Slow Released Fertilizer of Fe2+ and Mn2+ from Composite Micronutrient Chitosan-Silica

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Slow Released Fertilizer of Fe^{2+} and Mn^{2+} from Composite Micronutrient Chitosan-Silica

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ABSTRACT

This study aims to synthesize slow released fertilizer in the form of Chitosan-Silica micro nutrient composite (CSiMN) by utilizing mining waste as a source of micronutrients whose release can be controlled by the presence of silica ash supporting material in rice chitosan as chelating from agricultural and fishery industrial wastes. The research method includes the synthesis of composite fertilizers in the ratio of chitosan: silica: tailings extract (TE) which is 1:1:2; 1:2:2; 1:3:2; 1:4:2 (v/w/v); swelling capacity test, and water retention capacity test from soil containing CSiMN composite fertilizer. The results showed that the CSiMN composite pellet in formula 1: 2: 2 was stable for 8 days in incubation with 100 mL distilled water. The ability to absorb water (swelling ratio) of chitosan silica composites in all comparisons, increased until the 120th minute and tended to be constant after the 120th minute. Chitosan-silica-ET composite at a ratio of 1: 2: 2, is the composition with the highest swelling power. The water retention capacity of soils containing CSiMN composite fertilizers is higher than soils without composite fertilizers. Increased silica composition in CSiMN composites can improve the retention of water capacity in soil. The release profile Fe^{2+} is different from Mn^{2+}. After an incubation time of 20 days, the release of Fe^{2+} has increased while the release of Mn^{2+} tends to be constant.

Keywords: tailing extract, chitosan, slow released fertilizer, silica.

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INTRODUCTION

Chemical and physical properties of the soil in the study area, Wondama, is classified into the order Inceptisol, soil pH ranged from 4.7 to 5.0, classified as very acid to acidic with sandy clay soil, dusty clay, low C-organic , N-total low, P-available 8.5 to 25.5 ppm (low). The availability of micronutrients of manganese (Mn), iron (Fe), copper (Cu), zinc (Zn) in locations with high rainfall levels and soil characteristics with acidic pH and low organic matter, tend to be at critical limits for plant needs. High levels of rainfall cause micro-nutrient leaching from the soil[1]. Several methods have been used in order to prevent and overcome the occurrence of micronutrient deficiencies in plants such as direct fertilization at the roots of plants using inorganic salt fertilizers. However, the use of dissolved salts as micro-nutrient fertilizers causes serious environmental problems such as the use of fertilizer doses that far exceed the plant's absorption ability causing the accumulation of metal ions in the soil, water pollution and leaching of nutrients by rainwater. For this reason, we need a compound that is not soluble in water that functions as a micronutrient fertilizer that can be released slowly into the soil solution by hydrolysis or diffusion. Chitosan is very effective in chelating metal ions because the amine group in the chitosan ring can be used as a chelating side for the metal[2,4-6].

Chitosan in fact have excellent biodegradability and a swelling ability of lower rate when it generates hydrogel because of the slower relaxation rate of polymer chains[7-9]. As a result, blending chitosan with other hydrophilic polymers assist to increase the water absorbency at gel state. Silica from rice husk waste can be used as an environmentally friendly supporting material. In order to improve the efficiency of chemical fertilizers and reduce the loss of the nutrients they supply, many research has been focusing on the development of Slow-Release Fertilizers (SRF) in an attempt to minimize the difference between solubility and uptake[10,11] Development of slow released fertilizer (SRF) synthesis method in the form of Chitosan-Silica micro nutrient composites by utilizing mining waste as a source of Fe and Mn micronutrients whose release can be controlled by the presence of silica ash and chitosan as supporting materials for chelating from agricultural industrial wastes and fisheries will be effectively and efficiently applied to crops especially those growing on agricultural land that lack micronutrients.

MATERIALS AND METHODS

1. Production of Chitosan-Silica Micronutrient Composite Fertilizer

   Samples were prepared by direct wet mixing method using an experimental set consisting of beaker, hot plate and magnetic stirrer. Chitosan was dissolved in 2% acetic acid and stirred with magnetic stirrer until homogeneous then sodium silicate ash was added with rice husk stirred with magnetic stirrer for 1 hour. Then tailings extract was added with the ration of chitosan-silica-TE ratio 1:1:2;1:2:2;1:3:2;1:4:2 (v/w/v)) into the beaker and stirred at 60 ^{o}C. Next, the mixture was poured into aluminum molds and allowed to harden for 12 hours at room temperature. Then removed from the mold and dried in an oven at 60^{o}C for 8 hours. Composite fertilizer testing was performed after one day conditioned at room temperature.

