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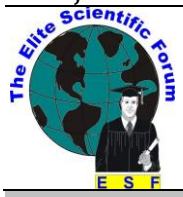

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RESEARCH ARTICLE

Simple and Environmental Friendly Preparation and Characterization of Slow Release Urea Tablet Made of Rice Husk Ash Composite with Chitosan Coating

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ABSTRACT

Slow release and coated urea has been commercially available, but the studies are still growing. Most of the studies used synthetic polymers and involved relatively complicated procedures. This study aimed to explore preparation of environmental friendly slow release urea tablet (SR-urea). The effect of composite composition, chitosan coating on the SR-urea tablet stability and nitrogen release were studied prior to the fertilizing characterization on growth parameters of corn. A composite containing prilled urea, rice husk ash, sago starch and chitosan in appropriate composition were used to fabricate stable SR-urea tablets that survived without decomposition in water up to 30 days of incubation. The nitrogen content was 12.27% (w/w) per tablet. The rate of urea leaching from SR-urea tablet in 100 mL water decreased from 0.048 g to 0.01 g per day, if SR-urea tablets were coated with chitosan film. Chitosan coating protected SR-urea tablet from excessive leaching, functioned as water storage and fungal growth retardation for at least one month. Growth parameters of fertilizing corn with 0.5 g SR-urea tablet showed non-significant difference from fertilizing with 2 g of prilled urea after 30 days of cultivation, but the nitrogen uptake efficiency (NUE) within dried plant was higher (12.37%) in treatment of SR-Urea tablet fertilizing.

INTRODUCTION

Urea is known as an effective fertilizer since it quickly supplies nitrogen (N) for plant, relatively cheap, readily available and easy in transportation. However, it has low efficiency in uses due to excessive leaching. Excessive urea leaching has been identified as a major contaminant to ground water and surrounding environment (Conrad and Fohrer, 2009; Qiao et al., 2013). Only 38.2–44.8% nitrogen of urea fertilizing is taken up by rice crop (Rahman et al., 2014). Approaches to reduce nitrogen losses during fertilization are by using urea slow release fertilizers and other by employing nitrification inhibitors (Carreres et al., 2003).

Urea slow and control release fertilizers known as control-release coated-urea (CRCU) have been commercially available and some are still under intensive studied using various composites as shown in many relevant publications (Azeem et al., 2014). The CRCU were coated either by using sulfur, polyolefin, methacrylic acid copolymer, 4,4-diphenylmethane di-isocyanate, triethanolamine, diethyleneglycol polyols or other synthetic polymeric materials (Azeem et al., 2014). In the preparation process, it is often used spray coating methods using organic solvent that has potential source for environmental pollution. Using slow release urea was not always better than common urea for all plants and for all seasons therefore the studies are still growing (Rodrigues et al., 2010). Slow release fertilizer using environmental friendly matrixes were reported previously (Khan et al., 2008; Adlim et al, 2018). Wheat straws and attapulgite were also used for preparation of nitrogen and boron slow release fertilizer; however, the process still involved copolymerization of acrylic acid (Xie et al., 2011). Chitosan has been introduced in preparation of control release fertilizer to prepare phosphor slow release. In

the formula chitosan-hydrogel was made by blending chitosan with PVA (Polyvinylalcohol) and crosslink with glutaraldehyde (Jamnongkan and Kaewpirom, 2010a, b). Corradini et al. (2010) incorporated NPK fertilizer in a nanoparticle matrix prepared by polymerization methacryclic acid in chitosan solution but the fertilizer performance test has not been reported. Similar work on chitosan use but using combination technique between emulsification and cross-linking methods has been also known (Hussain et al., 2012; Tao et al., 2012). However, the processes are considered relatively complicated especially if it is applied in home industries.

The environmental friendly materials used in the present study were rice husk ash, sago (*metroxylon sp.*) starch and chitosan. The rice husk ash was used as the support for urea, sago powder as the adhesive and chitosan as the coating material. The rice husk ash is waste in rice milling process and chitosan is originally isolated from shrimp shell, the waste of fishery industries. The rice husk ash is available in large quantity in Indonesia which is around 20% of 71, 279, 709 tons of grain production in 2013 (http://www.bps.go.id/). The utility of rice husk ash has been reported as an absorbent (Tavlieva et al., 2013); a concrete supplement (Zain et al., 2011) and as a raw material for organic fertilizers or as fertilizers especially for wheat crop due to high content of silica and other important trace minerals including P, K, S, Fe, Ca, Mg, and N (Thind et al., 2012; Lim et al., 2012).

