

## Synthesis of Zeolite/NPK Coated with Cu-Alginate-PVA-Glutaraldehyde as a Slow-Release Fertilizer

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**Abstract:** The objectives of this study were to synthesize zeolite/NPK coated with Cu-alginate-PVA-glutaraldehyde as a material for slow-release fertilizers and to study the effect of various Cu concentrations in the coating material on the resistance of the zeolite/NPK fertilizer and to study the release rate reaction in citric acid. The study began with the synthesis of the zeolite/NPK fertilizer and the Cu-alginate-PVA-glutaraldehyde coating materials with variations of Cu concentration of 0.0; 0.2; 0.4; 0.6; 0.8; and 1.0 M. The Zeolite/NPK fertilizer and the coated NPK fertilizer were characterized by XRD and FTIR. The determination of the released N and P was conducted using a UV-Visible spectrophotometer, while released K and Cu was analyzed using AAS. XRD showed that the composite had a crystalline structure. The FTIR spectra showed characteristic cross-linking interactions between PVA-glutaraldehyde and Cu-alginate. A study of the release kinetics of zeolite/NPK coated with Cu-alginate-PVA-glutaraldehyde showed that increasing Cu concentration to 0.4 M decreased the amount of nutrition released, and the release process followed the pseudo-second-order kinetics. The release rate constants of N,P,K and Cu in the citric acid medium on zeolite/NPK coated with Cu 0.4 M were  $8.49 \times 10^{-3}$ ,  $17.48 \times 10^{-3}$ ,  $21.73 \times 10^{-3}$ , and  $8.57 \times 10^{-3} \text{ mg g}^{-1} \text{ h}^{-1}$ , respectively.

**Keywords:** alginate; cross-link; Cu; glutaraldehyde; PVA

### ■ INTRODUCTION

Plants need an adequate amount of nutrition to grow. There are two kinds of nutrients for plants: macronutrients and micronutrients. The former are those which are required in relatively large amounts: carbon, hydrogen, oxygen, nitrogen, phosphorus, calcium, sulfur, potassium and magnesium. The micronutrients are those required in small amounts, such as chlorine, iron, manganese, boron, zinc, copper, molybdenum, sodium and selenium [1]. Even though micronutrients are not necessarily needed in a huge amount, they have an equal role in the growth of plants. Copper (Cu) is a type of micronutrient that is crucially needed though in a small amount. One of the functions of Cu is to activate some of the enzymes involved in lignin synthesis. Cu is also very crucial for photosynthesis, respiration, and also helps the metabolism of carbohydrates and protein. Lack of Cu in plants can cause withered-looking young leaves, which

will die eventually, and it can also cause the branches to turn brown and eventually die [2].

Nutrients needed by plants can be fulfilled by providing fertilizers, an important material in plant growth. Commercial NPK (Nitrogen Phosphorus Kalium) fertilizers in the market have a disadvantage, in that they are easily soluble in water, so they can pollute the environment. Besides that, commercial fertilizers have reduced efficiency and need to be frequently applied to optimize nutrient intake [3]. Zeolite is used as an additive in slow-release fertilizers. Zeolites added to fertilizers give double results when applied to soil: provide long lasting action of the fertilizer (prolongation effect) and prevent nutrient leaching [4]. One of the methods to reduce the rate of release of nutrients in fertilizers is by using slow-release or controlled fertilizers. Slow-release fertilizers are fertilizers that have low solubility and can provide a gradual supply of

nutrients over a long period of time, thereby increasing the efficiency of nutrient uptake by plants and reducing their loss due to the leaching process [5-7]. One type of slow-release fertilizer is coated fertilizers [8].

The constituent materials in slow-release fertilizers consist of two components, namely carrier material or support material and minerals needed by plants [9]. Zeolite is a support material used in agriculture because it is environmentally friendly, relatively stable to acids and easy to obtain. In the manufacture of fertilizers, zeolite is often used as carrier material and ballast or filler material. Sustainable development of agricultural products could also be assisted by zeolite as a slow-release fertilizer and to control pests [10]. NPK is a nutrient needed by plants to grow and can be mixed with zeolite with the help of starch as an adhesive material. The interaction between zeolite and NPK is a physical interaction that can cause NPK to be easily released by water, so zeolite/NPK fertilizers require coating materials to control or slow down the nutrient release rate from the fertilizers [11].

The synthesis of slow-release fertilizers has undergone many developments. Sodium alginate can be used as a coating material for fertilizers to produce slow-release fertilizers. The alginate-gelatin hydrogel can be a slow-release nutrient to plant an environmentally friendly fertilizer [12]. Sodium alginate can be cross-linked with divalent and trivalent metals such as Ca(II), and Fe(III) [13-14]. Alginate and Cu(II) as a divalent metal ion create intermolecular bonds forming a nonplanar geometry [15]. These cross-links can decrease the solubility of alginate membranes in water [16]. The  $\text{CuSO}_4$  solution was also used as a cross-linking agent because Cu(II) ions belong to the group of essential micronutrients [17]. In the presence of divalent metal cations such as  $\text{Cu}^{2+}$ , alginates can form gels where cross-linking occurs due to the presence of chelating complexes between divalent ions and carboxylate anions of the G-G block. The cross-link interaction between alginate and Cu metal will increase the binding strength and stability of the fertilizer composite [18]. The CMC/PVA blend film may be a potential coating material for the application in the control-release fertilizer [19]. In addition to alginate, polyvinyl alcohol (PVA) can also form cross-links with

glutaraldehyde so that it can release K slowly from chitosan/PVA composites [20]. These studies show that the fertilizers synthesized using a single cross-linker have good resistance and are able to release nutrients slowly.

Based on the previous research, a study was conducted on slow-release fertilizers that have better resistance by using a double cross-linker. In this research, the synthesis of Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK was carried out as a slow-release fertilizer material, where Cu and glutaraldehyde act as cross-linkers.

## ■ EXPERIMENTAL SECTION

### Materials

Natural zeolite was taken from Klaten, and technical-grade sodium alginate was obtained from Sigma-Aldrich. Urea (commercial quality), SP36 (commercial quality), KCl (commercial quality), technical-grade PVA, glutaraldehyde, copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), ethanol 95%, *p*-dimethylamino benzaldehyde (PDAB), vanadic acid, ammonium molybdate, concentrated  $\text{HNO}_3$ , and citric acid were purchased from Sigma-Aldrich. Other materials include filter paper, double distilled water, and distilled water.

### Instrumentation

The release of K and Cu nutrients test was carried out using atomic absorption spectroscopy (Perkin Elmer 3110), and the release of N and P nutrients was carried out using a UV-Vis spectrophotometer (Thermo Scientific Evolution 201). The samples were characterized using an infrared spectrophotometer (Shimadzu FTIR Prestige 21) and an X-ray diffractometer (PANalytical X'pert Pro).

### Procedure

#### **Preparation of zeolite/NPK fertilizer**

The Zeolite/NPK fertilizer was made by mixing 316 g of previously sieved natural zeolite (200 mesh) with 100 g urea, 30 g KCl, and 30 g SP36. As much as 10 g of starch was weighed, dissolved in 100 mL of hot water, and stirred until thickened. The starch solution

prepared was mixed in the previous mixture, then the mixture was stirred until evenly distributed, and the resulting mixture was formed into granules with a mass that is made as similar in size as possible. The zeolite/NPK granules were then dried.

