Bioplastic Composite of Carboxymethyl Cellulose/Tannic Acid/Glycerol/Iron for Slow-Release Iron Micronutrient Fertilizer

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Abstract—Iron (Fe) is an important micronutrient in plants, aiding in photosynthesis and chlorophyll production. Insufficient iron leads to pale leaves and slow plant development. This study successfully produced a bioplastic with slow-release iron micronutrients for plants. The composites were synthesized using a solvent casting method utilizing Carboxymethyl Cellulose (CMC) as a plastic matrix, tannic acid as a crosslinker, glycerol as a plasticizer, and Fe³⁺ as the micronutrient. Mechanical and water resistance tests were performed, along with X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) analysis for chemical properties. Atomic Absorption Spectroscopy (AAS) was used to monitor Fe release. The optimal composition of bioplastic comprised 4.5% CMC, 3% tannic acid, 0.7% Fe³⁺, and 3 mL glycerol, exhibiting a tensile strength of 4.92 MPa and 31.67% elongation. This bioplastic composite holds promise as an eco-friendly material that can slow-release Fe micronutrients when discarded, serving as a plant fertilizer.

Keywords—bioplastic, fertilizer, iron micronutrient, slow release

I. INTRODUCTION

The global issues in the agricultural sector are the deficiency of micronutrients such as iron in the soil. Direct application of micronutrients to the soil is not effective as most of the active ingredients added can be leached out by the water [1]. Therefore, a solution is needed to provide constant and sustainable micronutrients. Iron is one of the soil micronutrients that plays a very important role in plant growth. Iron deficiency in soil can have significant impacts on plant growth and productivity such as chlorosis, impaired photosynthesis and metabolic changes. However, excess will cause metabolic disorders in plant tissues [2]. Therefore, in order for the application of iron fertilizers to be effective and efficient, it is necessary to apply sufficient amounts and the right duration of time.

One of the fertilizer application strategies is slow-release fertilizer. The advantages of fertilization with a slow-release fertilizer approach are able to control the absorption of nutrients in plants gradually [3], can increase fertilizer efficiency, reduce fertilizer loss due to rainwater or irrigation water and save fertilizer consumption [4]. The development of slow-release fertilizer can use biopolymer as a carrier [5]. In recent studies, plant nutrients have been incorporated into a bioplastic system called slow-release fertilizer [6].

This research aims to synthesize bioplastic fertilizer, using carboxymethyl cellulose as matrix, tannic acid as crosslinker, glycerol as plasticizer, and iron as micronutrient source. This bioplastic fertilizer is expected to have the ability to slowrelease iron micronutrient so that it can overcome iron micronutrient deficiency.

II. LITERATURE REVIEW

Iron is one of the soil micronutrients that has a very important role in plant growth. Iron plays a role in the electron transfer process and chlorophyll biosynthesis [7]. Plants require 10 to 1000 mg/L of iron with sufficiency levels within the range of 50 to 200 mg/L. Plants are categorized as iron deficient if they contain only 10–30 ppm [8]. Iron deficiency in soil can have a significant impact on plant growth and productivity such as chlorosis, disturbances in photosynthesis and metabolic changes. However, excess will cause metabolic disorders in plant tissues [2]. Therefore, in order for iron fertilizer application to be effective and efficient, it is necessary to apply sufficient amounts and the right duration of time.

Slow-release fertilizer is a type of fertilizer designed to deliver nutrients gradually and sustainably to plants over a longer period of time compared to conventional fertilizers. The slow-release process in these fertilizers can occur through several mechanisms, such as controlled release of nutrients through a protective membrane, controlled release through binding of nutrients in a more stable chemical form, or controlled release through chemical reactions and microorganisms in the soil [9]. According to the European Standardization Committee (CEN), Slow-Release Fertilizers (SRF) fall into three categories. Category 1 states that no more than 15% of the nutrients are released within 24 hours after application. Category 2 no more than 75% of the nutrients are released within 28 days after application. Category 3 involves the release of nutrients at a minimum of 75%, lasting for 40-360 hours. The development of slowrelease fertilizer can use biopolymer as a carrier [5]. In recent studies, plant nutrients are incorporated into a bioplastic system called bioplastic fertilizer.

Bioplastics can be made from natural polymers such as cellulose [10]. However, cellulose is insoluble in water and requires special reagents to dissolve it. One of the cellulosederived compounds that has water-soluble properties is Carboxymethyl Cellulose (CMC). CMC has non-toxic properties, is easily soluble in water and easily degraded [11]. CMC has been used as a matrix in the manufacture of bioplastic for slow-release fertilizer applications [6]. However, the disadvantage of the resulting bioplastic is that it is easily soluble in water, so a crosslinking agent is needed to increase the resistance of bioplastic fertilizer in water.

