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Wood Ash Additive for Performance Improvement of Gelatin-Based Slow-Release Urea Fertilizer

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Abstract: Urea is a crucial nutrient for plant growth, but because of its substantial losses due to nitrification, ammonification, and subsurface leaching, there is currently a push to reduce these losses. Urea is frequently uploaded and trapped in gelatin. In this research, the improvement of urea uploading and encapsulation efficiency is investigated using wood ash made from plant biomass (*Pinus roxburghii*). The 8 g w/v of gelatin was mixed with various concentrations of wood ash (from 4 to 16 g w/w), urea (from 4 to 24 g w/w), and glutaraldehyde (from 0.5 to 3 mL g⁻¹) to prepare various formulations of slow-release fertilizer (SRF). According to this study, adding wood ash to gelatin increases its ability to upload and encapsulate urea. The urea on its surface and the metal in wood ash both considerably contribute to the compositional alterations in gelatin in SRFs, which were demonstrated by IR spectroscopy. Visualization from photographs revealed that the homogenous dispersion of wood ash improved structural compatibility. The water content of the SRF formulation showed that wood ash can reduce water absorption by changing how hydrophobic gelatin is. Wood ash improves the gelatin's ability to reduce the rapid release of urea over time, according to testing of cumulative urea release from SRF. The optimal combinations for achieving the maximum 53.43% of urea uploading were 2.44 g of urea, 2.47 mL of glutaraldehyde, and 1.50 g of wood ash, according to the Box–Behnken model. The gelatin-based SRF that had been amended with wood ash was applied to the *Mentha spicata* plant, and the plant's healthy development and higher chlorophyll content revealed its agronomic potential. This study has a significant contribution to the development of an affordable and more effective wood ash-modified gelatin-based SRF.

Keywords: Gelatin; wood ash; urea; Box–Behnken design; slow-release fertilizer; *Mentha spicata*

1. Introduction

Major issues that the world is currently facing include extensive industrialization, fast urbanization, a rising population worldwide, increased food supply demand, increased environmental pollution, and a variety of changes in climatic patterns. Over the ensuing years, the world's population will surpass 8.5 billion [1]. Due to high food prices, grain shortages, and a disruption in the global fertilizer supply chain, the present Ukraine–Russian conflict threatens the world's food security [2]. Therefore, fertilizers should be enclosed in a biopolymer to affect their slow dissolving and release qualities in soil, preventing losses

of soil fertility and accelerating the rate of uptake by plants. Farmers can ensure minimal fertilizer usage, minimize fertilizer losses via agricultural field practices, and increase crop yield by trapping fertilizer for the desired release to the plant's roots. It has already been demonstrated that safe and consistent agricultural production of wheat in various ecological zones may be achieved with the use of appropriate SRFs (slow-release fertilizers). Under the existing and emerging climate changes, SRF increases yield, nitrogen efficiency, and benefits in terms of reducing labor input and improving economic returns [3].

The most widely used nitrogen fertilizer in the world is urea, although it is quickly lost from the soil when it volatilizes into ammonia. Enhanced efficient and eco-friendly fertilizers have been created to boost crop yield and primary productivity, reduce nitrogen losses, and improve nutrient recycling and reuse efficiency [4]. To reduce the on-field release of ammonia into the environment, one of the main issues facing the worldwide agriculture sector is reducing the usage of synthetic fertilizer. A substantial loss of nitrogen results in losses for the farmers to achieve the potential estimated and desired crop yield. In order to maintain environmental sustainability development goals No. 2 and 15, the United Nations and European Union passed legislation that limits 30% of urea fertilizer's ammonia emissions [5]. The most typical method for reducing urea solubilization is to entrap it in a matrix, which is typically made of natural biopolymers. These include lignin, starch, pectin, gelatin, chitosan, and gum, and each of their various compositions has been used so far [6]. In recent years, polymer-based controlled-release formulations have significantly outperformed chemical fertilizers because they help to maintain soil fertility by lowering soil pollution and plant toxicity in agricultural areas [7].

Gelatin is a biocompatible, inexpensive, biodegradable macromolecule with superior melting and gel-forming natural potential, which is an efficient characteristic. Numerous applications of these characteristics can be found in agricultural fields and for research purposes as well. The controlled-release urea gelatin microspheres were created using an emulsion cross-linking technique. The urea uploading and release are more effectively managed to optimize the urea-to-glutaraldehyde ratio, water absorption, and gelatin microsphere reaction time [8]. In another research, it was discovered that chitosan-alginate composite beads outperformed gelatin-alginate composite beads in terms of their capacity to entrap urea. When urea was trapped in gelatin-alginate beads rather than chitosan-alginate beads, the release of urea was also significantly restricted [7]. To improve the solubility of phosphate fertilizers, interpenetrating network hydrogels based on gelatin and polyacrylamide have been used to control the release of maleic acid [9]. To manage the soil environment system, slow-release fertilizers, urea, and sawdust were combined with gelatin as a binding material. After being treated with sawdust and gelatin, the time for the release of urea was prolonged [10].

For many years, it has been well-known that wood ash from bonfires is a possible source of lime and potash frequently used in agriculture. Applying ash to crops often improves the quality of the nutrients since it contains many of the trace elements that plants require for healthy growth.

Essentially, a direct supply of wood ash provides important elements, such as P, Ca, Mg, and K, in soil [11]. The ash may also contain a number of trace elements, such as Fe, Mn, Zn, and Cu, which would strengthen its beneficial effects in soil [12]. According to an assessment of the potential for nutrient recovery from industrial wood energy plants in southwest Germany, ash may replace about 3.1% (P), 7.5% (K), and 22.8% (Ca) of the raw materials used to make fertilizers [13]. It has been reported that the salt in wood ash helps to manage the pests on agricultural land [14]. An essential liming agent for agricultural land that is both environmentally friendly and revenue-generating is wood ash [15]. The use of ash increases the variety of microorganisms in soil [16]. According to reports, fertilizing the soil with wood ash reduced the amount of N_2O [17,18].

This study aims to control and improve urea's lease qualities by modifying the urea/gelatin film with wood ash. Consequently, wood ash has been added to urea that is trapped in gelatin and examined under IR and optical microscopes to describe it in

detail. The effectiveness of urea uploading, urea encapsulation, water absorption, urea release kinetics, and response surface approach optimization were assessed for these films' various ash compositions. Following growth experiments on the *Mentha spicata* plant, the agronomic parameters were evaluated.

2. Methodology

The following material and methods have been used to design and execution of this study.

2.1. Materials

Ammonium sulfate dodecahydrate (99%, Sigma Aldrich, USA), Granular urea (U) (borrowed from a local supplier), Gelatin (G) (Rossmorr, Pakistan), sulphuric acid (95–98%, Merck, Germany), Sodium hydroxide (>98% Merck, Germany), Glutaraldehyde (GA) (25% Aqueous solution, Merck, Germany), Nutrient agar (BioTrend, Germany), Absolute ethanol (99.5%, Merck, Germany), *p*-dimethylaminobenzaldehyde (99%, Sigma Aldrich, USA). *Pinus roxburghii* biomass was collected locally and burned to produce wood ash (A).