#### **Preparation of Cu-alginate-PVA-glutaraldehyde coating solution with variations in Cu concentration**

A total of 10 mL of 5% w/v PVA solution (5 mixed systems) was mixed with 10 mL of 2% w/v alginate solution (5 mixed systems), then stirred until homogeneous. The five mixed systems were then added with 10 mL of 1.25 v/v glutaraldehyde and stirred until homogeneous. Furthermore, 10 mL of CuSO<sub>4</sub> solution were added into five mixed systems with a concentration of 0.00; 0.20; 0.40; 0.60; 0.80; and 1.00 M. The dried zeolite/NPK fertilizer was then soaked in the five mixed systems for 30 min. Furthermore, the zeolite/NPK fertilizer which had been coated with a mixture of alginate-PVA-glutaraldehyde with various concentrations of CuSO<sub>4</sub>, was dried at room temperature.

#### **Characterization of zeolite/NPK and zeolite/NPK fertilizers coated with Cu-alginate-PVA-glutaraldehyde**

The composite sample to be analyzed was first grounded to form a powder. Characterization was carried out using FTIR and XRD with the powder sample method.

#### **Swelling test on the release of NPK and Cu from the zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde in citric acid media**

Each composite sample in a dry state was weighed and put in a container and was then added with 20 mL of 0.33 M citric acid solution. The citric acid solution was used because it has similar pH as the soil. On the 7<sup>th</sup> day, each sample that was soaked in citric acid was taken and weighed again. The swelling percentage can be obtained by calculating the difference (Eq. (1)) between the mass of the composite in a wet state ( $W_w$ ) and the mass of the composite in a dry state ( $W_0$ ) and then dividing it by the mass of the composite in a dry state.

$$Q_w = \frac{W_w - W_0}{W_0} \quad (1)$$

#### **Test of the release of NPK and Cu from zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde in citric acid media**

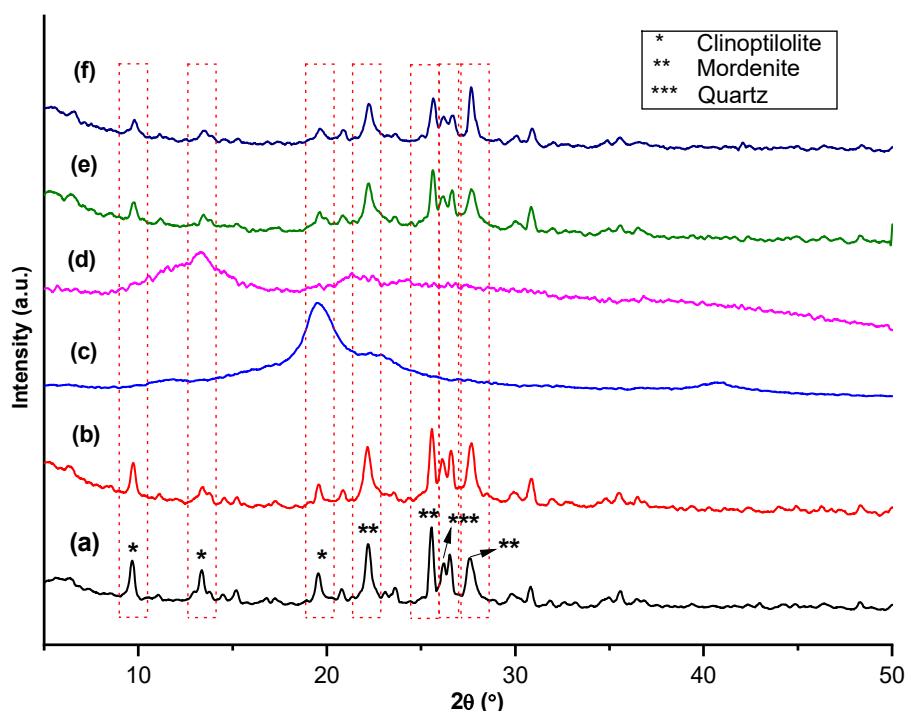
A total of 0.20 g of each composite sample was put in a container and added with 20 mL of 0.33 M citric acid solution. The fertilizer immersion in the solution was allowed to sit, and 1 mL was taken for analysis of N, P, K, and Cu at intervals 3, 6, 12, 24, 48, 72, 96, 120, 144, 168, 192, 216, 240, 264, 288, 312, and 336 h. The filtrate containing N and P was then diluted, and a complexified solution was added and analyzed using a UV-Vis spectrophotometer, while the filtrate containing K and Cu was then diluted and analyzed using atomic absorption spectroscopy (AAS). The filtrate containing P was complexed with molybdovanadate and measured using a UV-Vis spectrophotometer at 400 nm, while the filtrate containing N was complexed with PDAB and measured using a UV-Vis spectrophotometer at 410 nm.

## **RESULTS AND DISCUSSION**

### **XRD Spectroscopy**

Zeolite/NPK fertilizers, alginate-PVA-glutaraldehyde-coated zeolite/NPK fertilizers, and Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK fertilizers were characterized using XRD and FTIR spectroscopy. Characterization using XRD spectroscopy was carried out to obtain information related to the crystallinity of zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde as a result of the synthesis and the minerals contained in it. The crystallinity of a material indicates the regularity of the bonds in it. Crystallinity increases along with the increasing bond regularity. The sharper (pointer) diffraction peaks indicate the more crystalline the material, meaning that the regularity of the bonds within the material is also getting higher.

Fig. 1 shows the comparison of X-ray diffractograms between natural zeolite, Na-alginate, PVA, zeolite/NPK, zeolite/NPK alginate-PVA-glutaraldehyde, and zeolite/NPK Cu-alginate-PVA-glutaraldehyde with a Cu concentration of 0.4 M. The choice of X-ray diffractogram with variations in Cu concentration of 0.4 M was made



**Fig 1.** XRD diffractogram (a) natural zeolite, (b) zeolite/NPK, (c) PVA, (d) alginate, (e) zeolite/NPK alginate-PVA-glutaraldehyde, and (f) zeolite/NPK Cu (0.4 M)-alginate-PVA-glutaraldehyde

because at that concentration, the nutrient release was best, it had the slowest nutrient release compared to other concentration variations and also the smallest development value. This will be explained in detail in the next sub-chapter. It was expected that the Cu concentration of 0.4 M might be able to represent all samples using other variations of Cu.

The results of characterization using X-ray diffraction of natural zeolite-based material showed several sharp peaks at  $2\theta = 26.5^\circ$ , which identified the presence of quartz minerals according to JCPDS 05-0490, sharp peaks at  $2\theta = 9.676$ ;  $13.02$ ; and  $20.6^\circ$  indicate the presence of clinoptilolite minerals according to JCPDS 25-1349, and sharp peaks at  $2\theta = 15.17$ ;  $22.15$ ;  $26.21$ ;  $27.57$ ; and  $30.67^\circ$  indicate the presence of mineral mordenite in accordance with JCPDS 11-0155. The results of the characterization of the alginate base material showed that there were three peaks of alginate characteristics at  $2\theta = 19.06$ ;  $28.93$ ; and  $32.08^\circ$ . The three peaks have a high intensity which indicates the formation of very strong hydrogen bond interactions in the guluronate and mannuronic units in alginate through

intermolecular interactions. The hydrogen bonds formed between the carboxyl and hydroxyl groups in the alginate structure. The results of the comparison of the zeolite/NPK fertilizer composite diffractogram with the natural zeolite diffractogram provide information that the same peak appears as the zeolite peak at  $2\theta = 25.68$ ;  $28.60$ ; and  $27.73^\circ$  which indicates the presence of the mineral mordenite. Overall, zeolite/NPK fertilizer produced sharp diffractogram peaks, indicating that the zeolite/NPK fertilizer was crystalline.