Sago plant also grows almost in every province in Indonesia with production of 5,640 million tons of dry sago starch per year (Timisela, 2006). The native sago starch was reported as good for gelling agent (Teng et al., 2013) and important material for control release drug (Singh and Nath, 2013; Hasyim et al., 2011; Chin et al., 2011). This study aims to search the best composition for SR-urea tablet preparation, the effect of chitosan coating on the rate of urea leaching in water and the fertilizing performance of SR-urea tablet on corn growth parameters.

MATERIALS AND METHODS

Materials and equipment

Chitosan medium molecular weight (~400000, "Fluka", Switzerland), urea (prilled /crystal), sago (starch, market available), rice husk ash (from rice milling waste). Para dimethylamino-benzaldehyde (p.a grade, "Fluka", Switzerland), hybrid corn seeds (Pioneer 19 variety), Spectrophotometer UV/Vis spekol 2000, Microscope trinokuler Olympus CX41 with camera DP12, microscope stereo bellstone with optical camera and Kjeldahl equipment and the chemicals for N total analysis by Kjeldahl method.

Preparation of Slow Release Urea Tablet denoted as SR-urea tablet

Around 3 kg of each sundried rice husk ash and sago starch (commercially available) were ground separately and each was sieved with 200 mesh sieve and shaker. The powder which passed through the sieve (< 200 mesh of the particle size) was collected and dried in an oven at 105°C until for 2 hours.

The composite composition weight was maintained at 50 g with several combinations of rice husk ash: sago starch; (45:5), (40:10), (35:15), (20:30), (25:25). Each of combination was added slowly into solution of 10 g of dissolved prilled urea in 20 mL distillated water and mixed thoroughly using a heater mixer at around 50°C for 10 minutes. Stirring rate was adjusted several times according to the viscosity of mixture. Additional 5 mL of urea solution (0.5 g/mL) was added carefully to adjust the viscosity till it formed dried pasta. The pasta was inserted into a tablet mull (9 holes with each diameter of 12 mm) prior to be pressed as SR-urea tablets using a hydraulic press machine at pressure of 100 kg/cm^2. The control tablets were prepared without addition of urea.

The tablets were air dried for 2 days before being coated with chitosan. The dried tablets were submersed for 2 minutes in 100 mL solution of chitosan-acetic acid solution made of 0.2 g of chitosan flake in 100 mL of 5% acetic acid solution (Adlim and Bakar, 2013). As the control, SR-urea-tablets were prepared without chitosan coat. The chitosan-coated tablets and the control ones were air dried for 2 days before being dried in oven at 60°C for 2 hours to evaporate water and trace amount of acetic acid from the chitosan layer.

Screening the best composition based on the stability urea-tablets in water

SR-urea-tablets coated with chitosan and the control ones (uncoated) were soaked in 100 mL distillated water and each has three replications. Daily observation was done and the decomposition time was recorded. SR-urea tablets decomposition within water was considered occur when it started to crack, melt, dissolve the tablet or form a turbid solution. The number of tablets decomposed per day was counted and converted to percent of tablet decomposition. After finding the right composite composition, then the urea composite was reproduced in larger quantity.

Determination of N total in urea tablets

After finding the best composition of the tablet, the study was focused on determination of N total in tablets using Kjeldahl methods. Prior to N total determination, the urea tablets were oven dried for one hour in an oven at 60^{o}C until a constant weight and randomly sampled several tablets. The results were weighted with an analytical balance and the water content was determined. One tablet was sampled and grinded prior to weight, then 1.022 g of the powder was transferred to a Kjeldahl flask.

Several steps and several chemicals were added to the flask as the common procedure for N total determination with Kjeldahl methods (AOAC, 1980).