2.2. Preparation of Ash Modified Urea-Gelatin Films

Gelatin was used to entrap urea to create urea-gelatin films as SRF, and casting and drying techniques were used to create the modified films. The 300 mL glass beaker was filled with different concentrations of urea, such as 4, 8, 16, and 24 g w/w, and 100 mL of distilled water was then added. Then, 8 g of gelatin (at 8% w/v) was added. For 30 min, the entire mixture was heated to 60 °C. Wood ash levels of 4, 8, 12, and 16 g w/w were added to the mixture of urea and gelatin. To create a uniform slurry, the mixture was agitated for the next 1 h at 60 °C. As a crosslinking agent for gelatin, from 0.5 to 3 mL g⁻¹ glutaraldehyde (25%) is added, and the process is continued for an additional 1 h. After the mixture was put into the Petri dishes, the film was left to cure at room temperature. These films were then further dried for 1 h at 80 °C after they had dried. The dried films were immediately dried in an oven after being photographed and processed for two minutes with 70% ethanol. After that, these films were labeled and preserved on silica gel for later analysis. The SRF films made exclusively of urea-gelatin were known as UG, whereas the SRF films that also contained varying amounts of ash were known as A/UG. In the formulations of SRF films, the letters A, U, and G stand for ash, urea, and gelatin, respectively. The comprehensive plan for creating SRF films is shown in Figure 1.

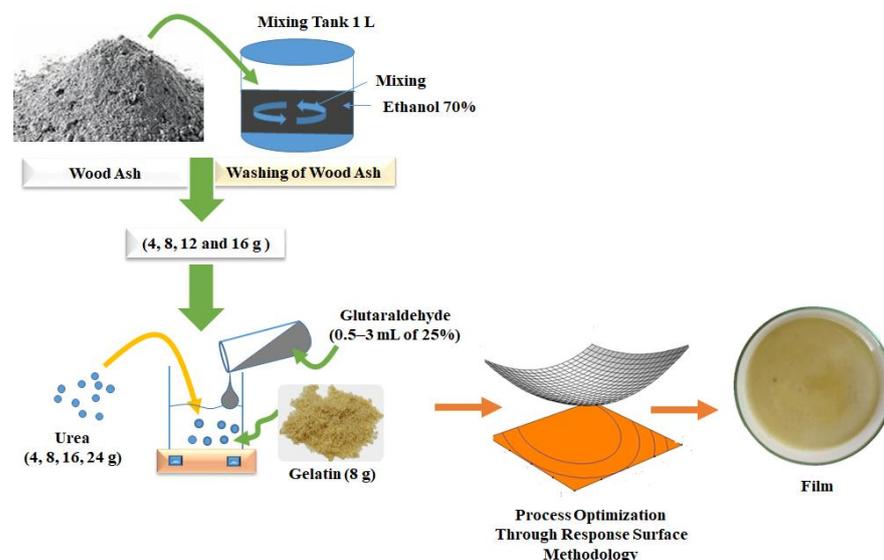


Figure 1. Gelatin film with urea modified by wood ash is being prepared as a slow-release fertilizer.

2.3. Urea Uploading and Encapsulation Efficiency

For uploading and encapsulation efficiency of urea, a UV-visible spectrophotometer (Model T60, PG Instruments, UK) was used the amount of urea uploaded from the solution into the ash-modified gelatin was also calculated [18]. For determining the UL and EE, a 300 mg film was quickly pulverized in a pestle and mortar in order to release the urea. After this, gently centrifuged this filtrate at 10,000 rpm for three (03) minutes. The supernatant is collected and given a 10-min reaction with *p*-dimethylamine benzaldehyde before the sample is run through a spectrophotometer. The solution turned light yellow because of the urea and *p*-dimethylamine benzaldehyde reaction. The relationship between urea concentration and color intensity is straightforward. The solution's absorbance was then measured using a UV-visible spectrophotometer at 420 nm wavelength. The amount of urea was also estimated by comparing the results to the urea standard curve.

UL represents the urea uploading, and EE describes encapsulation efficiency. Calculations for the urea's UL (%) and EE (%) are as follows:

$$UL = \frac{w_{ul}}{W_f} \times 100 \quad (1)$$

$$EE = \frac{w_{ul}}{w_{u0}} \times 100 \quad (2)$$

where w_{u0} is the initial weight of the urea in the mixture, w_{ul} is the weight of uploaded urea, and W_f is the weight of the film.

2.4. IR Spectroscopy

To verify the chemical stability of urea in the SRF films, infrared spectroscopy was carried out using a spectrophotometer (Shimadzu-8400S, Japan). By combining the crushed materials with KBr powder, pristine IR spectra of gelatin, pristine urea, and pristine SRF films were obtained. The spectra were averaged across 32 scans with a resolution of 4 cm^{-1} and a range from 500 to 4000 cm^{-1} .

2.5. Surface Visualization

On the Petri plates, the SRF films with a smooth surface and no increases were put. The films were then subjected to a morphological study employing visual analysis and a $10\times$ magnification. The homogeneity, smoothness of the surface, color variations, and any other changes, if any, were noted. After that, pixels of the films were taken with a Nikon Coolpix-S6700 (Japan), a 20 Megapixel camera.

2.6. Cumulative Urea Release Experiment

The cumulative urea release experiment for SRF films was conducted in distilled water [19]. The slow release of urea from these films was observed underwater. In practice, 1 g of SRF film was added to a 250 mL Erlenmeyer flask with double-distilled water at room temperature. A starting time (in minutes) is specified for the experiment, with a maximum of 360 min. The volume of the reaction flask is maintained throughout the experiment by infusing 1 mL of distilled water into the same reaction flask each time 1 mL of the solution is pipetted out. A triple urea solution was tested using a T60UV-Visible Spectrophotometer (PG Instruments, UK).

2.7. Swelling Measurements

A 0.5 g film was dissolved in 100 mL of deionized water at 25°C . Film was swollen for 16–36 h to reach equilibrium, and it took 24 h for imbibition/swelling. s. After the film has been submerged in water for 24 h, the water is decanted, and any remaining water is

delicately wiped away using high-quality tissue paper. Equation (3), mentioned below was used to calculate the degree of swelling (DS), according to a literature source [20].

$$DS = \frac{M_1 - M_2 - M_\mu}{M_2} \times 100 \quad (3)$$

where the M_1 is the weight of swollen SRF film, and M_μ represents the urea content in water, M_2 is the weight of dry SRF film, which was calculated by subtracting the content of urea from the dry film. Every experiment used in this study was repeated in triplicate trials.