The results of the comparison of the diffractogram of zeolite/NPK alginate-PVA-glutaraldehyde fertilizer with the diffractogram of natural zeolite and alginate provide information on peaks at  $2\theta = 25.84^\circ$  and  $27.87^\circ$  that indicate the presence of mordenite minerals from zeolite, and there is a low-intensity peak at  $2\theta = 32.12^\circ$  which is the typical peak of alginate. The presence of more zeolite in the composite material allows the zeolite to cover the alginate so that the crystalline peaks of the alginate mineral are not clearly visible. Polyvinyl alcohol is an amorphous material, but in this composite, the presence of amorphous PVA did not reduce the

crystallinity of the fertilizer. It is possible because there is a cross-link between PVA and glutaraldehyde which can improve the chemical properties of the material so that the fertilizer material remains crystalline. The diffractogram of alginate-PVA-glutaraldehyde-coated zeolite/NPK fertilizer showed sharp peaks, which indicates that the addition of coating material in the form of alginate-PVA-glutaraldehyde to zeolite/NPK fertilizer did not change the crystalline nature of the fertilizer.

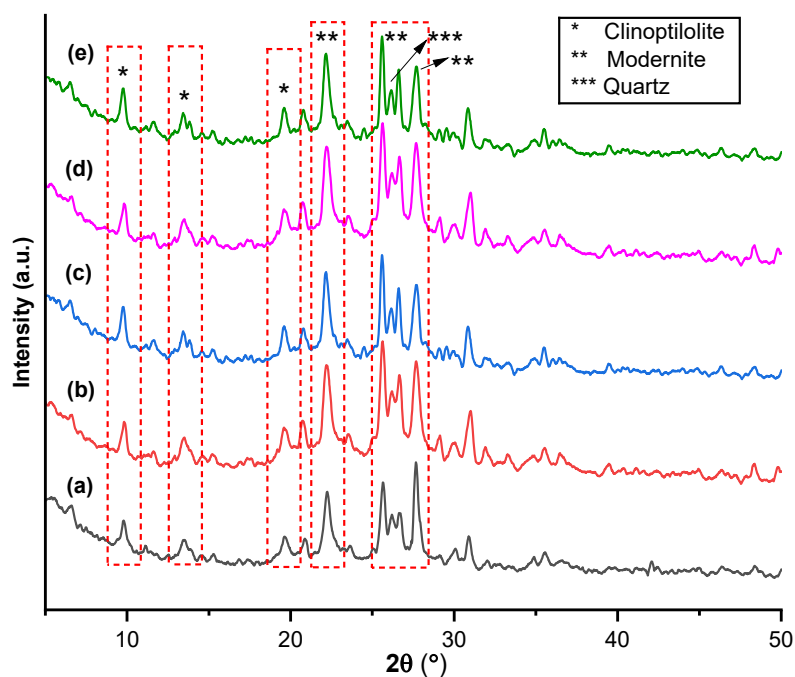
Furthermore, the diffractogram of zeolite/NPK alginate-PVA-glutaraldehyde fertilizer was compared with that of zeolite/NPK Cu-alginate-PVA-glutaraldehyde fertilizer with variations in Cu concentration of 0.4 M. It can be seen that the diffractograms of the two composites were relatively the same, indicating that the addition of Cu in the composite did not decrease the crystallinity of the fertilizer which means that the regularity of the bonds in the material did not decrease due to the addition of Cu. This can happen because Cu itself has crystalline properties, so the addition of Cu in the composite does not damage the crystallinity of zeolite/NPK fertilizers.

Fig. 2 shows the comparison of the zeolite/NPK diffractogram of Cu-alginate-PVA-glutaraldehyde with

variations in Cu concentration 0.2; 0.4; 0.6; 0.8; and 1.0 M. Increasing the concentration of Cu in the coating material did not change the crystallinity of the fertilizer material even though Cu was crystalline. This is because the Cu in the composite acts as an alginate cross-linker in the coating material and does not directly interact with the zeolite/NPK fertilizers, so the crystallinity of the fertilizer does not increase significantly. In addition, the addition of a relatively small concentration of Cu in the composite system also resulted in the intensity of the diffractogram tending to remain constant even though Cu with varying concentrations was added.

### FTIR Spectroscopy

The goal of the characterization using FTIR spectroscopy is to determine the presence of functional groups contained in the starting material, which includes natural zeolite, PVA, and alginate, as well as interactions/bonds between polymer chains of PVA, alginate and glutaraldehyde in the coating material for zeolite/NPK fertilizers which are interpreted into absorption peaks in the FTIR spectra. The absorption peak that indicates the interaction between PVA and



**Fig 2.** XRD diffractogram of zeolite/NPK Cu-alginate-PVA-glutaraldehyde with various concentrations of Cu; (a) 0.20 M, (b) 0.4 M, (c) 0.6 M, (d) 0.8 M, and (e) 1.0 M



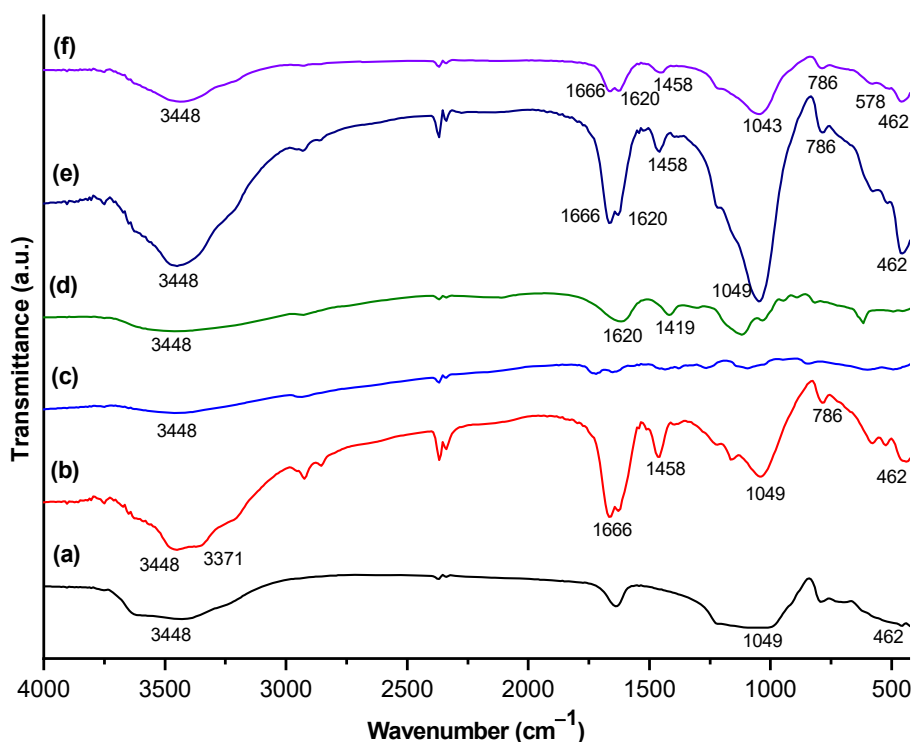
glutaraldehyde is visible, as well as the absorption peak that indicates the interaction between Cu and alginate, in which this interaction indicates that the double cross-linking process had been successful.