Rate of urea leaching from urea tablet

One chitosan-coated SR-urea-tablet was randomly taken from 100 dried tablets and soaked in 100 mL of distilled water. This procedure was done three replications and each solution was placed in a water bath to maintain the temperature at around 29°C and covered up with plastic film to avoid evaporation. The solution was stirred gently using a stirring rod and every 3 days, 5 mL of the aliquot was taken for urea determination using spectrophotometric method. In a separate glass beaker; 0.2015 g of p-dimethylamino-benzaldehyde was dissolved in 0.25 mL of H_2SO_4 (36 N) and 70 mL of CH_3OH (labeled as DB solution). Three milliliters of aliquot were mixed with 2 mL of DB solution and recorded the absorbance with the spectrophotometer (Husain et al., 2002).

Urea standard solutions were made from urea solution at concentration of 1, 2, 3, 4, dan 5 ppm. It was taken 3 mL aliquot from each solution was added 2 ml of DB solution, mixed truly and recorded the absorbance at 420 nm using a UV-Vis spectrophotometer model Spekol 2000. The absorbencies were plotted with the concentration to form a calibration curve.

Performance test of urea tablet on corn growth

SR-urea tablet was applied on corn fertilization by using prilled urea and without urea as controls. The experiments were carried out using randomized complete block design with 5 treatments and 3 replications. There were 15 unit experiments distributed in 5 blocks that were Block P_1 (without urea, "control-1"), Block P_2 (2 g of prilled urea per plant, "control-2"), Block P_3 (1.5 g urea in urea tablet per plant), Block P_4 (1 g urea in urea tablet per plant) and P_5 (0.5 g urea in urea tablet per plant). Phosphor (SP-36) and KCl fertilizers were consistently treated for each plant with doses of 2 g and 1 g per plant respectively.

Germination

Hybrid corn seeds (Pioneer 19 variety) obtained from Department of Agriculture, Republic of Indonesia was planted in a wet-river-sand as the seedling media. The study plot area was 0.80 m x 0.50 m and the seeds were planted in area of 0.05 m x 0.05 m. The seeding was placed in shade area and watered 2 times a day following the reported procedure (Kartasapoetra, 2003).

Soil testing before cultivation

Soil sample was collected and tested at Soil Testing Laboratory of Syiah Kuala University. Parameters observed were soil texture, total Nitrogen (Kjeldahl), ratio of C/N (Walkey & Black), cation exchange capacity CEC (NH_4O_{AC} pH 7), and soil pH (Electrometric). Soil samples were taken from various plots and mixed homogenously prior to laboratory testing (Rosmarkam and Yuwono, 2002).

Cultivation

The corn seeds were planted on gardening type of soil (inceptisol). Corn parameters used were stem length and stem diameter. Stem length was measured from the bottom stem till the highest node, while the stem diameter was measured at 5 cm above the lowest brace root.

Experiments were conducted in garden-enciptisol soil protected by a perimeter fence as common practices in Indonesian community. Soil was processed with conventional tillage with two times of plowing. There were 15 plots (1 m x 1 m) with distance of 0.25 m and 0.5 m wide of drainages verified the literature (Kasinius, 1993).

Plantings with various treatments were labeled and placed randomly in several plots. After 8 days germination, the growing seeds were sorted and those that were healthy thriving and have 7 cm height were selected for planting. The seeds were planted in ~ 3 cm depth with a single plant per plot (Kartasapoetra, 2003). Watering was in the morning and in afternoon. Prilled urea, KCl and phosphor (SP-36) or urea tablet-(SR) were distributed around 7 cm from the plants in 5 cm deep (Purwono and Hartono. 2008). Weeding and insect spraying were after 15 days after planting (DAP) (Kasinius, 1993).

Soil test after fertilizer application and nitrogen absorption

Soil around the plants was sampled after 30 DAP for Total-N determination with Kjeldahl methods. The diameter of corn stalks was measured at 5 cm from based of the root using a caliper at 30 DAP (Ramlan and Yufniati, 2009).

The Total-N absorbed by the plant was analyzed at 30 DAP using Kjeldahl method. Prior to analysis, the whole part of the sample plants (roots, stems & leaves) was cleaned from the soil and washed several times. The sample was finely chopped, weighted and dried in an oven at 60ºC for 48 h until it has relatively constant weight. The dried sample was weighted again prior to wet destruction and followed with total-N determination with Kjeldahl method (AOAC, 1980).

The NUE might have various definitions (Dawson et al., 2008) but this study, NUE was calculated based on total N in treated plants tissue subtract the total N in control plant and divided by total N added to the soil.

