Composite of amorphous silica encapsulated urea as a slow-release fertilizer

M Idris¹, Sutarno¹*, and B Rusdiarso¹
¹Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia.
*Corresponding author: sutarno@ugm.ac.id

Abstract. Composite of amorphous silica encapsulated urea as a slow-release fertilizer has been performed. Amorphous silica was obtained from dealumination of natural clay by the reflux method using HCl 6M. Encapsulation composite was prepared with amorphous silica mass variations of 0.50; 0.75; 1.00; 1.50; and 2.00 g. The preparation of encapsulation composite aimed to study the effect of amorphous silica mass on compressive strength and water absorption of composite. The XRD data showed that the dealumination process was successfully prepared by the formation of an amorphous diffraction pattern. The dealumination process was also supported by EDX data that indicated a decrease in the percentage of Al atomic weight from 11.29 to 0.36%. The optimum compressive strength and water absorption results were obtained at amorphous silica mass of 0.75 g with values of 5.40 MPa and 42.60%, respectively. The kinetics model followed the pseudo-second order for urea as a control and Korsmeyer-Peppas for composite of amorphous silica encapsulated urea with rate values of 0.847 mg g⁻¹ hour⁻⁰.⁸ and 0.012 mg g⁻¹ hour⁻¹, respectively.

1. Introduction

Urea is the most popular fertilizer used in agriculture. Urea is widely used because it has properties such as high nitrogen content of around 46.6%, low cost of production, non-corrosive, high water solubility and easily mixed with other compounds [1]. The main challenge in the use of urea fertilizer is that nutrients are the high rate of loss to the environment through leaching and volatilization. Urea left in the soil is only half of the total amount of urea given to plants but it also depends on the climate, soil conditions, and application technologies, thereby causing environmental pollution and increasing the costs of crop production [2].

Research that conducted by Ni et al [3] produces a natural attapulgite (APT) based clay fertilizer, ethylcellulose film (EC), and sodium carboxymethyl cellulose/hydroxyethyl cellulose (CMC/HEC) hydrogel. These materials and their derivatives are biodegradable polymer materials so they do not contaminate the environment. The weakness of this type of fertilizer is that the synthesis process is complicated. In addition, uniformity in coating thickness is difficult to achieve. Therefore a new solution in the form of encapsulated urea is needed because it has uniform thickness dimensions. This can be realized by producing mold equipments that can be adjusted in dimensions and are easy to use.

Encapsulation composite has been made in this research as urea wrapper for slow-release fertilizer. The materials used in this study are amorphous silica from natural clay as matrix and glutinous rice flour (starch) as binder for preparation of encapsulation composite. Glutinous rice has amylose and amylopectin constituents which can form aggregation in encapsulation composites thereby increasing the permeability of composites. In addition, white cement as a cross-linker material then acts as the main bearer of a burden on the encapsulation composite.

Recently, encapsulation composite as a slow-release material has not been explored in much. This condition has encouraged researchers to prepare encapsulation composites as urea encapsulant for designing slow release fertilizer. The slow-release properties of fertilizer are mainly influenced by the composition of the encapsulation composite that can be assessed from its compressive strength and water absorption capacity.
2. Experimental Section

2.1. Materials

Natural clay used was obtained from Boyolali, Central Java, Indonesia. Urea fertilizer and glutinous rice were obtained from the traditional market. White cement used was a product from Tiga Roda Indocement. Other chemicals with a purity of analysis such as 4-(dimethylamino) benzaldehyde and hydrochloric acid (HCl) 36% were obtained from Merck.

2.2. Preparation of amorphous silica

As much as 25 g of natural clay which had been stirred for 24 hours was put into a round bottom flask with 150 ml HCl 6M then refluxed for 24 hours at 100-110 °C.

2.3. Preparation and characterization of encapsulant composite

A mount of 25% (w/w) white cement, 1 g of sticky rice, and amorphous silica (with various weight: 0.5; 0.75; 1.0; 1.50; and 2.00 g) were homogeneously mixed and then added with 4 ml distilled water. Casting is prepared using cylindrical mold with height of 2 cm and diameter of 8.2 mm so as to ensure same dimensions to all the tablets. The formed composite was dried for 24 hours at room temperature and then tested for water absorption capacity and compressive strength. The results showed in Figure 6. Fourier Transform Infrared (FTIR) spectroscopy of composite was carried out with a KBr disk using a Shimadzu Prestige 21 FTIR spectrometer (Figure 4). A Shimadzu XRD 6000 diffractometer was used to conduct diffraction patterns of the composite. With similar procedure, the optimum composition was taken to produce the composite encapsulated urea fertilizer by the addition of 0.50 g of urea.