Fig. 3 shows the FTIR spectra of natural zeolite, showing a wide absorption at  $3448\text{ cm}^{-1}$ , indicating the presence of hydrogen bonds from water [21]. The peak at the wavenumber of  $1435\text{ cm}^{-1}$  indicates the presence of H-O-H bending vibrations. The peak characteristic of the zeolite is shown at the wavenumber of  $1049\text{ cm}^{-1}$ , which is a characteristic of the asymmetric stretching vibration of Si-O-Al, and  $462\text{ cm}^{-1}$ , which is the bending vibration of Si-O/Al-O.

The FTIR spectra of alginate showed strong absorption at the wavenumber of  $1620\text{ cm}^{-1}$ , which is a characteristic of the asymmetric stretching vibration of the  $\text{COO}^-$  group and a weak absorption peak at  $1419\text{ cm}^{-1}$ , which is an indication of the  $\text{COO}^-$  symmetric stretching vibration. The FTIR spectra of PVA showed that there were several peaks that appeared at wavenumbers of  $1435$ ,  $1635$ , and  $3448\text{ cm}^{-1}$ . The absorption peak at wavenumber  $3448\text{ cm}^{-1}$  is considered as the stretching vibration of the

hydroxyl group ( $\text{OH}^-$ ) originating from the hydroxyl group of the PVA chain and the hydroxyl group from water. The FTIR spectra of the zeolite/NPK fertilizer showed an absorption peak at wavenumber  $3371\text{ cm}^{-1}$  which indicated the presence of N-H stretching vibrations in urea. At wavenumber  $1666\text{ cm}^{-1}$ , there is a peak indicating the presence of C=O bonds in urea, and at wavenumber  $1458\text{ cm}^{-1}$ , there is a peak indicating the presence of C-N vibrations from urea. An absorption peak is also formed at  $786\text{ cm}^{-1}$ , which is a characteristic of the P-O symmetric stretching vibration. The peak that shows the characteristics of the zeolite is still visible at the wavenumber of  $1165\text{ cm}^{-1}$ , which is the asymmetry range of Si-O-Si/Al-O-Al. The absorption peak at wavenumber  $3448\text{ cm}^{-1}$  indicates the presence of hydroxyl groups from PVA and water that are also still visible.

In the FTIR spectra of the alginate-PVA-glutaraldehyde-coated zeolite/NPK fertilizer, there is a sharp absorption peak at wavenumber  $1049\text{ cm}^{-1}$ . This indicates that there are other vibrations besides the asymmetric stretching vibration of Si-O(Si) or Si-O(Al);



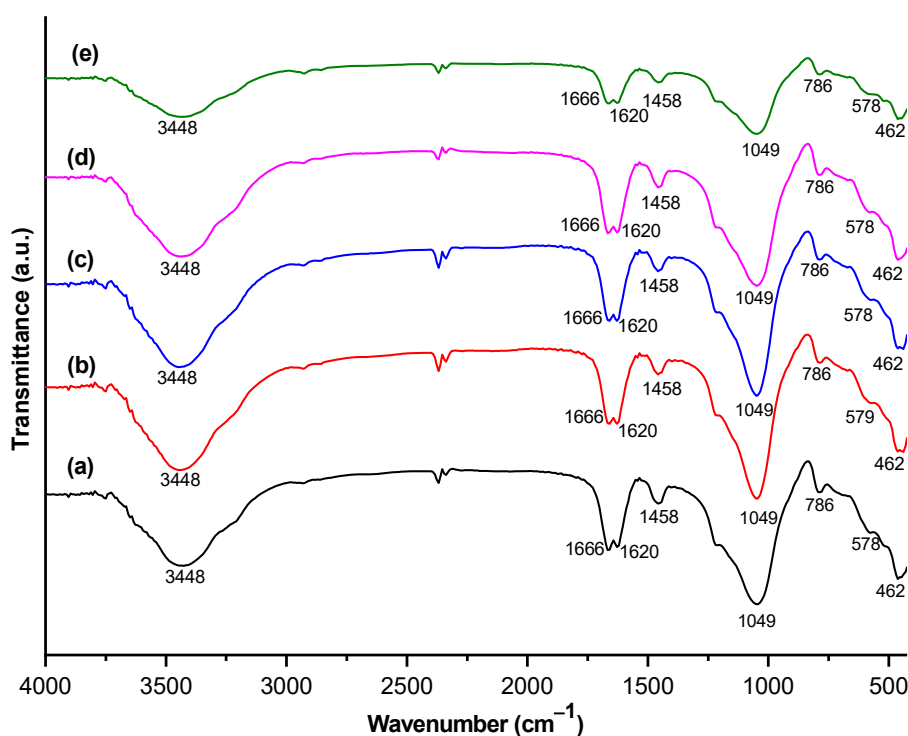
**Fig 3.** FTIR spectra (a) natural zeolite, (b) zeolite/NPK, (c) PVA, (d) alginate, (e) zeolite/NPK alginate-PVA-glutaraldehyde, and (f) zeolite/NPK Cu (0.4 M)-alginate-PVA-glutaraldehyde

it is the presence of C-O ether bonds produced by the cross-linking process of PVA and glutaraldehyde so that at this wavenumber, it produces a sharper peak than the peak in the zeolite/NPK fertilizer without alginate-PVA-glutaraldehyde coating. The appearance of a sharp peak at the wavenumber of  $1049\text{ cm}^{-1}$  also indicates that the cross-linking process occurred in the zeolite/NPK fertilizer coating. In addition, the characteristic peaks of the zeolite/NPK fertilizer were also clearly visible in the alginate-PVA glutaraldehyde-coated zeolite/NPK fertilizer, which indicated that the cross-linking process in the coating material did not interfere with the interaction of compounds in the initial composite.

Furthermore, the FTIR spectra of zeolite/NPK fertilizer coated with alginate-PVA-glutaraldehyde were compared with the FTIR spectra of zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde with a Cu concentration of 0.4 M. Spectra from the sample with the addition of 0.4 M Cu concentration was selected because it was the best composite which has a late release of nutrients proven by the nutrient release test. Overall, it can be seen that there is a new absorption peak due to the

addition of Cu at wavenumber  $579\text{ cm}^{-1}$ . The absorption peak indicates the formation of Cu-O bonds from cross-linking between Cu and alginate. The characteristic peaks of the alginate-PVA-glutaraldehyde-coated zeolite/NPK fertilizer were also seen in the composites with the addition of Cu.

Fig. 4 shows that the addition of Cu will decrease the peak intensity of the characteristic C=O in urea at a wavenumber of  $1666\text{ cm}^{-1}$  and the peak characteristic of  $\text{COO}^-$  belonging to alginate at a wavenumber of  $1620\text{ cm}^{-1}$ . This is possible because Cu, which has a positive charge, will interact with the carbonyl group of urea and the carboxyl group of alginate. The interaction between Cu and the two groups will increase the bond length between the groups themselves. The elongation of the bond that occurs has an impact on the weakening of the bonds in both C=O in urea and  $\text{COO}^-$  in alginate. When more Cu is added, the number of C=O bonds in urea and  $\text{COO}^-$  in alginate will decrease because they have formed new bonds with Cu. This causes a decrease in the intensity of the absorption peak as seen in the FTIR spectra above.