RESULTS AND DISCUSSION

Preparation and stability test of SR-Urea tablet

During the SR-urea tablet preparation, higher water content in composition matrix lead to decrease solidity and eventually SR-urea could not be produced. This was due to water and sago starch influenced the viscosity and solidity of the mixture (Pimpa et al., 2007). High concentration of sago starch caused high

viscosity of the mixture and subsequently decreased the urea solubility and formed a heterogeneous matrix as well as higher cost processing. When rice husk ash was dominant within composition, it caused decrease the urea tablet stability in water as shown the composition test of SR-tablet in water (Table 1).

The average dried weight of SR-urea tablet was 1.92 g each with 4.17% of water content and the mean urea content was 0.538 g per tablet. The urea evaporation from tablet during preparation was not significant amount since the melting point of urea was 135°C which is above preparation temperature (Ebrahimian et al., 2012). Nitrification in tablet during sample preparation also might not plausible theoretically since processing temperature was above 40°C (Frederick, 1956).

The composition test was carried out by soaking dried SR-urea tablet in water. Table 1 shows that the optimum weight ratio of tablet composition was 2:2:3 for water, sago starch and rice husk ash respectively (Table 1 entry #4). In fact, the most stable was on the ratio of 2:2.5:2.5 (entry #5), but it was high content of sago starch that cause difficulty in urea distribution in tablet matrix and high cost preparation.

Urea leaching in water

Although physically the SR-urea tablet did not decompose after 7 days but leaching urea started as soon as the tablet soaked in distilled water. Within three days soaking (one tablet containing 0.538 g of urea within 100 ml distillated water), the urea has leached 10-25 weight percent (wt %) and the rate of urea leaching was much slower when urea tablet coated with chitosan (Figure 1). The image chitosan coating and the chitosan film are displayed in Figure 2 (a-b). The average leaching rate without chitosan coating was 0.048 g per day or 9wt% per day in 0.1 liter of water and with chitosan coating the rate was only 0.01 g per day or 2 wt%. This leaching rate is much slower than previously reported. Xie et al. (2011) published that slow release nitrogen and boron fertilizer (SNBF) released 60.1 wt% within three days in soil. Xiaoyu and co-workers reported urea sulfur-coated released 75 wt% of urea in 14 h with condition of 12 g per liter water and common urea has rate of <0.5 h (Xiaoyu et al., 2013).

The prilled urea displayed as white area was trapped in matrix of sago powder and rice husk (Figure 2). The trapped urea has spot area of < 100 μm and distributed in the matrix. Chitosan film covered the tablet as marked with a solid line and compared to the border of SR-urea tablet (dash line). This coating protected urea from leaching until water penetrated the film and decomposed the matrix. Chitosan thin film was transparent, sticky and swelled in water (Figure 3). The chitosan film also protected the matrix from excessive dryness and fungi growth. There were no fungi hives observed on the urea tablet although it has been stored for three months. The sterilization might have connection with low water content (<10%) and the presence of chitosan as known has antimicrobial activities (Goy et al., 2009).

Properties of chitosan swelling and water absorption also gave advantage as the water storage into SR-urea tablet when it is applied for a dry planting media such as in orchid fertilizing. Water holding average of the SR-urea tablet after 10 minutes soaking in water was 16.31wt% compared to the weight of SR-urea tablet. This water holding is higher than SNBF fertilizer reported previously (Xie et al., 2011).

The mean of nitrogen content of SR-urea tablet analyzed with Kjeldahl method was 12.27% (w/w) for each tablet. The percentage is closed to the theoretical amount of nitrogen (13%) from 0.538 g of urea content within 1.92 g SR-urea tablet according to spectrophotometric methods. The nitrogen weight comparison between prilled urea and SR-urea tablet were 2 g of prilled urea = 7.49 g of SR-urea tablet; 1.5 g of prilled urea = 3.74 g of SR-urea tablet and 0.5 g of prilled urea = 1.87 g of SR-urea tablet.

Soil properties before cultivation

Soil properties were analyzed on the surface with 0-20 cm depth and it was found that the texture was sandy-clay loam, pH (neutral), C total (1.81%, considered low), N total (0.19%, considered low), C/N (9.53, considered low) ratio and cation exchange capacity (CEC, 17.6 cm $_{(+)}$ kg^{-1}, considered moderate) . The soil condition was suitable for corn plantation. Based on these data, it was indicated that the soil was low organic content and fertilizing is necessary.