Crosslinkers are materials used to bind polymer chains to prevent bond breakage in an aqueous environment. Several types of acids are usually used as crosslinker agents such as citric acid [12], tartaric acid [13], malic acid [14] and tannic acid [15]. In this study, tannic acid was chosen as a crosslinker because it has non-toxic properties and is easily available. The use of tannic acid can increase the resistance of bioplastics to water and can increase their mechanical strength [15]. This research aims to make bioplastic fertilizer containing iron micronutrient. This iron micronutrient is expected to release gradually and the resulting bioplastics have high water resistance and good mechanical properties.

III. MATERIALS AND METHODS

A. Materials

The materials used in this study with pro analysis quality produced by Sigma Aldrich include sodium carboxymethyl cellulose (Na-CMC). Materials with pro analysis quality produced by Merck include tannic acid ($C_{76}H_{52}O_{46}$) and Iron (II) Chloride Hexahydrate (FeCl₃·6H₂O).

B. Preparation of CMC/TA-Fe³⁺Bioplastic

The bioplastic matrix consists of Carboxymethyl Cellulose (CMC) and Tannic Acid (TA). The concentration of CMC used was 4.5% and 3% tannic acid and the variations of FeCl₃·6H₂O were 1%, 4%, 7%, and 10% (w/v). A total of 50 mL of TA with various variations of FeCl₃·6H₂O concentration, each added 60 ml of 4.5% KMS. The KMS/AT-Fe³⁺ mixture was stirred for 1 hour, then melded on a 10×13 cm glass meld and dried at 60 °C for 24 h. The resulting bioplastics were tested for mechanical properties. FeCl₃·6H₂O variation that gives the best results will be used for the production of further bioplastics with the addition of glycerol.

C. Preparation of CMC/TA/Fe³⁺/Glycerol Bioplastics

The production of bioplastics with the addition of glycerol used three variations, namely 1 mL, 3 mL and 5 mL. The CMC/TA-Fe³⁺ mixture after stirring for 1 h, then added glycerol and stirred again for 30 mins. Then melded and dried at 60 °C. The resulting bioplastics were then tested for mechanical properties.

D. Characterization of Bioplastics

Bioplastics were analyzed with Fourier Transform Infrared (FTIR) Thermo Nicolet iS10 and X-ray diffraction BRUKER D8 ADVANCE ECO. Mechanical tests were conducted with a Zwick Z 0.5 Universal Testing Machine (UTM). Each bioplastic was cut using a dumbbell-shaped cutting mold with a size of 3×10 cm and tested using a universal testing machine at a speed of 10 mm/minute to obtain elongation and tensile strength data.

E. Determination of Iron Concentration by Using Atomic Absorption Spectrometer (AAS)

Bioplastic samples were weighed with a mass of 0.1 g, then dissolved in 15 mL of 1M HNO₃ solution and heated until dissolved. The solution was filtered using filter paper. Filtrate was taken as much as 0.1 mL and diluted using DI water up to 10 mL. Next, the absorbance of the solution was measured with an atomic absorption spectrometer.

F. Evaluation of Slow-Release Performance

Slow-release experiment in water Bioplastic samples were weighed with a mass of 0.1 g, then immersed in 10 mL of DI water. During the time span of 0, 3, 9, 24, 48 h. the solution was taken as much as 0.1 mL and diluted in a 10 mL volumetric flask with DI water. The absorbance of the solution was measured with an atomic absorption spectrometer.

Slow-release kinetic to identify the mechanism of iron release in bioplastic fertilizer, Korsmeyer-Peppas, pseudosecond order and Higuchi kinetic equation models were used.

IV. RESULT AND DISCUSSION

Fig. 1 shows the resulting bioplastics infrared spectra incorporating TA, Fe^{3+} and glycerol. The CMC spectra are included for comparison. At wave numbers around 3000–3500, which indicate the presence of O-H groups, there is a shift indicating that CMC interacts hydrogen with TA. This indicates that TA acts as a crosslink. The formation of tannic acid complexes with Fe^{3+} is evidenced by a shift in the wave number in the 1309 cm⁻¹ region of the C-O group experiencing a shift [10]. This is due to the coordination bond between the O atom of the carboxyl group with Fe^{3+} ions. Wavelengths around 1584 cm⁻¹ indicate the presence of - COO- groups [16], after the addition of Fe^{3+} experienced a shift indicating an interaction. This indicates that Fe^{3+} ions not only interact with carboxyl groups of tannic acid but also interact with -COO- groups derived from CMC.