**Fig 4.** FTIR spectra of zeolite/NPK Cu-alginate-PVA-glutaraldehyde with various concentrations of Cu; (a) 0.20 M, (b) 0.4 M, (c) 0.6 M, (d) 0.8 M, and (e) 1.0 M

Determination of the optimum conditions for the Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK composite with a Cu concentration of 0.4 M was based on the results of the minimum data release occurring at that particular concentration. In addition, it can be seen that under these optimum conditions, there is a characteristic wavenumber belonging to the Cu-O cross-link bond in the Cu-alginate, which initially shifted from 578 to 579  $\text{cm}^{-1}$ . The shift in the wavenumber towards a larger direction indicates that the bond distance was getting shorter, resulting in a stronger Cu-O bond. When the addition of Cu is above 0.4 M, the Cu-O absorption peak reappears at the wavenumber of 578  $\text{cm}^{-1}$ . From the data obtained, it can be concluded that the strongest alginate-Cu cross-linked bond occurred at the addition of 0.4 M Cu.

### Swelling Properties

In this study, some of the active sites of alginate bind to PVA and some are cross-linked by Cu. PVA and alginate form hydrogen bonds, while alginate and Cu form cross-links in the form of an egg box, making it stronger than alginate-PVA. The higher the concentration of Cu added, the more cross-linked alginate will form. This causes the bond between PVA and alginate to be reduced. The reduced interaction between PVA and alginate will also disrupt the PVA-glutaraldehyde cross-link bond, which causes the composite system to not be

optimally protected, causing water from the environment to enter the composite easily. In this sub-chapter, the effect of variations in Cu concentration on the swelling of the zeolite/NPK fertilizer composites is discussed. The swelling test was carried out by measuring the change in mass of the Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK fertilizer in a dry state and after experiencing swelling for a certain time. The swelling test was carried out on zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde with variations of Cu 0.00; 0.20; 0.40; 0.60; 0.80; and 1.00 M. Swelling measurements were carried out on the 7<sup>th</sup> day of immersion of the fertilizer in 0.33 M citric acid. The results of swelling measurements are presented in Fig. 5.

Fig. 5 shows that the increase in Cu concentration reduces the swelling rate of the zeolite/NPK fertilizer composite up to the Cu concentration of 0.40 M. At Cu concentrations of 0.00; 0.20; and 0.40 there was a decrease in the swelling rate. Furthermore, when more Cu was added to the composite, the swelling increased, as seen in Cu concentration of 0.60; 0.80; and 1.00 M; in which the swelling number rose consecutively. This indicates that the bond between Cu-alginate-PVA-glutaraldehyde is optimum when the Cu concentration was 0.40 M. Cu concentration of above 0.40 M caused the bond between Cu and alginate to increase, thereby

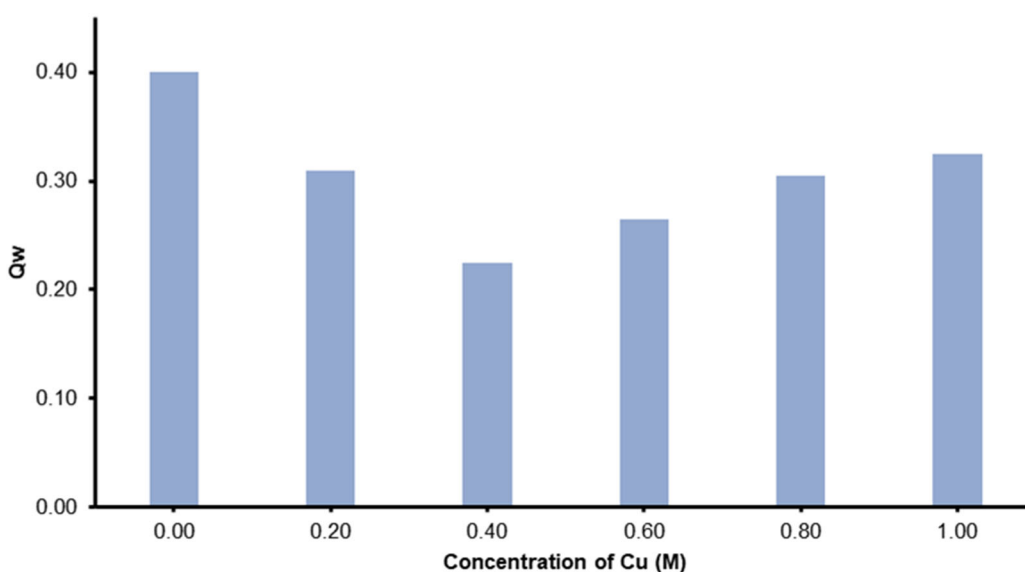


Fig 5. Effect of variations in glutaraldehyde concentration on swelling of zeolite/NPK fertilizer composites on day 7



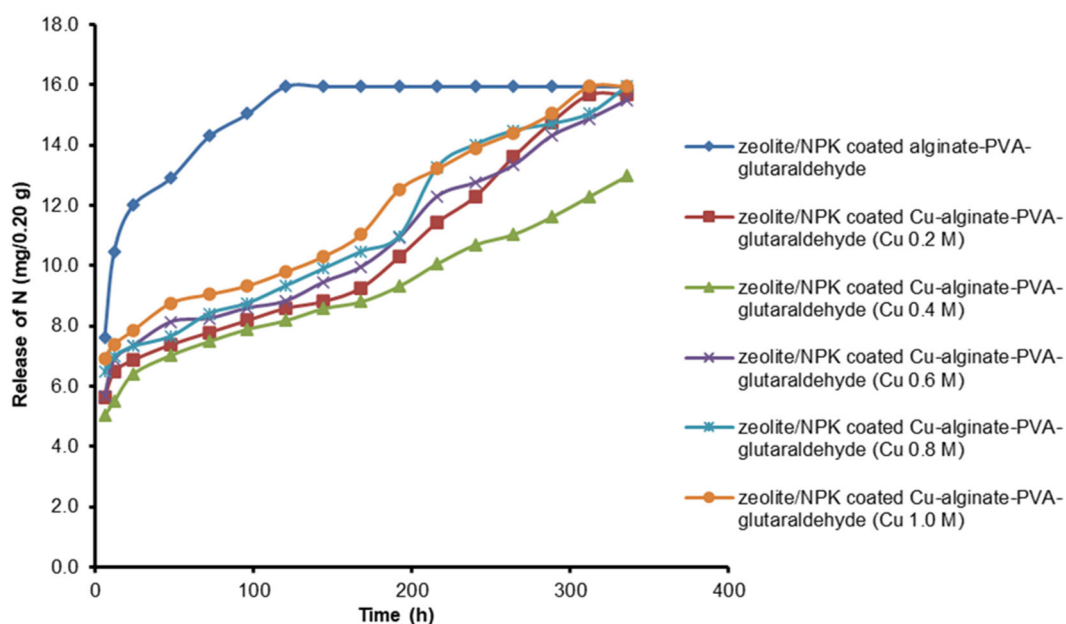
reducing the interaction between PVA and alginate, which causes the bond between PVA-glutaraldehyde to the composite to also weaken, increasing the swelling value. Greater swelling allows water to enter the composite more easily and will accelerate the rate of release of the NPK and Cu nutrients in zeolite/NPK fertilizers. Thus, the addition of Cu above 0.40 M will make the application of the double cross-linker not optimum in which the aqueous solution from the environment will enter the composite system more easily.

### Study of the Effect of Variations in Cu Concentration in Cu-Alginate-PVA-Glutaraldehyde Coating Materials on N Release from Zeolite/NPK Fertilizers

Fig. 6 shows the release of N from the Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK composite in the citric acid system through two mechanisms: the fast mechanism and the slow mechanism, according to the results of Sukma's research [22]. The slow mechanism is shown in the relatively gentle slope of the graph from the 6<sup>th</sup> to the 144<sup>th</sup> h. Meanwhile, the fast mechanism is shown on the fairly steep slope from the 144<sup>th</sup> to the 336<sup>th</sup> h. This indicates that the release of N from the composite after 144 h experienced a significant increase which could be

caused by the weakening of the cross-link system in the coating material. The weak cross-linking between PVA-glutaraldehyde and Cu-alginate can cause a decrease in the density of the composite so that the release of the nutrients in it also increases.