Corn growth response towards SR-urea tablet fertilizing

The corn respond on the fertilizers were monitored on the stem diameter and stem extension. The stem length and diameter were measured from the brace root up to the node. Statistical analysis showed that there were significantly different diameters of corn at various doses and type of urea fertilizers ($P<0.05$). Similar finding was also observed for stem length differences ($P<0.05$).

As shown in Table 2 that fertilizing affect significantly on the stem diameter and extension of corn. However, there was no significant different on the corn growth fertilized with either 2 g of prilled urea or with 0.5 g of SR-urea tablet. Fertilizing corn with 2 g of prilled urea per plant is common practice in society. This suggests that the common dose urea (2 g per plant) for corn growth could be reduced up to 0.5 g or 75% reduction when it was applied SR-urea tablet. Increasing the SR-urea tablet doses also let to increase the stem extension but no different on the stem diameter. Doses reduction will reduce the crop operational cost since the production cost for SR-urea tablet is still comparable to prilled urea cost and reduce the potential pollution.

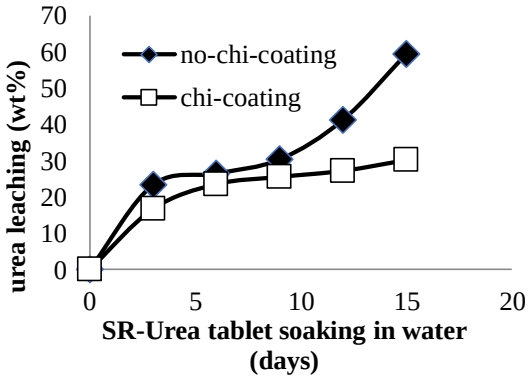

Fig. 1: Urea leaching from SR-urea tablet in water

Table 1: The average condition of urea tablet in water (one tablet within 100 mL distillated water)

No	Water (mL)	Sago (g)	Rice husk ash (g)	Stability SR-urea tablet in water before started to decompose(days)
1	20	5	45	7.00±1
2	20	10	40	10.67±1
3	20	15	35	23.67±1
4	20	20	30	30.00±1
5	20	25	25	35.67±1

Table 2: Mean of the stem length and the stem diameter of corn on various treatments at 30 DAP

Treatment with/o urea fertilizing per plant	stem length (cm)	stem diameter (cm)
P_0 (no urea)	15.20±0.4	0.57±0.02
P_1 (2.0 g within prilled urea)	17.10±0.7	0.62±0.01
P_2 (1.5 g within SR-urea tablet)	23.20±0.4	0.74±0.03
P_3(1.0 g within SR-urea tablet)	20.77±1.3	0.72±0.03
P_4 (0.5 g within SR-urea tablet)	17.50±0.6	0.65±0.02
Least Significant Different (0.05 with LSD)	1.45	0.04

Table 3: Mean of total N in the dried plant, nitrogen uptake per plant at various fertilizing treatments

Treatment per plant	Wight of dried plant (g)	N uptake per plant (g)	NUE (%)
P_0 (no urea)	1.34±0.1	0.02±0.01	NA
P_1 (2.0 g within prilled-urea)	1.67±0.3	0.04±0.01	2.03±0.7
P_2 (1.5 g within SR-urea tablet)	3.71±0.6	0.09±0.02	10.07±3.0
P_3(1.0 g within urea SR-tablet)	2.94±0.6	0.07±0.01	10.35±2.3
P_4 (0.5 g within SR-urea tablet)	2.13±0.2	0.05±0.01	12.37±5.3
Least significant different (0.05 with LSD)	0.72	0.04	5.69

Confirmation of the effect on nitrogen fertilizing was also studied based on the nitrogen content in the dried-whole-part of each plant and the nitrogen uptake as displayed at Table 3. The corn fertilized with urea had more nitrogen content in the ash and had more nitrogen uptake than the control except at treatment with 2 g prilled-urea. Corn fertilized with 0.5 g of SR-urea tablet had no different nitrogen content and nitrogen uptake from corn fertilized with 2 g of prilled urea. A similar trend was also observed for the total N in the dried plant and nitrogen uptake of the corn. However, the nitrogen uptake efficiency (NUE) was much higher (12.37%) at treatment of 0.5 g of SR-urea compared to those of 2 g of prilled urea treatment but it was not significantly different from other SR-urea tablet treatments.