2. Swelling Ability Testing for Chitosan-Silica Micronutrient Composite Fertilizer

   Chitosan-Silica Micronutrient Composite Fertilizer immersed in 100 mL aquades for 30; 60; 90; 120, 150 and 180 minutes. At this time interval, fertilizer was filtered, and the sample weight was weighed. Swelling ability (% SR) of Chitosan-Silica Micronutrient Composite fertilizer was calculated using the following equation:

$$\%SR = \frac{W_s - W_d}{W_d} \; x\; 100\%$$

3. Water Retention Testing (%WR)
Water retention testing of soil containing slow release fertilizer is carried out by mixing soil and CSiMN composite fertilizer samples (formula: 1:1:2; 1:2:2; and 1:3:2;) in a cup A, and soils without fertilizer was placed in cup B. Each cup was weighed, and distilled water was added to each cup and the weight of each cup (W_0) was measured again. The cups were placed at room temperature and weighed every day for 20 days (W_t). Water retention (% WR) was determined by the following equation:

$$\%WR = \frac{W_t - W}{W_0 - W} \; x\; 100\%$$

4. Testing of Fe^{2+} and Mn^{2+} release from soil containing composite fertilizer.
A total of 1 gram of slow release fertilizer micronutrient-chitosan-silica composite was mixed evenly on 200 grams of soil. At 0 days, 5 days, 10 days, 15 days, 20 days, and 30 days watered 100 mL water. Water that has been splashed was collected and tested for Fe, and Mn levels using AAS.

RESULTS AND DISCUSSION

The low release fertilizers development is according to the required in order to increase the performance of conventional fertilizers and reduce socio-environmental problems by minimizing pollution due to the excess nutrients used in agriculture practice[12]. The slow-release Chitosan-Silica Micronutrient composite can also increase absorption of micronutrients and prevent potential loss of micronutrients due to washing and volatilization.

1. Screening of the formula of Chitosan-Silica Micronutrient Composite Fertilizer

CSiMN composite fertilizers were synthesized in several ratios of chitosan:silica:tailings extract namely 1:1:2; 1:2:2; 1:3:2; 1:4:2 (v/w/v) then shaped in pellet form (Figure 1).

Figure 1. Pellet of CSiMN Composite

The CSiMN composite pellet stability test during the incubation period of 8 days in water is presented in table 1.

Table 1. The stability of CSiMN composite pellets

No.	Formula of chitosan:silica:tailings	Texture	Stability in water (day)
1	1: 1: 2	Pelet	2
2	1: 2: 2	Pelet	>8
3	1: 3: 2	Pelet	>6
4	1: 4: 2	Pellet	>6

The stability of CSiMN composite pellets in formula 1:2:2 shows the stability of pellets for 8 days in incubation with 100 mL distilled water. Increasing the amount of silica ash from rice husk tends to reduce the stability of pellets from 8 days to 6 days. This is because an increase in the amount of silica ash from rice husk will form a composite texture of Chitosan-Silica Micronutrient that is not compact and tends to undergo mechanical decomposition.

2. Swelling capacity testing of CSiMN composite fertilizer

Swelling ability of CSiMN composites in several ratios of chitosan:silica:tailings extract, ie 1:1:2; 1:2:2; 1:3:2; and 1:4:2 shown in Figure 2.