Variations in Cu concentration affect the amount of N released in the composite. Zeolite/NPK fertilizer without coating material released 15.04 mg/0.20 g of N fertilizer at the 3<sup>rd</sup> h, then the N release was constant at the 12<sup>th</sup> h by releasing 16.02 mg/0.20 g of N fertilizer. The zeolite/NPK fertilizer coated with alginate-PVA-glutaraldehyde released 15.95 mg/0.20 g of N fertilizer after 120 h and afterwards remained constant. In zeolite/NPK coated with Cu-alginate-PVA-glutaraldehyde with a Cu concentration of 0.2 M, the release of N at 312 h was 15.67 mg/0.20 g of fertilizer. In zeolite/NPK coated with Cu-alginate-PVA-glutaraldehyde with a Cu concentration of 0.4 M, the release of N at 336 h was 12.98 mg/0.20 g of fertilizer. In zeolite/NPK coated with Cu-alginate-PVA-glutaraldehyde with the Cu concentration of 0.6 M, the release of N at 336 h was 15.50 mg/0.20 g of fertilizer. The Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK with a Cu concentration of 0.8 M at 336 h released 15.95 mg/0.20 g



**Fig 6.** Graph of effect of Cu concentration on N release in zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde in 0.33 M citric acid system for 14 d

of N fertilizer. Furthermore, in Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK with a Cu concentration of 1.0 M, the release of N at 312 h was 15.95 mg/0.20 g of N fertilizer, and afterwards remained constant. From the data obtained, it can be deduced that the minimum N release occurred in the composite with the addition of 0.4 M Cu. This indicated that the cross-link bond in the composite was strongest at the addition of 0.4 M Cu.

The N release kinetics followed the pseudo-second-order reaction kinetics with a value of  $R^2$  closest to 1 (Table 1). Meanwhile, the results of the calculation of the N release rate constant from the composite are shown in Table 2. Based on the rate constant data ( $k$ ) in Table 2, it is shown that the N release rate slows down with the addition of Cu concentration of 0.4 M, then the N release rate increased again at Cu concentrations above 0.4 M, causing the double cross-link system not to run optimally so that the release of nutrients will also increase. This indicates that the interaction between Cu-alginate-PVA-glutaraldehyde was optimum at the addition of 0.4 M Cu to produce a slow-release of nutrients. In addition, at the Cu concentration of 0.4 M, the application of double

cross-linker went well so that a strong and tight composite system was obtained, which can be seen from the low swelling value and the lowest release rate, causing the release of nutrients in fertilizers to run slowly at this concentration.

### Study of the Effect of Variations in Cu Concentration in Cu-Alginate-PVA-Glutaraldehyde Coating Materials on P Release from Zeolite/NPK Fertilizers

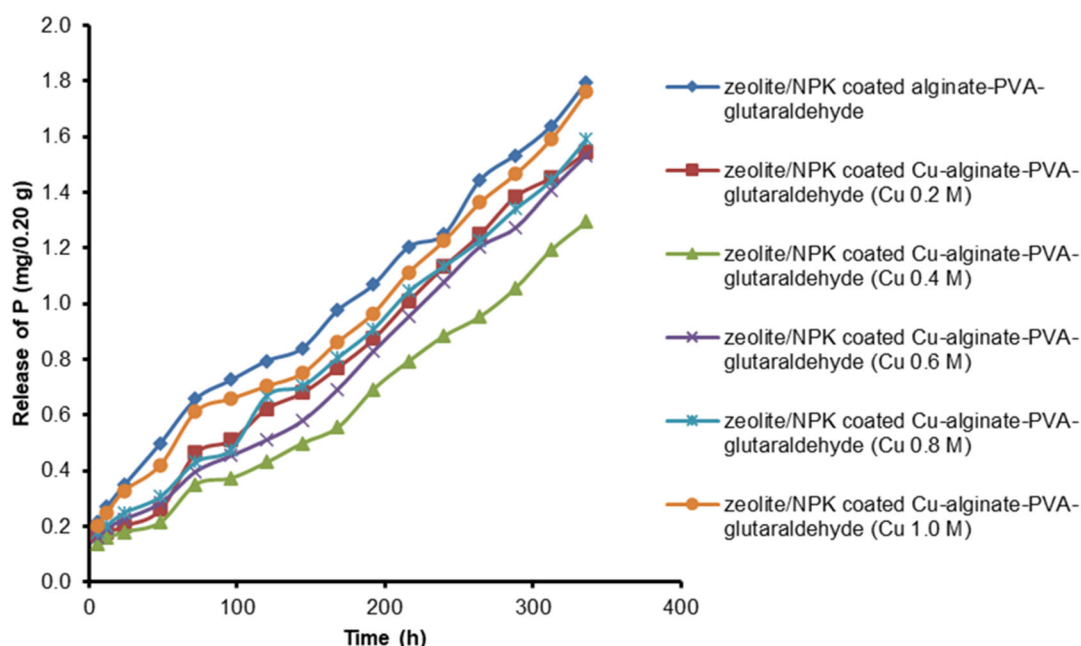
The graph of P release from zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde is shown in Fig. 7. The Cu concentration of 0.4 M in the coating material increased the cross-linking between Cu and alginate without reducing the interaction between alginate-PVA, resulting in a zeolite/NPK coating material which has optimum coating resistance and strength. The Cu concentration above 0.4 M in the Cu-alginate-PVA-glutaraldehyde coating material caused the Cu-alginate interaction to increase, and the interaction between PVA and alginate to decrease. The reduced interaction between PVA and alginate caused the PVA-glutaraldehyde cross-link bond to also be disrupted

**Table 1.** The results of the calculation of the value of  $R^2$  on the kinetics of N release from zeolite/NPK fertilizer composites coated with Cu-alginate-PVA-glutaraldehyde variations in Cu content

Cu concentration (M)	$R^2$				
	First-order	Second-order	Third-order	Pseudo-first-order	Pseudo-second-order
0.0	0.91	0.75	0.53	0.95	0.99
0.2	0.96	0.98	0.79	0.93	0.99
0.4	0.95	0.97	0.98	0.95	0.99
0.6	0.93	0.95	0.95	0.93	0.99
0.8	0.99	0.98	0.98	0.99	0.99
1.0	0.98	0.97	0.94	0.98	0.99

**Table 2.** The value of the N release rate constant with variations in Cu concentration from Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK composites

Cu concentration (M)	Pseudo-second-order	
	$R^2$	$k$ ( $\text{mg g}^{-1} \text{h}^{-1}$ )
0.0	0.99	$21.73 \times 10^{-3}$
0.2	0.99	$11.75 \times 10^{-3}$
0.4	0.99	$8.49 \times 10^{-3}$
0.6	0.99	$9.27 \times 10^{-3}$
0.8	0.99	$9.45 \times 10^{-3}$
1.0	0.99	$10.86 \times 10^{-3}$



**Fig 7.** Graph of effect of Cu concentration on P release in zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde in 0.33 M citric acid system for 14 d

so the double cross-linker composite system is not optimal. The non-optimal double cross-linker system will certainly have an impact on the faster release of nutrients compared to the optimum double cross-linker composite. Disruption of the bond between PVA-glutaraldehyde causes solutions from the environment to enter the system more easily so that the P nutrients in the zeolite/NPK fertilizer will diffuse out more easily, and the release of nutrients will be faster.