Soil properties after planting

Based on the stem length and diameter respond, P_4 treatment was considered the best fertilizing system. To analyze the urea supply in the soil media, then the soil was sampled and analyzed the physical and chemical parameters. The data were compared to control (P_1) at 15 DAP and 30 DAP. It is found that the properties were not much different in terms of sampling time, type of urea treatment and soil properties before planting. The pHs were all neutral (7.14), C total (1.75-1.91%,

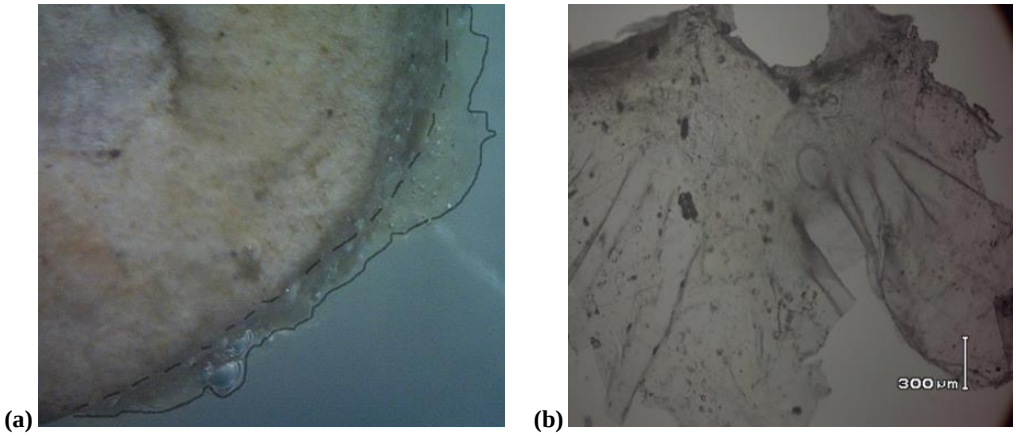

Fig. 2: (a) The border between SR-Urea tablet (the dash line) and chitosan coating layer (the solid line), (b) Chitosan thin film peeled off from SR-urea tablet.

considered low), N total (0.18-0.19%, considered low), C/N (9.7-10.0; considered low) ratio and cation exchange capacity (CEC, 17.6-20.0 cm $_{(+)}$ kg^{-1}, considered moderate). Moderate CEC gave good condition for nitrogen absorption when nitrification of urea took place, the nitrite ions moderately bonded and released by the soil to be available for the plant but it was prevented for excessive leaching.

The different properties of SR-urea tablet from the prilled urea might be affected by several factors. The present of sago starch and rice husk ash let to slow down urea leaching until water and microbe decompose sago starch. The urea mobility might be retarded due to urea absorbed by the rice husk ash which has been reported as good adsorbent for dissolved minerals (Feng et al., 2004; Naeem et al., 2010). Chitosan film which has known as absorbent for minerals and has antimicrobial properties could also inhibit the urea diffusion and nitrification (Roberts, 1992). However, trace of micro nutrients (K^+, P, N & S) contained in sago starch, rice husk ash and chitosan might not gave significant contribution to the plant since the larger quantity of the nutrients were available from the additional fertilizers (KCl and TSP) for all treatments including the control. According to previous report the potassium and phosphorous content in 1 g rice husk ash was only 3 mg and 7.5 mg respectively (Thind et al., 2012). In conclusion, the proportion of matrix is crucial for stability of dried SR-urea tablet in water. In the tablet preparation, the optimum weight ratio for water:sago:rice-husk-starch was 2:2:3. Chitosan coating reduced the urea leaching from the tablets when dried SR-urea tablets were soaked in water. The rate of urea leaching from the tablet in water decreased from 0.048 g to 0.01 g per day if the SR-urea tablets were coated with chitosan film. On the corn fertilizing performance test, application of 0.5 g SR-urea tablet to the plant gave no significant difference in the growth parameters compared to those of fertilizing with 2 g of prilled urea.

Authors' contribution

MA and DD designed the research, FZ supervised the students in lab works, ZZ conducted research work. All authors read and approved the final manuscript.

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