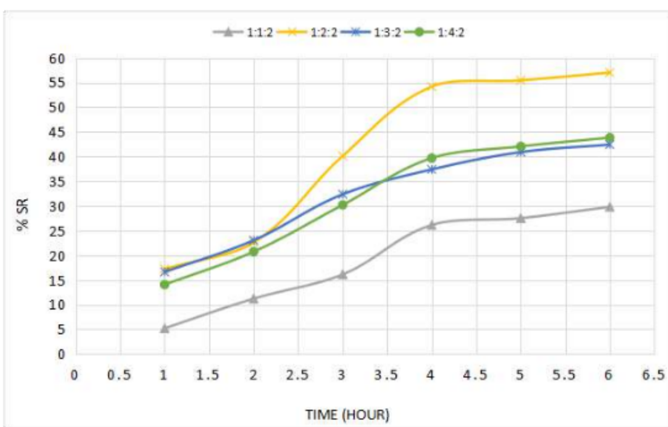

Figure 2. Swelling ability of CSiMN composite

Measurements were made for 3 (three) hours at 30-minute intervals. Figure 2 shows that the swelling ability of chitosan silica composites in all chitosan:silica ratios increased until the 120th minute and tended to be constant after the 120th minute. The chitosan-silica composites at a ratio of 1:2:2, showed the composition with the highest swelling ability. The addition of silica in chitosan-silica-tailing extract composites to reach 1:4, tends to reduce the swelling ability of chitosan-silica composites. The water absorption capacity of CSiMN Composite fertilizer is significant with the ability of the fertilizer as a slow release fertilizer. Mixing chitosan with silica can increase the absorption power of water from chitosan. This is possible because of the presence of silica as a supporting material, with the nature of the material which has a broad surface, is hygroscopic and has a high affinity for water molecules (Huang *et al*., 2009). In addition, thing that may also affects the swelling power of chitosan composites is its hydrophilic characteristics. Generally, membranes with chitosan with high properties of hydrophilicity. This is possible because active functional groups in chitosan such as the $-OH^-$ and $-NH_3^+$ groups can bind H_2O molecules. Interaction between chitosan and silica occurs through electrostatic attraction and hydrogen bonds. Chitosan has a high affinity to the surface due to the interaction between part of protonated amino groups of polymer and dissociated hydroxyl groups of silica, which are formed in aqueous solution[13-15]

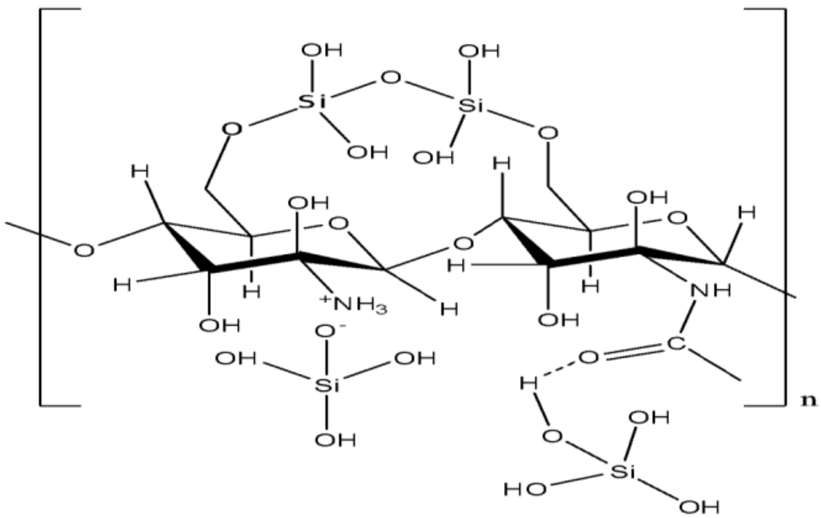

Figure 3. The scheme of chitosan-silica composite interaction

3. Water retention test of the soil (%WR)

Groundwater retention is a condition that provides the volume of water that is retained in the pores of the soil system. The water retention properties of soil containing CSiMN composite fertilizer are presented in Figure 4. The water retention capacity of soil containing CSiMN composite fertilizer decreases with increasing incubation time. The volume of water retained in the soil pore without containing CSiMN Composite was 2.36% on the 17th day, while the soil containing CSiMN Composite in formulas A, B, C, and D; each containing a volume of water retained in the soil pore of 9.18%; 12.86% and 15.74%. This shows that increasing silica levels in composite fertilizers can increase water retention in soils. This possibility due to the silica (SiO2) as a compound that has a high affinity for molecules of water, is hygroscopic and has a broad surface. All of those properties make it easy for composites to absorb water on the surface and increase the water resistance[16]. Hydrogel CSiMN composite to not only enhance the soil water retention capacity and porosity, but also to simultaneously improve the crop yield and productivity.