From Fig. 7, it is shown that variations in Cu concentration affect the amount of P released in the composite. The lowest P release occurred in the zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde with a Cu concentration of 0.4 M. This

indicates that the cross-linking process is optimum when adding 0.4 M Cu to the zeolite/NPK coating material, both for the cross-links between PVA and glutaraldehyde and the cross-links between Cu and alginate. Further observations can be made by calculating the kinetics of P release from Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK fertilizers.

The P release kinetics followed the pseudo-second-order reaction kinetics with  $R^2$  values closest to 1 (Table 3). Table 4 shows the results of the calculation of the P release rate constant from the composite.

Based on the constant rate data ( $k$ ) in Table 4, it is shown that with the increasing Cu concentration in the coating material, the value of the P release constant rate

**Table 3.** Calculation of the value of  $R^2$  on the kinetics of P release from zeolite/NPK fertilizer composites coated with Cu-alginate-PVA-glutaraldehyde variations in Cu content

Cu concentration (M)	$R^2$					
	First-order	Second-order	Third-order	Pseudo-first-order	Pseudo-second-order	
0.0	0.97	0.98	0.95	0.93	0.99	
0.2	0.91	0.98	0.96	0.94	0.99	
0.4	0.99	0.99	0.96	0.95	0.99	
0.6	0.99	0.95	0.94	0.92	0.99	
0.8	0.98	0.98	0.96	0.94	0.99	
1.0	0.96	0.97	0.95	0.93	0.99	

**Table 4.** P release constant rate value with the variation of Cu concentration from Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK composite

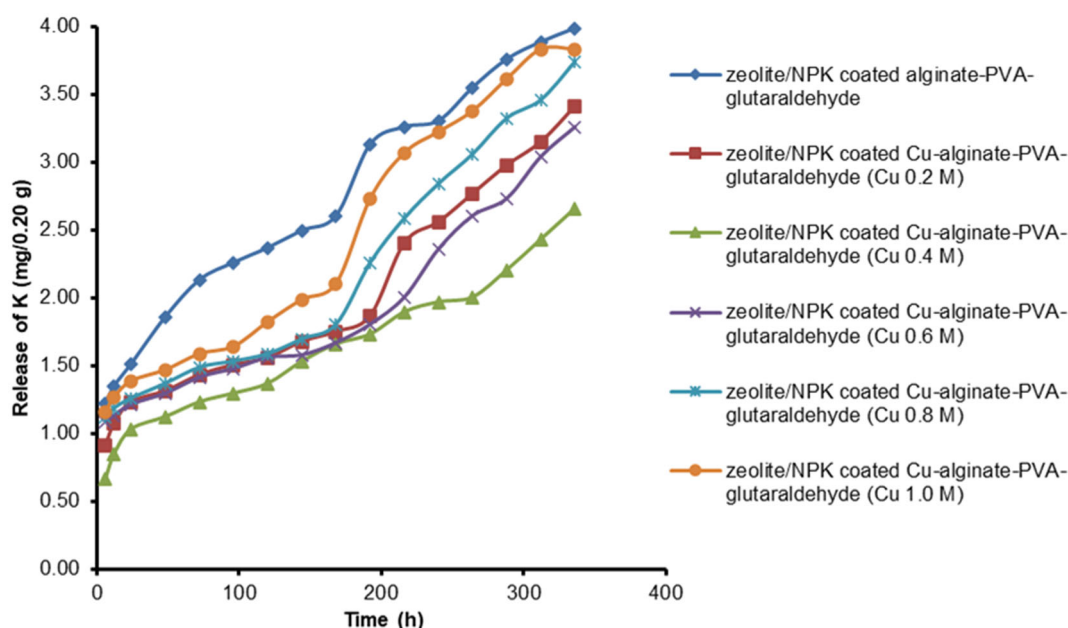
Cu concentration (M)	Pseudo-second-order	
	R <sup>2</sup>	k (mg g <sup>-1</sup> h <sup>-1</sup> )
0.0	0.99	29.08 × 10 <sup>-3</sup>
0.2	0.99	22.34 × 10 <sup>-3</sup>
0.4	0.99	17.48 × 10 <sup>-3</sup>
0.6	0.99	49.62 × 10 <sup>-3</sup>
0.8	0.99	29.04 × 10 <sup>-3</sup>
1.0	0.99	33.21 × 10 <sup>-3</sup>

in the composite fluctuates, starting with a decrease in the rate and followed by an increase. Overall, the P release rate was minimum when Cu with a concentration of 0.4 M was added. From the data obtained, it can be concluded that the lowest P release rate was found in the addition of 0.4 M Cu, which indicates that the double cross-link bond between PVA-glutaraldehyde and Cu-alginate was optimum at the Cu concentration of 0.4 M, meaning it had the best ability to withstand the release of P compared to the other Cu concentrations.

#### Study of the Effect of Variations in Cu Concentration in Cu-Alginate-PVA Glutaraldehyde Coating Material on K Release from Zeolite/NPK Fertilizers

The graph of K release from alginate-PVA-

glutaraldehyde-coated zeolite/NPK fertilizer is shown in Fig. 8. Fig. 8 shows that variations in Cu concentration affect the amount of K released in the composite. With the addition of variations of Cu concentrations of up to 0.4 M, the release of K experienced a slowdown. In the Cu concentration of 0.6 M, K release increased again to 1.08 mg/0.20 g fertilizer at the 6<sup>th</sup> h and 3.26 mg/0.20 g fertilizer on the 14<sup>th</sup> d. At Cu concentrations of 0.8 and 1.0 M, the release of K increased again by 1.12 and 1.16 mg/0.20 g at the 6<sup>th</sup> h, and 3.74 and 3.83 mg/0.20 g of fertilizer on the 14<sup>th</sup> d or 336<sup>th</sup> h. The slowest release of K occurred at Cu concentration of 0.4 M, where the double cross-link interaction between PVA-glutaraldehyde Cu-alginate was optimum, resulting in a composite with the

**Fig 8.** Graph of effect of Cu concentration on K release in zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde in 0.33 M citric acid system for 14 d

best coating material, which caused the release of K to be minimum. Further observations were made by calculating K release kinetics and K release efficiency from the zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde.

Based on the results of the plot of concentration data in a certain time set, it was discovered that the rate of K release follows the pseudo-second-order reaction kinetics with the  $R^2$  value closest to 1 (Table 5). The results of the calculation of the K release of the constant rate from the composite are shown in Table 6.

Based on the constant rate data ( $k$ ) in Table 5, it is shown that the addition of 0.4 M Cu had the lowest K release rate compared to the other Cu concentrations. This indicates that the interaction between Cu-alginate-PVA-glutaraldehyde is optimum at the addition of Cu 0.4 M, resulting in a slow-release of nutrients.

The release of N, P, and K, in general, shows a similar trend with the optimum condition represented by Cu 0.4 M. This can be proven by the FTIR spectra, in which the double-cross-linker bond between PVA-glutaraldehyde and Cu-alginate was optimum at 0.4 M.

Cu-alginate was optimal with a shift in wavenumber indicating a stronger bond, along with the PVA-glutaraldehyde bond which was still good. The addition of a higher concentration of Cu weakened the PVA-alginate bond causing the PVA-glutaraldehyde cross-link bond to also decrease, and the double cross-linker system to not be optimal and release more nutrients.