2.8. Optimization of Urea Release

Box–Behnken design has been chosen [21], and the experimental independent variables interaction for optimizing urea release is modeled using response surface methods. Three independent variables with three levels made up the design of the experiment. Ash/Gelatin ratio, reaction time, and Urea/Gelatin ratio (w/w) (minutes). The UV-Visible spectrophotometer evaluated the dependent variable, UL (%). The Design-Expert 6.0.8 portable version was used to process the data for the response quadratic polynomial and analysis of variance (ANOVA) has been used to calculate the interaction between the process factors (GA, U, and A) and the response (UL and EE).

2.9. Effect on Plant Growth

U/G and A/UG films were applied to the *Mentha spicata* (Spearmint) plant. The *M. spicata* was grown during a 45-day period in clay loam soil with a soil texture class of 40% sand, 30% silt, and 30% clay. At the conclusion of the experiment, the chlorophyll contents were also tested to gauge the health of the plant. Fresh leaves were minced and placed in 5 mL acetone to measure chlorophyll contents. Then pass it through a 0.20 μm syringe filter amount of the chlorophyll was measured [22]. At wavelengths of 680 nm and 720 nm, the amount of chlorophyll was measured. To obtain dry biomass, the plant biomass is heated to 105 °C. Using a pH meter, the pH of the soil slurry (1:2.5) was determined.

2.10. Statistical Analysis

The effect of U/G and A/UG films on the soil pH, *S. spicata* plant's chlorophyll, and dry biomass was determined for significant difference using a paired-sample *t*-test at $p < 0.05$. Statistical tests were performed using the OriginPro version 8.5.1 (Northampton, MA, USA).

3. Results and Discussions

3.1. Urea Uploading and Encapsulation Efficiency in Gelatin Films

3.1.1. Effect of Urea Ratio

The varied urea-to-gelatin ratios in U/G films are shown in Figure 2, which enhances the urea's uploading and encapsulation efficiency. The urea uploading in U/G films was improved by gradually increasing the urea-to-gelatin ratio from 1:2 to 3:1. However, when the urea-to-gelatin ratio changed from 1:2 to 2:1, there was an increase in urea encapsulation efficiency. In U/L film, the greatest urea uploading was observed at 3:1 (48.8%) and the maximum urea encapsulation efficiency was obtained at 2:1 (56.6%). We believe that the declining pattern in urea uploading and encapsulation efficiency is caused by the reduced gelatin-to-urea ratio. Additionally, it is known that using too much urea prevents H-H bonds from forming, which lowers the risk of further urea entrapment within gelatin's loose and poorly constructed inner structure [8]. To overcome this obstacle, wood ash has been added to find improvement in uploading and trapping efficiency.

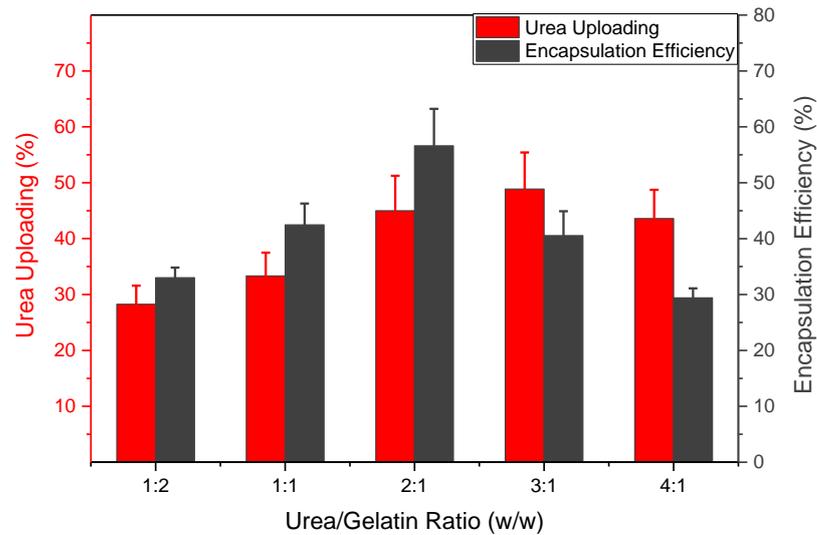


Figure 2. Effect of increasing the urea/gelatin ratio on the effectiveness of urea uploading and encapsulation in U/G film. U/G film was prepared with a 2 mL g^{-1} glutaraldehyde concentration and an hour-long reaction period. All values in the figure are represented as mean \pm standard deviation.

3.1.2. Effect of Wood Ash Ratio

The A/UG film's ability to upload and encapsulate urea was demonstrated in Figure 3, when different percentages of wood ash were applied. However, ratios of 1:1 to 2:1 failed to show any improvement or significant difference. Wood ash examined at ratios of 1:2 to 2:1 showed an increase in urea uploading and encapsulation efficiency. However, a wood ash ratio of 2:1 results in the highest urea uploading (54.03%). In contrast, when the wood ash ratio was 1:1, the urea encapsulation effectiveness increased to 59.94%. Wood ash is made up of numerous types of inorganic metals. The gelatin network may get stronger because of those metals. The ability of the gelatin network to upload and entrap urea is improved. It is understood that after being exposed to $\text{Zr}(\text{SO}_4)_2$, gelatin hydrogel's microspores shrank to tens of microns, and its water content also somewhat dropped [23]. As a result, it is believed that metals found in wood ash with positive charges may influence the gelatin's microporosity, facilitating the retention of urea and improving urea uploading.

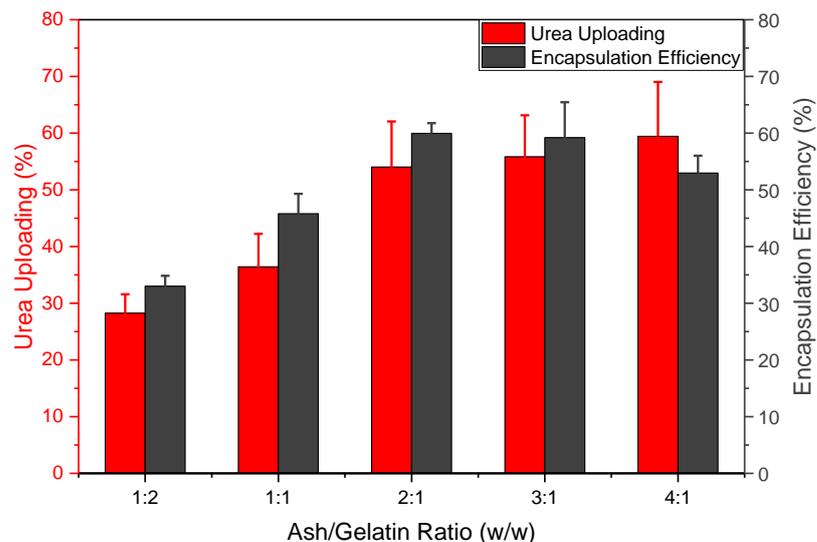


Figure 3. Effect of the increasing ash ratio on urea uploading and encapsulation efficiency in gelatin film. Gelatin film was prepared with a glutaraldehyde content of 2 mL g^{-1} and a reaction time of 1 h. All values in the figure are represented as mean \pm standard deviation.