Fig. 1. The FTIR spectra of bioplastic CMC, CMC/AT, CMC/AT/Fe³⁺, CMC/AT/Fe³⁺/G.



Fig. 2. The XRD patterns of bioplastic CMC, CMC/AT, CMC/AT/Fe^3+, CMC/AT/Fe^3+/G.

Fig. 2 shows the diffraction pattern of carboxymethyl cellulose, tannic acid, Fe^{3+} and glycerol. Carboxymethyl cellulose shows amorphous nature [16], peak formed at 21°. The addition of tannic acid shifted the peak to 23°. The addition of Fe³⁺ causes a very significant decrease in peak. Then, bioplastics containing Fe³⁺ after adding glycerol did not give significant changes, so it can be said that the Fe³⁺ bioplastic composite is amorphous.



Fig. 3. (a) Tensile strength and elongation of Bioplastic; (b) Bioplastic without iron; (c) Bioplastic with iron.



and elongation. The addition of glycerol can increase elongation [17]. However, it decreases the tensile strength, so the optimum 3 mL glycerol was chosen with a tensile strength of 4.992 MPa and elongation of 31.668%. This is due to the interaction of the -OH group in CMC with glycerol [18]. Fig. 3(b) and (c) show the color difference between before and after the addition of Fe³⁺. Before the addition of Fe³⁺, it gives a light brown color which comes from the basic colour of tannic acid. When after the addition of Fe³⁺, the bioplastic composite turns black. This is due to the complex of tannic acid with Fe³⁺, where Fe³⁺ acts as a metal center [10].

European Standard EN 132662001 sets the standard for slow-release fertilizers divided into 3 categories, namely category 1: for 24 hours showing a maximum SRF nutrient release of 15%, Category 2: for 28 days, maximum SRF nutrient release of 75%, Category 3: for 40–360 h, SRF nutrient release of at least 75%. Previous research shows that the release rate of fertilizers with slow-release systems at 24 hours should be no more than 15%, while at 28 days it should be no more than 75% [3]. The results that have been obtained for 24 h of bioplastic immersion in water, the iron release rate reaches 9.56%, that concluded bioplastics can be categorized as slow-release fertilizer.

Determination of slow-release fertilizer kinetics was carried out with different kinetics models used to determine the mechanism of iron micronutrient release. The fitting results and kinetics parameters are shown in Fig. 4. R² values close to 1 indicate a high level of fit [19]. Based on the fitting that has been done using three models namely pseudo second order, Higuchi and Korsmeyer Peppas. The R² value that is close to 1 is pseudo second order with an R² value of 0.99 and a K = 0.52 mg·g⁻¹·h⁻¹ value which indicates that iron micronutrients are released as much as 0.52 mg every hour.



Fig. 4. (a) Release of micronutrient iron; (b) Plots demonstrating Pseudo Second Order; (c) Plots demonstrating Korsmeyer-Peppas; (d) Plots demonstrating Higuchi.



Fig. 5. Possible interaction between CMC, TA and Fe³⁺.

Fig. 5 shows the interaction between CMC, AT and Fe^{3+} . CMC acts as a matrix, tannic acid acts as a crosslinker. The presence of -OH group in CMC makes the formation of hydrogen bond with tannic acid. In addition, the C-O group present in tannic acid binds coordination with Fe^{3+} ions.

V. CONCLUSION

Bioplastics based on carboxymethyl cellulose with tannic acid crosslinker have been successfully synthesized. The bioplastics may serve as an iron micronutrient for plants. The characteristics of bioplastics based on mechanical tests are tensile strength of 4.92 MPa and 31.67% elongation. In addition, it was also found that iron micronutrients release 9.56% in 24 hours, so it can be categorized as a slow-release fertilizer. The release kinetic follows a pseudo-second order with an R^2 value of 0.99 and a K = 0.52 mg·g⁻¹·h⁻¹.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Syahriani is responsible for conducting research, formal analysis, investigation, and drafting the initial version. Indriana Kartini focuses on conceptualization, validation, formal analysis, and reviewing as well as editing the writing. Bambang Rusdiarso plays a role in validation, formal analysis, and participates in the review and editing of the written material. All authors had approved the final version.

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