### Study of the Effect of Variations in Cu Concentration in Cu-Alginate-PVA-Glutaraldehyde Coating Materials on Cu Release from Zeolite/NPK Fertilizers

Fig. 9 shows that the Cu released from the composite decreased along with the increasing Cu concentration up to a concentration of 0.4 M. Afterwards, the Cu release increased again with the addition of Cu 0.6, 0.8, and 1.0 M.

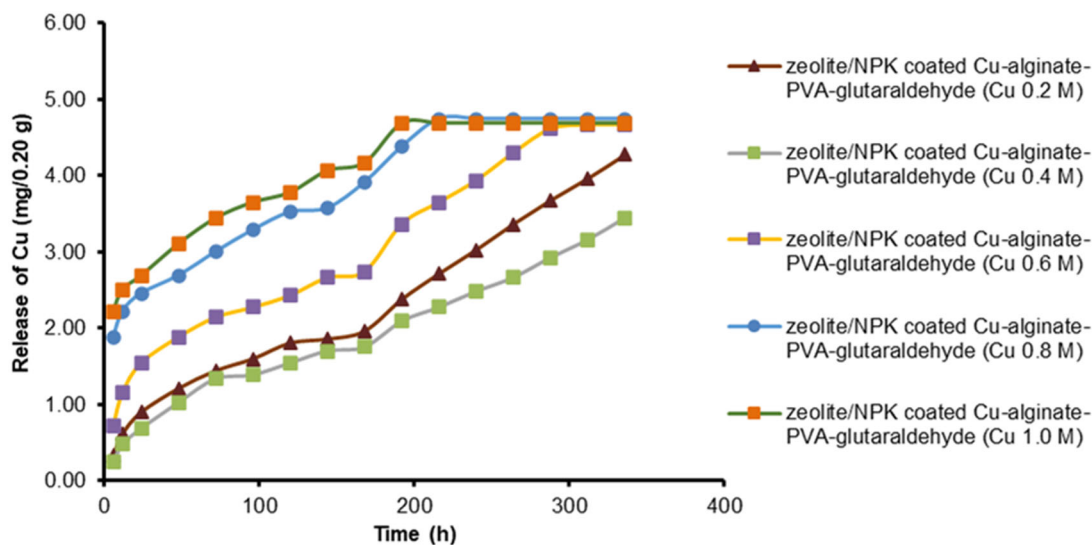
The slow mechanism is shown in the relatively gentle slope of the graph from the 6<sup>th</sup> to the 144<sup>th</sup> h. Meanwhile, the fast mechanism is shown in the steeper slope of the graph from the 144<sup>th</sup> to the 336<sup>th</sup> h. This indicates that the release of Cu from the composite after 144 h experienced a significant increase which could be

**Table 5.** Calculation of the value of  $R^2$  on the kinetics of K release from zeolite/NPK fertilizer composites coated with Cu-alginate-PVA-glutaraldehyde variations in Cu content

Cu concentration (M)	$R^2$				
	First-order	Second-order	Third-order	Pseudo-first-order	Pseudo-second-order
0.0	0.97	0.99	0.99	0.97	0.99
0.2	0.94	0.96	0.97	0.94	0.99
0.4	0.72	0.78	0.84	0.72	0.99
0.6	0.98	0.96	0.98	0.97	0.99
0.8	0.99	0.99	0.99	0.99	0.99
1.0	0.99	0.99	0.99	0.99	0.99

**Table 6.** K release constant rate value with the variation of Cu concentration from alginate-PVA-glutaraldehyde-coated zeolite/NPK composite

Cu concentration (M)	Pseudo-second-order	
	$R^2$	$k$ ( $\text{mg g}^{-1} \text{h}^{-1}$ )
0.0	0.99	$46.52 \times 10^{-3}$
0.2	0.99	$36.24 \times 10^{-3}$
0.4	0.99	$21.73 \times 10^{-3}$
0.6	0.99	$63.63 \times 10^{-3}$
0.8	0.99	$54.79 \times 10^{-3}$
1.0	0.99	$51.43 \times 10^{-3}$



**Fig 9.** Graph of effect of Cu concentration on Cu release in zeolite/NPK fertilizer coated with Cu-alginate-PVA-glutaraldehyde in 0.33 M citric acid system for 14 d

caused by the weakening of the cross-linking system in the coating material. From the data obtained, it can be deduced that the minimum Cu release occurred in the composite with the addition of Cu 0.4 M. This indicated that the cross-link bond in the composite was strongest at the addition of Cu 0.4 M. Further observations were made by calculating the release kinetics of Cu and efficiency of Cu release from the zeolite/NPK fertilizer coated with Cu-

alginate-PVA-glutaraldehyde.

The kinetics of Cu release followed the pseudo-second-order reaction kinetics with the  $R^2$  value closest to 1 (Table 7). In contrast, the results of the calculation of the Cu release rate constant from the composite are shown in Table 8.

Based on the rate constant data ( $k$ ) in Table 8, it is shown that the Cu release rate slows down with the

**Table 7.** Calculation of the value of  $R^2$  on the kinetics of Cu release from zeolite/NPK fertilizer composites coated with Cu-alginate-PVA-glutaraldehyde variations in Cu content

Cu concentration (M)	$R^2$				
	First-order	Second-order	Third-order	Pseudo-first-order	Pseudo-second-order
0.2	0.94	0.96	0.98	0.94	0.99
0.4	0.77	0.97	0.98	0.95	0.99
0.6	0.94	0.98	0.99	0.94	0.99
0.8	0.97	0.99	0.98	0.97	0.99
1.0	0.99	0.96	0.87	0.99	0.99

**Table 8.** The value of Cu constant release rate with the variation of Cu concentration from Cu-alginate-PVA-glutaraldehyde-coated zeolite/NPK composite

Cu concentration (M)	Pseudo-second-order	
	$R^2$	$k$ ( $\text{mg g}^{-1} \text{h}^{-1}$ )
0.2	0.99	$10.33 \times 10^{-3}$
0.4	0.99	$8.57 \times 10^{-3}$
0.6	0.99	$13.61 \times 10^{-3}$
0.8	0.99	$17.44 \times 10^{-3}$
1.0	0.99	$19.72 \times 10^{-3}$



addition of 0.4 M Cu, then the Cu release rate increases again at Cu concentrations above 0.4 M. This indicates that the interaction between Cu-alginate-PVA-glutaraldehyde was optimum at the addition of 0.4 M Cu resulting in a slow-release of nutrients. In addition, at the concentration of Cu 0.4 M, the application of a double cross-linker went well so a strong and tight composite system was obtained, which caused the release of nutrients in the fertilizer to run slowly. The addition of Cu concentration above 0.4 M increased the interaction between Cu and alginate, reducing the number of PVA and alginate bonds which resulted in the disruption of the PVA-glutaraldehyde cross-link bond. The addition of Cu above 0.4 M will make the double cross-linker system unable to run optimally so the release of N, P, K, and Cu nutrients in the fertilizer will also increase.

## ■ CONCLUSION

Zeolite/NPK coated with Cu-alginate-PVA-glutaraldehyde as a double cross-linker slow-release fertilizer has been successfully synthesized by the coating method. The addition of Cu concentration up to 0.4 M in the coating material increased the resistance in citric acid and decreased the amount of N, P, K, and Cu released. The release process of N, P, K, and Cu follows pseudo-second-order release kinetics. The release rate constants of N, P, K, and Cu were  $8.49 \times 10^{-3}$ ,  $17.48 \times 10^{-3}$ ,  $21.73 \times 10^{-3}$ , and  $8.57 \times 10^{-3} \text{ mg g}^{-1} \text{ h}^{-1}$ , respectively.

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