3.1.3. Effect of Glutaraldehyde

Figure 4 illustrates the impact of various GA mL g^{-1} concentrations on the effectiveness of urea uploading and encapsulation. The uploading of the urea was significantly improved, and the effectiveness of encapsulation was further improved by increasing the GA concentration up to 2.5 mL, as shown by analysis. The effectiveness of encapsulation differed more from urea uploading. The highest urea uploading was 41.01% at a GA concentration of 2.5 mL g^{-1} , and the maximum encapsulation efficiency was 61.96%. GA was observed to increase the effectiveness of both urea uploading and encapsulation. GA is a well-known and frequently utilized gelatin cross-linker for film formation [24,25]. A 2.5 mL g^{-1} ratio of what? is ideal. The efficiency of additional urea uploading and encapsulation may be reduced by 3 mL g^{-1} due to minor changes in porosity. Different GA concentrations can be employed to alter the physico-chemical characteristics of gelatin films depending on the demands of a certain application. The results indicated that too much GA can make gelatin tougher and even cause trapped urea to escape from the matrix of the gelatin. Adding GA at concentrations between 0.1 and 1 w% has been shown to boost crosslinking from 60% to nearly 100%. The thermal, mechanical, swelling, and gelatin release in the solution of the films may all be slightly increased by the further addition of GA at concentrations of over 1 w% [25].

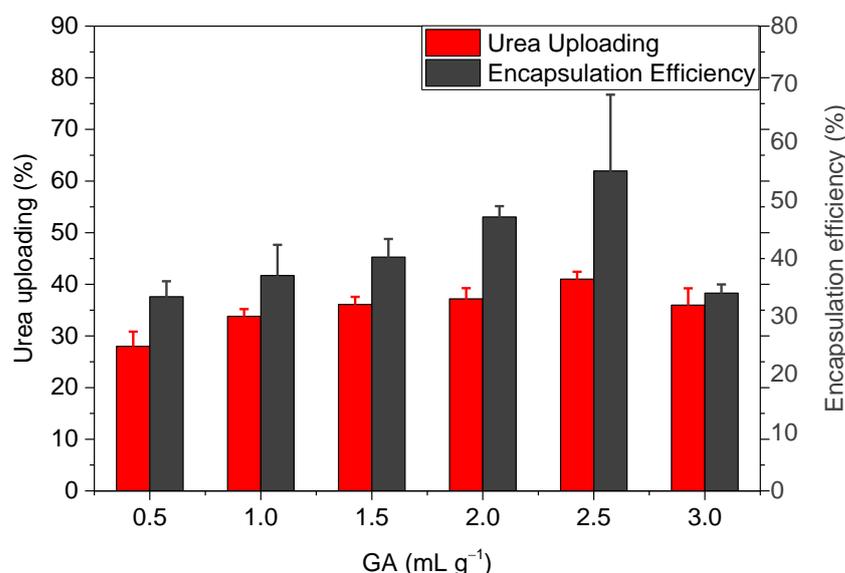


Figure 4. Effect of the GA content on the UG 2:1 films' urea uploading (%) and encapsulation efficiency (%). (Bars represents stand deviation). All values in the figure are represented as mean \pm standard deviation.

The effect of GA concentration on urea uploading and encapsulation efficiency for film added with wood ash is highlighted in Figure 5. Data indicated that the highest urea uploading in the A/UG 2:1 film was necessary for the GA concentration of 2.0 mL g^{-1} . Urea uploading at this GA content was 44.25 percent. It is interesting to note that the inclusion of wood ash improved urea encapsulation effectiveness more than other factors. The change in urea encapsulation efficiency remained essentially unchanged when the GA concentration was increased from 2.0 to 3.0 mL g^{-1} . The lowest concentration (2.0 mL g^{-1}) is the ideal limit to affect the properties of the A/UG 2:1 film because GA concentrations of 2.0 mL g^{-1} and above have the same impact. From past investigations, it has been concluded that urea concentrations of 50, 10, and 150 mg, which are trapped in gelatin and alginate beads, have an impact on the urea's regulated release [7]. Fly ash, a byproduct of coal combustion, has been utilized as filler in polyurethane at concentrations of 50, 10, and 20 weight percent because it enhances the thermal, mechanical, and cellular structure of biopolymers [26]. Therefore, using the ash may have enhanced the gelatin's physical and

chemical qualities, increasing the effectiveness of urea uploading and encapsulation in the current work.

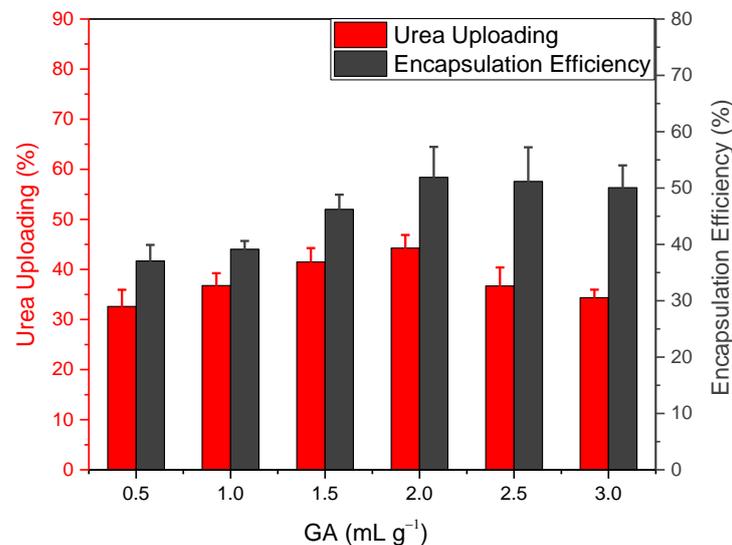


Figure 5. Urea uploading (%) and encapsulation efficiency (%) of A/UG 2:1 film as a function of GA content. All values in the figure are represented as mean \pm standard deviation.

3.2. Water Uptake

The water uptake in U/G film and A/UG film was compared in Table 1. It was found that the absorption is slowed down in both types of compositions as GA is increased from 0.5 to 3 mL g⁻¹. For both U/G and U/AG films, the water intake was reduced. When compared to the U/G film, the water uptake was reduced by 6.14% because of the addition of wood ash to the A/UG film. Wood ash can be added to films to boost their hydrophobicity.

Table 1. Equilibrium water absorption for several films with differing GA contents.

