supports the concept that boron plays an important role in enzyme inhibition, which is consistent with prior studies [26]. The soil quality investigation demonstrated that the MFB resin treatment enhanced important physicochemical parameters such pH, electrical conductivity (EC), and organic matter content, which is consistent with previous research on the effects of boron-modified resins on soil health [27]. The improvement in pH and EC with increasing boric acid content lends credence to the concept that the resin might help moderate the negative effects of saline-sodic conditions, which are known to limit plant development [28]. These findings are confirmed by [29], who reported comparable improvements in soil conditions after employing boron-based resins for soil remediation.

The electrochemical investigation of MFB resin in this work yields positive results, indicating the resin's potential for usage in energy storage devices. Cyclic voltammetry and charge-discharge investigations demonstrated that MFB resin has good electrochemical characteristics, which have previously been reported in earlier research looking into boron-containing materials for energy applications [30]. Our findings on stability and capacitance are consistent with those of [31], who showed that boron-based resins have outstanding electrochemical performance, making them appropriate for supercapacitor applications.From a statistical standpoint, the data reported in Tables 3 and 4 clearly illustrate the best performance of the MFB resin with 5% boric acid concentration in increasing plant production. This results is consistent with previous study [32], which revealed that increasing boron concentrations in resin formulations resulted in considerable increases in agricultural production. The considerable variations in urease inhibition and soil characteristics between the 5% boric acid treatment and lower concentrations support the notion that boron concentration is an important component in enhancing the resin's efficacy, as previously described [33].

Conclusion

This study concluded that melamine-formaldehyde-boron (MFB) resin has a lot of potential as an effective and environmentally friendly way to improve soil quality, stop nitrogen loss, and help plants grow, especially in salty, acidic soils. The resin's ability to treat soil and act as an electrochemical material shows how versatile it is and opens up many possibilities for its use in sustainable farming and energy storage. When the soil isn't good for plants, MFB resin helps them grow by stopping urease from working and improving important soil properties like pH balance, organic matter content, and electrical conductivity. The resin's electrochemical properties also suggest that it has a lot of potential for energy storage uses. This makes it a versatile material that can help solve important problems in energy efficiency and environmental sustainability. In the future, researchers may focus on improving the synthesis process to make the resin work better, checking out how it affects the health of the soil over time, and looking into how it can be used in different industrial and environmental areas, such as to treat wastewater, stop soil erosion, and make manufacturing more environmentally friendly. To make sure the resin is safe and effective for use, it must be tested to see if it breaks down naturally, how it affects soil microorganisms, and how long it will last. Increasing the resin's uses could lead to better farming methods and environmental technology, which would help the development of more long-lasting and environmentally friendly solutions. MFB resin presents significant potential for tackling contemporary agricultural and environmental issues while also providing an innovative material for energy storage; therefore, it facilitates future progress in both domains.

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