2.4. Slow-release test

The resulted composites were dipped in 100 ml distilled water then sampled at 5; 10; 15; 20; 25; 30; and 60 minutes. The next sampling was taken in the interval of one hour during 25 hours. The content of urea in the composite was determined by Spectrophotometer Uv-visible ThermoScientific Genesys 10S with the addition of the 4-(dimethylamino) benzaldehyde which was adopted from Giraldo and Rivas's research [4].

3. Results and Discussion

The infrared spectrophotometer was used to determine the absorption area of functional groups from prepared composites. It also could identify the types of bonds found in natural clays before and after the process of dealumination (amorphous silica). The IR spectra of natural clays before and after dealumination are shown in Figure 1. The absorption bands at 1033 cm\(^{-1}\) show a stretching vibration of TO\(_4\) (T= Si or Al), symmetrical stretching vibration of O-Si-O and O-Al-O (794 cm\(^{-1}\)), and bending vibration of Si-O-Al (Al is an octahedral cation) in 532 cm\(^{-1}\). This result is in accordance with the study by Alabarse et al. [5] and Paluszkiwicz et al. [6]. The absorption of the band 3425 cm\(^{-1}\) indicate the stretching vibration of the -OH group and the absorption at 1635 cm\(^{-1}\) also indicate the bending vibration of H-O-H of water molecules bound physically at aluminosilicate framework.

Results of XRD analyses, which were used to verify type of natural clay before and after dealumination, are shown in Figure 2. The XRD pattern of natural clay (Figure 2a) shows typical features of this material, with the peaks at 20: 21.94 and 26.63° indicate the presence of quartz. This diffractogram are compared to JCPDS No. 01-086-1560 which has a hexagonal crystal system. In addition, at 20: 19.81; 20.85; 25.03 and 34.77° were appeared that has been adapted to JCPDS No. 00-002-0014.
Figure 1. Infrared spectra (a) natural clay and (b) amorphous silica (b) amorphous silica

Figure 2. X-ray diffractogram (a) natural clay and (b) amorphous silica (b) amorphous silica

X-ray diffractograms after dealumination (amorphous silica) (Figure 2b) provides major peaks at 2θ 20.82; 26.61; 36.49; 39.46; 40.24; 42.37 and 50.05°. This indicates that the formation of alpha quartz after being compared with JCPDS No. 01-089-8935 which has hexagonal ring crystal system formed from SiO$_2$ tetrahedral and oxygen atoms. In addition, the presence of peaks at 2θ 21.90° indicates the formation of amorphous silica as reported by Martínez et al [7].

Analysis using SEM (Scanning Electron Microscope) aims to investigate the surface and particle size of natural clay and amorphous silica directly. The presence of Energy Dispersive X-ray (EDX) allows qualitative and semi-quantitative determination of the constituent elements of material such as many elements of silicon, aluminium, oxygen and hydrogen. The SEM images of natural clay and amorphous silica were shown in Figure 3.

Figure 3. SEM images (a) natural clay and (b) amorphous silica

SEM characterizations were performed to observe the morphology of natural clay and amorphous silica (Figure 3). Natural clay (Figure 3a) has large spherical particles and amorphous silica (Figure 3b) takes the form of small flakes and the distribution of particles is not uniform.

The results of the per cent element of natural clay and amorphos silica are shown in Table 1. Natural clays have major compositions namely Al, Si and O atoms, in which these atoms compose the octahedral and tetrahedral natural clay frameworks. The minor compositions (Mg, K, Ca, and Fe) are balancing cations found in the interlayer or intralayer in natural clay. EDX spectra for amorphous silica only consists of four atomic compositions (Al, Si, O, and C) reduction in the number of this composition...
that indicates the process of dealumination with acids in this case hydrochloric acid, is successfully carried out. Other indications are seen by decreasing the percentage of Al atomic weight from 11.29% to 0.36% and increasing the percentage of Si atomic weight from 22.32% to 29.50%. However, EDX spectra results are not representative of the justification of changes in overall atomic weight per cent.