GA (mL g ⁻¹)	Water Uptake at Equilibrium (%)		Difference (%)
	U/G (2:1)	A/UG (2:1)	
0.5	298	251	15.77
1	282	246	12.76
1.5	270	244	9.62
2	266	234	12.03
2.5	261	231	11.49
3	257	228	11.28
Difference	13.75%	9.16%	6.14

It has been reported that bone ash has been used to strengthen the gelatin/alginate/hyaluronic acid film. In these films, the change in pH to an alkaline state and the neural charge, or negative charge, of the carboxylic acid groups augment the within-chain repulsion. This encourages the intake of more water [27]. However, as the GA concentration rises, the gelatin network becomes more cross-linked, further reducing chain relaxation and, in turn, water uptake. This was more apparent when comparing A/UG films to U/G films, which had a water uptake reduction of 11.28–15.77%.

3.3. Visual Analysis Optimization through Response Surface Methodology

The visual observations from the images indicated why the distribution of the wood ash in Figure 6 was more uniform. The opacity of the U/G film increases as the concentration of wood ash increases. The film was stronger, the surface was smoother, and the shelf

life was increased. Compared to the U/G film, which did not obtain wood ash and showed poor characteristics.

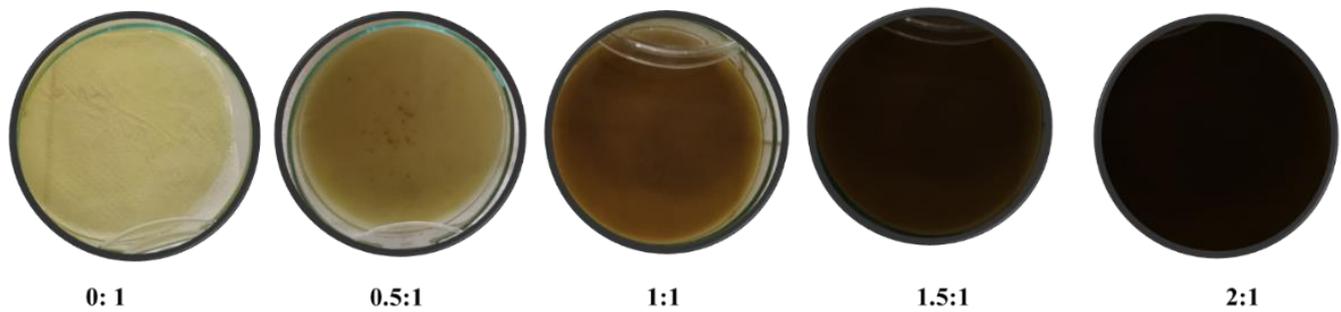


Figure 6. The A/UG film's morphology changes as the proportion of wood ash to gelatin increases.

When ash was added to A/UG films, a faint yellowish tint that had previously appeared in U/G films darkened. It is understood that the bonds formed between the amine groups of the gelatin and the hydroxyl groups of the glutaraldehyde, which result in the production of a Schiff base, cause the glutaraldehyde-promoted crosslinking to occur [28]. The primary visual characteristic caused by glutaraldehyde's action in cross-linking the gelatin strands is a yellowish color. The color is caused by a Schiff base, which is identified by the presence of a C=N group in which the carbon is connected to two groups other than hydrogen atoms. This base is created when the NH₂ groups of some of the amino acids that make up the protein react with the C=O group of the aldehyde [29]; see Figure 7.

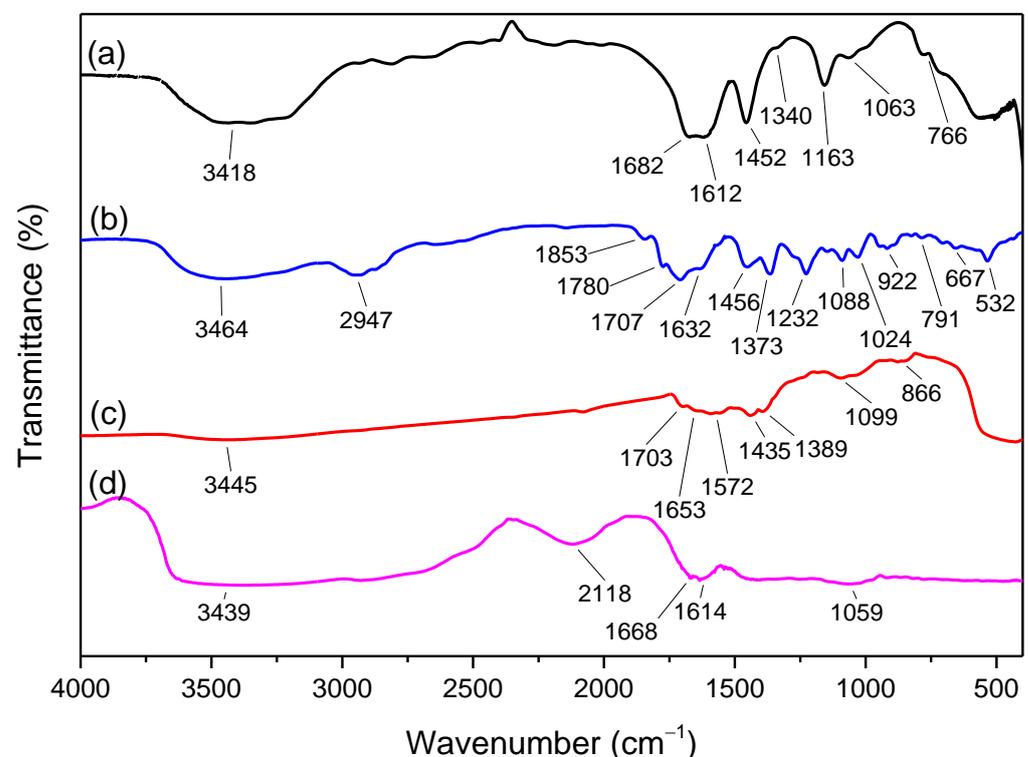


Figure 7. IR spectra: (a) urea, (b) ash, (c) gelatin, (d) A/UG film at urea/gelatin ratio 1:1 and ash/gelatin ratio 2:1 over time of 60 min.