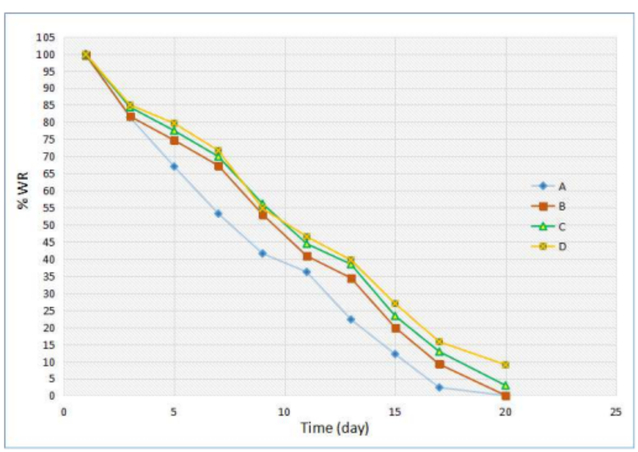

Figure 4. Water retention capacity from soil: (A) without composite fertilizers; and contain CSiMN composite fertilizers in composition (B) 1: 1: 2; (C) 1: 2: 2; (D) 1: 3: 2 (v/w/v)

4. Testing of Fe^{2+} and Mn^{2+} release from soil containing CSiMN composite fertilizer

The release of Fe^{2+} and Mn^{2+} from soil containing CSiMN composite fertilizers was observed in the period of 0 - 30 days (Figure 5).

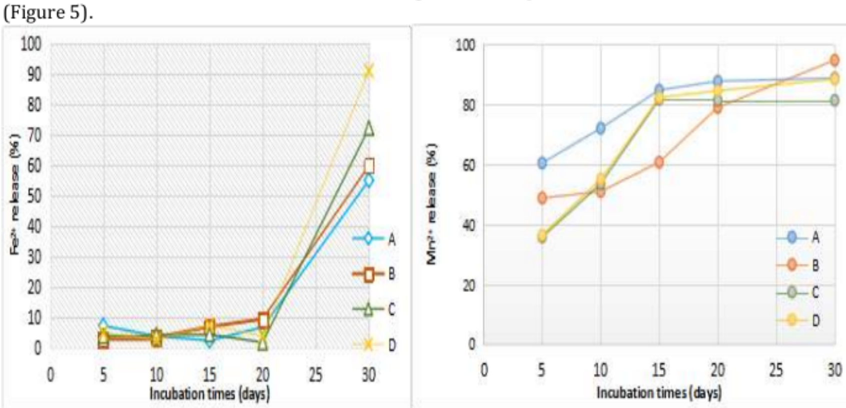

Figure 5. Percentage of release (a) Fe^{2+} (b) Mn^{2+} from soil containing CSiMN composite fertilizer

Figure 5 shows that the release of Fe^{+2} is slower than the Mn^{+2} ion. The release of Fe^{2+} in the incubation period of 5-20 days tends to be constant, until the 20th day, the release of Fe^{+2} for composites of formulas A, B, C, and D only reaches 7%; 10%; 2%; and 4%. After an incubation time of 20 days, the release of Fe^{2+} has increased until the 30th day reaching 55%; 60%; 72%; and 91% for each of the composites of formulas A, B, C, and D. The profile of Mn^{2+} release is different from Fe^{2+}, the release of Mn^{2+} in the incubation period of 5 - 20 days tends to increase and in the incubation period of 20-30 days tends to be constant. Until the 20th day, the release of Mn^{+2} for composites of formulas A, B, C and D each reached 87.67%; 78.96%; 81.33%; and 84.52%. The difference in the release profile of Fe^{+2} and Mn^{+2} is influenced by the difference in the radius of the ion and the electronegativity of the Fe ion is smaller than the Mn ion. This affects the adsorption capacity of CSiMN composite fertilizer to Fe^{2+} greater than to Mn^{2+}, so that the release of Mn^{2+} from SRF composite fertilizer is faster than the release of Fe^{2+}. The same thing happened in the study of adsorption of Fe^{+2} and Mn^{+2} ions in several materials containing Si-OH, Al-OH and -COOH functional groups namely silica, gibbsite and humic acid, showing that the affinity of adsorption of Fe^{+2} ions greater than Mn^{+2} ions [17-24].

CONCLUSION

The results showed that the CSiMN composite pellet in formula 1: 2: 2 was stable for 8 days in incubation with distilled water. Swelling ratio of CSiMN composites in all comparisons increased until the 120th minute and tended to be constant after the 120th minute. The water retention capacity of soils containing CSiMN composite fertilizers is higher than soils without composite fertilizers. Increased silica composition in CSiMN composites can improve the retention of capacity of at soil. The release profile Fe^{2+} is different from Mn^{2+}. After an incubation time of 20 days, the release of Fe^{2+} has increased while the release of Mn^{2+} tends to be constant.

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CONFLICT OF INTEREST

The authors declare no commercial or financial conflict of interest.

ETHICAL APPROVAL

This article does not contain any studies with animals performed by any of the authors.

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