Table 1. Composition of atomic weights from EDX spectra

| Element | Natural clay | Amorphous silica |
|---------|-------------|------------------|
| Al      | 11.29%      | 0.36%            |
| Si      | 22.32%      | 29.50%           |
| O       | 50.35%      | 55.91%           |
| C       | 9.11%       | 14.23%           |
| Mg      | 1.43%       | nd               |
| K       | 0.73%       | nd               |
| Ca      | 0.48%       | nd               |
| Fe      | 4.30%       | nd               |

*) nd = not detected

The infrared spectra of amorphous silica with variation of weight (Figure 4) showed the absorption of 3425, 1635, 794 and 470 cm\(^{-1}\) respectively. This indicates T-OH stretching vibrations (T = Si or Al), TOH stretching vibrations (T = H), Si-O stretching vibrations and Si-O bending vibrations in the plane. However, the amorphous silica experienced a decrease of intensity in the absorption region at 3425 and 1635 cm\(^{-1}\) in which the absorption region is stretching and bending -OH vibrations. This decrease in peaks is caused by an increase in the amount of amorphous silica and accompanied by a decrease in the amount of sticky rice in the composite.

To assess the effect of amorphous silica weight variations in the formation of encapsulated composites, an analysis using XRD is required. The results of X-ray diffractogram of amorphous silica weight variation are shown in Figure 5. The results of encapsulation composite with amorphous silica weight variations were observed by X-ray diffraction at 2θ 18.34; 20.83; 21.90 and 22.96\(^{\circ}\) with a widening d-spacing peak is caused by a mixture of silica and sticky rice in which both materials have an amorphous structure. X-ray diffraction at 2θ 26.61; 29.31 and 39.40\(^{\circ}\) were compared to JCPDS Calcite No. 00-005-0586 with the rhombohedral structural system. The results of X-ray diffraction indicate the formation of products by the hydration reaction.

Composites with variations in the weight of amorphous silica as a base material of urea encapsulation composites were also examined for their effect on the water absorption and compressive strength of the composites. The results water absorption and compressive strength tests are shown in Figure 6. The water absorption test results (Figure 6a) show that amorphous silica, in general, provides greater water absorption to the composite, however, the optimum amorphous silica variation results that provide the lowest water absorption was at a weight of 0.75 g. This weight is the optimum ratio between amorphous silica with calcium hydroxide in white cement to achieve complete pozzolanic reactions. Amorphous silica weighing 0.75 g was used to make urea encapsulation composites.
Figure 4. Infrared spectra of composite variation (a) composite amorphous silica variation (a) 0.50; (b) 0.75; (c) 1.00; (d) 1.50; and (e) 2.00 g

Figure 5. X-ray diffractogram of encapsulated amorphous silica variation (a) composite amorphous silica variation (a) 0.50; (b) 0.75; (c) 1.00; (d) 1.50; and (e) 2.00 g

Figure 6. Test results (a) water absorption and (b) compressive strength for amorphous silica weight variations

The compressive strength test results (Figure 6b) provide information that amorphous silica gives an alteration in the compressive strength value of the composite. The greater the amount of amorphous silica given, the compressive strength of composites has a tendency to increase. The highest compressive strength was obtained at 2.00 g of amorphous silica. This compressive strength is caused by the pozzolanic activity of the reaction of amorphous silica with calcium hydroxide to form calcium silicate hydrate (C-S-H). In addition, amorphous silica can increase the C-S-H chain length from the hydration of white cement and hydration stability for ettringite [8].
The release rates of composite encapsulated (Figure 7) urea were initiated by the slow release mechanism of urea in which at the 5th, 10th and 15th minutes, there was no increase in the concentration of urea that was released significantly. This phenomenon is caused in the early minutes of release, water undergoes hydro diffusion first on the composite wall to be able to dissolve urea. The observation of urea release every hour showed that the rate of urea release was faster than the initial minutes before. This is because of the hydro diffusion of water out of the composite system. This phenomenon is caused by differences in concentration between inside the composite and outside the encapsulation composite. The release of urea from encapsulation composites can be studied by creating several kinetic models such as first-order, second-order, third-order, pseudo-first order, pseudo-second order and Korsmeyer-Peppas. Based on the results of the plot data, the kinetics of the rate of release of urea from the optimum encapsulation composite follows the Korsmeyer-Peppas kinetics model and a pseudo-second-order reaction to conventional urea with rate values of 0.847 mg⁻¹ hour⁻¹ and 0.012 mg⁻¹ hour⁻¹.

![Figure 7. Graph of the release of urea (a) composite encapsulation and (b) control urea](image)

4. Conclusion

Amorphous silica had been synthesized by the reflux method. The composite encapsulated urea were made with amorphous silica mass variations to study the effect of compressive strength and water absorption on encapsulated composites. The urea release test on the composite was studied by creating a kinetics model. The composite encapsulated urea followed the Korsmeyer-Peppas model and the urea as a control followed a pseudo-second-order with successive rate values of 0.847 mg⁻¹ hour⁻¹ and 0.012 mg⁻¹ hour⁻¹.

5. References

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