3.4. IR Spectroscopy

In A/UG films, chemical changes were discovered using FTIR. The IR spectra for gelatin cross-linking, wood ash metal reactivity, and urea are displayed in Figure 7 to explain the chemical reactivity or alterations in film A/UG film. The urea molecule's

N-H stretching vibration is shown in Figure 7a at 3442 and 3346 cm^{-1} . The stretching vibration caused by C=O is indicated by the peak that was seen at 1682 cm^{-1} . The N-CO-N bonding was associated with the peak at 766 cm^{-1} , while the stretching vibration of the C-N bond was associated with the peak at 1452 cm^{-1} . The phases of the chemical structure and the distinguishing features of the wood ash are shown in detail in Figure 7b's IR spectrum. Si-O band vibrations at 1088 and 1024 cm^{-1} , and Al-Si-O symmetric bridge stretching vibrations at 532 cm^{-1} . It is also easy to see the consistently dispersed OH band at 3418 cm^{-1} . The water molecules are what caused the tiny peak to appear at 1632 cm^{-1} . The asymmetric stretching vibrations caused by the carbonyl group (C=O) are what give the band at 1546 cm^{-1} its characteristic shape. The carbonyl group in wood ash is a sign of the existence of carbonate compounds. Peak vibrations at 513 and 532 cm^{-1} also support silica production, as do vibrations at 667 cm^{-1} and 532 cm^{-1} . Stretching C-H vibrations are linked to the 2947 cm^{-1} peak. Figure 7c depicts the bending of the N-H link in the gelatin's chemical structure. The vibration at peak 1703 cm^{-1} , which is connected to amide I, causes the N-H bond to flex. An amide group makes up a protein's peptide link. The peaks of the infrared characterization of amide are the absorption spectrum bands of amide infrared radiation (IR), amide I (1600–1800 cm^{-1}), amide II (1470–1570 cm^{-1}), amide III (1250–1350 cm^{-1}). The C=O stretching vibration is mostly connected to the amide I band (between 1600 and 1700 cm^{-1}) and is directly related to the backbone conformation. Amide II is produced by both the C-N stretching vibration and the N-H bending vibration. The N-H in-plane bending and C-N stretching are present in the amide III area (1350–1200 cm^{-1}), as well as C-H and N-H deformation vibrations [30]. The amide I banding pattern is indicated by the band location at 1553 cm^{-1} . Amide II and III stretching frequencies relate to the peak positions at 1572 cm^{-1} and 1389 cm^{-1} , respectively. The C-H bend or scissoring stretching causes the band to be present at 1435 cm^{-1} . Figure 7d shows the gelatin film containing urea and additional wood ash (A/UG 2:1). Many of the peaks that are caused by wood ash, urea, and gelatin in the fingerprint region of the IR spectrum vanished from the film. This implies that gelatin has chemical and conformational changes that result in physical and chemical interaction with the surfaces of urea molecules and wood ash particles. However, a few peaks at 1059, 1641, 2118, and 3439 cm^{-1} were still discernible. Due to C-O stretching, the peak at 1059 cm^{-1} is present. The N-H bending in the amino groups of urea and gelatin is what causes the peak at 1614 cm^{-1} . The quartz formation is responsible for the peak at 2118 cm^{-1} [31]. The N-H of the -CONH- stretching vibration in the structures of gelatin and urea is what causes the peak at 3439 cm^{-1} . The stretching vibrations of the imine group (C=N) of the Schiff base, which is produced by the interaction of the aldehyde group of GA with the amino group of gelatins, also account for the sharp peak at 1666 cm^{-1} .

3.5. Slow Urea Release Study in Water

The release of urea from A/UG film containing various amounts of wood ash was carefully investigated in deionized water at room temperature. Figure 8 shows a comparison of the release of urea. After 20 min, burst release was detected for all compositions. However, there was a difference in the burst release. When wood ash was added to UG film at ratios of 0:1, 1:2, 1:1, 1.5:1, and 2:1, the burst release measured in terms of cumulative release was 66.62% (control), 56.01%, 41.21%, 35.13%, and 29.26%, respectively. The urea that is either poorly confined or readily present on the surface is released quickly during the initial burst release. It might possibly be because of film cracks, however, soft films such as the ones under study do not crack and expand when submerged. The urea that is fully trapped in the cross-linked network of the gelatin is released over time through a diffusion process, as evidenced by the later release after 20 min, which is comparatively slower. Due to metal interaction with gelatin, the wood ash's insoluble nature in water might have increased the strength of the cross-linked network of the gelatin and lowered its porosity. In A/UG (0:1), the maximum cumulative urea release was recorded at 91.25%. Whereas A/UG (2:1) had the lowest cumulative urea release, which was 55.55%.

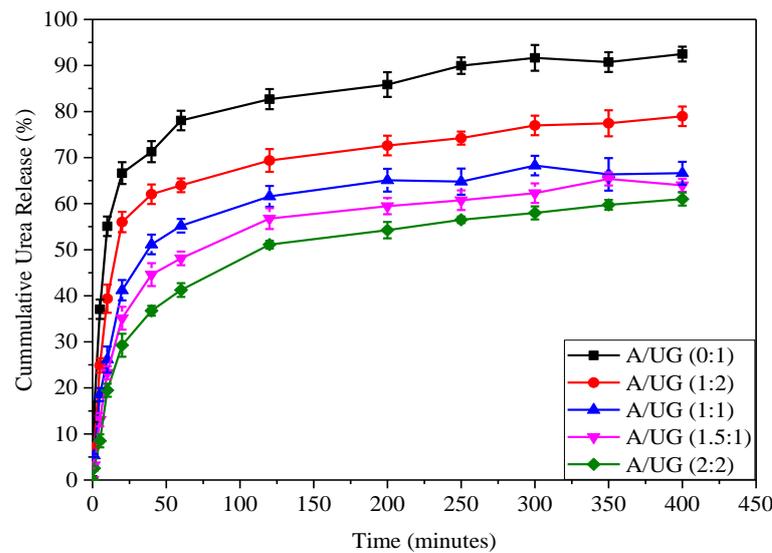


Figure 8. The impact of adding wood ash on the A/UG film’s urea release pattern (2:1). All values in the figure are represented as mean ± standard deviation.

3.6. Optimization by Box–Behnken Design

3.6.1. Urea Uploading

Table 2 displays the Box–Behnken design with three different factor levels and response. Equation (4) represents the quadratic model for urea uploading in terms of coded components, including U to G mass ratio (X_1), A to UG mass ratio (X_2), and GA concentration (X_3).

$$Y = +50.18 + 9.88X_1 + 4.50X_2 + 1.76X_3 - 2.16X_1^2 - 3.02X_2^2 - 0.66X_3^2 + 7.50X_1X_2 + 4.87X_3 - 1.50X_2X_3 \quad (4)$$

Table 2. Runs, factor levels, and response variable for the Box–Behnken experimental design.

Runs	Factor Levels			Response
	U/G (X_1)	A/UG (X_2)	GA (X_3)	Urea Uploading (%) (Y_1)
1	2	2	3	49.25
2	1	1	2	40.25
3	3	1.5	3	68.01
4	2	1	1	40.75
5	2	1.5	2	48.50
6	2	1.5	2	48.99
7	3	1	2	40.75
8	1	2	2	34.25
9	2	1.5	2	51.24
10	2	1	3	43.25
11	1	1.5	1	36.46
12	2	2	1	52.75
13	2	1.5	2	52.36
14	1	1.5	3	34.25
15	3	1.5	1	50.73
16	2	1.5	2	49.80
17	3	2	2	64.75

The analysis of variance (ANOVA) was used to evaluate the quadratic model equation’s importance (Table 3). The best-fitting quadratic model had a p -value of 0.0012 (significant), and the least-fitting model had a p -value of 0.0072 (significant). The corrected and anticipated R-squared differences were significantly more than 0.2, indicating that

observations may not follow regression lines. Figure 9 displays a plot of experimental and expected values for the urea-uploaded response using the ANOVA test. Both the experimental and forecasted data points clearly lie close to the regression line, indicating a good match. For response visualization through surface changes, the urea uploading to gelatin film for various combinations of independent factors has been shown in a 3D graph (Figure 10a–c).

Table 3. ANOVA for response surface quadratic model.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	1361.28	9	151.25	13.44	0.0012	Significant
Residual	78.79	7	11.26			
Lack of Fit	68.53	3	22.84	19.91	0.0072	Significant
Pure Error	10.26	4	2.56			
Total	1440.08	16				
R2		0.9453	Predicted R2			0.2274
Adjusted R2		0.8749	Adequate precision			13.508

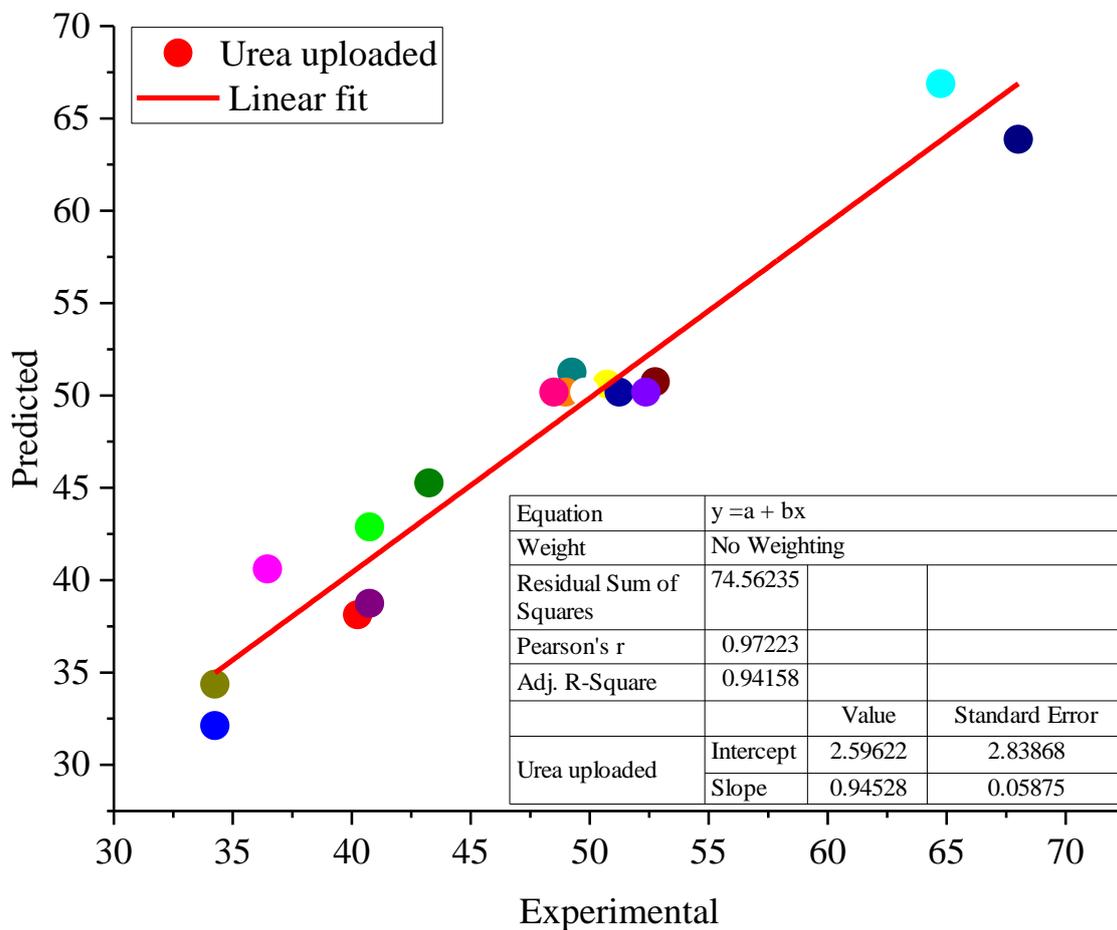


Figure 9. Plot shows the experimental and expected values of the urea uploaded in the urea/gelatin film under the interaction of the independent variables.

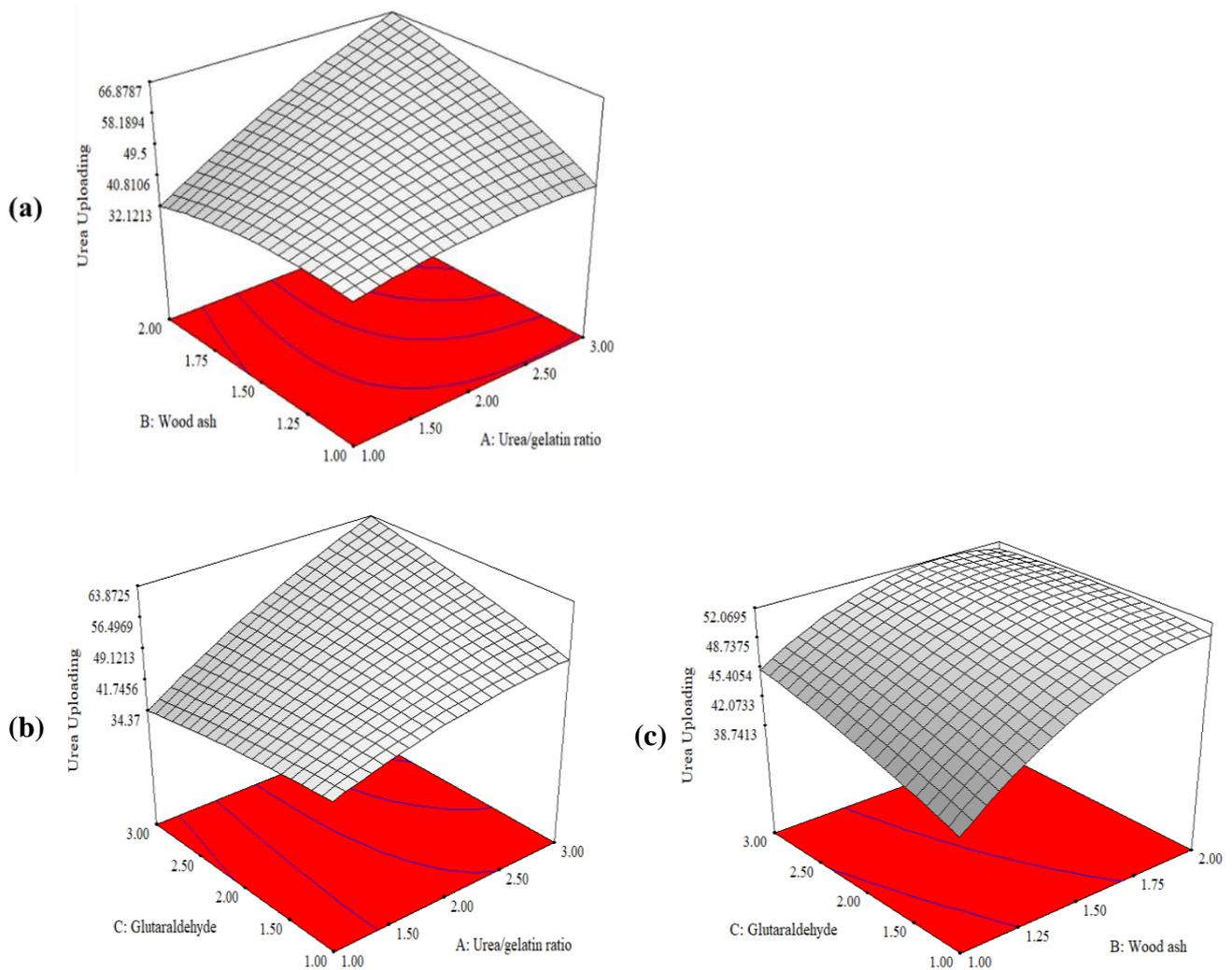


Figure 10. The effect of independent variables on urea uploading is shown in a three-dimensional response surface graphic. (a) The interaction between the urea/gelatin ratio and the amount of wood ash at a GA concentration of 2 mL g⁻¹; (b) The interaction between the urea/gelatin ratio and the amount of wood ash at 1.5 g; (c) The interaction between the amount of wood ash and GA at a 2:1 urea/gelatin ratio.

The interaction effect of urea on gelatin and the wood ash content on urea uploading is shown in Figure 10a. The uploading of urea into the gelatin grew steadily until it reached its maximum when the wood ash content was held constant within the range of 1–2 g. A maximum rise of 34.76% has been noted. However, maintaining the urea-to-gelatin ratio within the range of 1–3 g while altering the wood ash levels from 1 to 2 g revealed a similar upward trend in the amount of urea that was uploaded into the gelatin. The increase, nevertheless, was 24.0%. As a result, wood ash makes a positive contribution and raises the urea uploading to 10.74% at glutaraldehyde 2 mL g⁻¹. Therefore, increasing the ratio of urea to gelatin film may not have the same good impact on urea uploading as increasing the ratio of wood ash to urea.

From Figure 10b, when the ratio of glutaraldehyde is constant between 1 and 3 mL g⁻¹ at a wood ash fixed mass of 1.5 g, the uploading of the urea to gelatin showed an increasing trend with a maximum increment of 13.69%. When the urea is set to constant 1–3 g to gelatin then varying the glutaraldehyde the increase in urea uploading depicted the same trend with a higher increase rate of 29.5%. Therefore, glutaraldehyde contributed to urea uploading in gelatin film up to 15.81% and has a positive effect on urea uploading.

When urea uploading was compared with the interaction of glutaraldehyde and wood ash at a fixed urea concentration of 2.0 g, it was found that when the wood ash was fixed at 1–2 g and the glutaraldehyde was varied, the uploading of urea increased quickly, reached its maximum, and then decreased (Figure 10c). The considerable effect of glutaraldehyde in the presence of wood ash on the urea uploading is shown by the curve. When glutaraldehyde is fixed at 1–3 mL g⁻¹, changing the amount of wood ash causes the uploading of urea to increase by 0.52%. At ideal conditions, which included a urea-to-gelatin ratio of 2.22 g, a GA concentration of 2.47 mL g⁻¹, and a wood ash to U/G ratio of 1.50 g, a maximum urea uploading efficiency of 54.43% was projected. Several experiments were carried out under ideal circumstances to verify the expected values. Experimental results showed an average urea uploading efficiency of 53.49%, which was close to the expected figure.

3.6.2. Effect on Growth of *M. spicata* Plant

Table 4 shows the growth evaluation performed on the *M. spicata* plant following exposure to U/G (2:1) and A/UG (2:1) compositions of SRF films put on soil. Monitoring the changes in the plant's dry biomass, chlorophyll, growth, and soil pH allowed us to quantify the effect of these SRF films on *M. spicata*. Compared to U/G (2:1), the dry biomass of *M. spicata* rose by 3.33 g after treatment with A/UG (2:1). Chlorophyll buildup in *M. spicata* increases in response to A/UG (2:1) treatment up to 8.02 mg g⁻¹. When SRF film A/UG (2:1) was used to amend the soil, the pH dropped from 7.23 in the SRF film U/G (2:1)-treated soil to 6.66. Growth was seen in *M. spicata* after visual investigation. The paired-sample *t*-test revealed a difference was non-significant ($p > 0.05$) between the treatment of U/G and A/UG films on dry biomass and chlorophyll of the *M. spicata* plant and the soil's pH. Our study's findings have close conformity with those of the earlier researchers and are also supported by the scientific community in this field. In sandy loam soil (pH 5.18), the development of wintering Chinese chives (*Allium tuberm* Rottler ex Spreng.) has been boosted with SRFs (a resin-coated compound fertilizer). In comparison to conventional fertilizers, these SRFs are known for their effect on an increase in leaf length (from 8.3 to 13%), chlorophyll content (7.1% to 8.2%), accumulation of roots' dry matter (22%), and shoots' dry matter (36%) [32].

Table 4. The comparison of wood ash added urea gelatin film effect on growth performance of *M. spicata* plant and soil quality.

Parameters	U/G (2:1)	A/UG (2:1)	Difference	Paired-Sample <i>t</i> -Test $p < 0.05$
Dry biomass (g)	10.60 ± 0.84	13.95 ± 0.26	3.33	0.07881
Chlorophyll (mg g ⁻¹)	37.54 ± 4.29	45.56 ± 4.21	8.02	0.40992
pH	7.23 ± 0.16	6.66 ± 0.29	0.57	0.32751
Growth Visuals				



4. Conclusions

Utilizing cheap, plant biomass burning waste known as wood ash, the effectiveness of the urea/gelatin film as a slow-release fertilizer was improved. Wood ash improved the urea uploading capability while reducing the capacity for water uptake. The wood ash's gelatin surface coating will improve its impact on urea uploading and encapsulation, according to the results of the visual surface examination and IR spectroscopy. The three main factors that affect how the urea is uploaded and encapsulated in the gelatin are urea, wood ash, and glutaraldehyde. The maximum urea uploading efficiency of 54.43% was estimated successfully under a urea-to-gelatin ratio of 2.22 g, a GA concentration of 2.47 mL g⁻¹, and a wood ash to U/G ratio of 1.50 g using response surface methodology. Additionally, wood ash modification of film has a positive effect on the *M. spicata* plant's dry biomass and chlorophyll content. Moreover, such a film has an environmentally positive effect on stabilizing the soil pH (by maintaining the soil's pH). With the use of a wood ash ingredient, a slow-release urea fertilizer based on gelatin has been produced effectively.

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