



Research Article

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Increasing the effectiveness of pesticides based urea nanofertilizer encapsulated nanosilica with addition of rice husk TiO_2 additive substances

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ABSTRACT

Increasing effectiveness of the encapsulated urea pesticide nanofertilizer based nanosilica from rice husk with the addition of additives TiO_2 had been achieved. The analysis showed that SiO_2 content in rice husk ash amounted to 82.12%, while 17.88% is the amount of oxide compounds other than major elements K, Ca, Al, P, Cl, Fe and Mn uptake S. Characteristics Fourier Transform Infra Red (FTIR) pure silica of rice husk ash showed absorption widened at 3418.01 cm^{-1} and 1634.74 cm^{-1} which the stretching vibration and bending vibration-OH of silanol (Si-OH) are hydrophilic. The dominant absorption peaks showing the presence of siloxane groups (Si-O-Si) contained in the catchment area 1110.08 cm^{-1} , 796.64 cm^{-1} , and 465.83 cm^{-1} . Modification of the structure of the silica produced nanosilica done through the sol gel reaction involving acid-base reaction. An average pore size of rice husk ash obtained 5.996 nm, whereas the average pore size nanosilica 7.752 nm. Nanosilica surface area increased to $25.591\text{ m}^2/\text{g}$ compared with the prior modified only amounted to $1.780\text{ m}^2/\text{g}$. Results of analysis using FTIR, nanosilica encapsulated urea had formed, it could be confirmed from the dominant absorption peaks indicating siloxane groups (Si-O-Si) are at 1121.65 cm^{-1} , 784.10 cm^{-1} and 461.01 cm^{-1} . While at 1158.30 cm^{-1} is the uptake for CN. In the measurement% urea-nanosilica release, the release without silica urea has almost reached 100% in the early minutes, 15 minutes..

Keywords: pesticides, encapsulated nanofertilizer urea, rice husk ash

INTRODUCTION

As an agricultural country, Indonesia has agricultural, forestry, plantation, animal husbandry and fisheries are abundant. These conditions provide opportunities for the majority of the Indonesian people to conduct business activities in agriculture or related to agriculture. Agriculture is one of the most fundamental activity for humans. As one agricultural country, Indonesia including consumer urea sizable approximately 5.1 million tons per year in 2010 (Ministry of Agriculture 2010). While the total fertilizer usage reached 11.1 million tons in 2012. Indonesia is also one of the countries with the largest nitrogen fertilizer use. One type of artificial nitrogen fertilizer is urea which is widely used in the agricultural sector reached 3.6 million tons (Directorate General of Horticulture, Department of Agriculture, 2008). In addition to the use of urea fertilizer to increase crop productivity, also performed eradication of pests and diseases by using pesticides. Excessive use of synthetic pesticides can adversely affect the environment. Nitrogen fertilizer demand in plants because plants have to extract nitrogen from the soil needs. The use of inorganic fertilizers have caused agricultural productivity this will only last a short time. This is due to the use of inorganic fertilizers are constantly result in changes in soil structure, compaction, nutrient content in the soil decreased, and environmental pollution [7].

Various efforts to increase the efficiency of the increase in agricultural production has been carried out, one of them is to manufacture urea tablet. However, the application of fertilizer with urea tablet is less popular among people

because the process is too complicated with urea immerse tablets into the ground. Increased food productivity can be achieved with the use of modern technology, among which is that nanotechnology has the potential to improve agricultural systems [2]. Began to develop innovation-based encapsulation or encapsulation technology. Encapsulation on pesticides is done in micro size, later release of pesticides into the environment can be maintained and regulated by the levels allowed [1].

Meanwhile, about 20% of agricultural waste obtained in the process of milling rice is rice husk whose potential has not been fully utilized. Ash from rice husk containing silica with levels high enough so that the base material can be used silica-based material.

Nanofertilizer or fertilizer with nano size will balance the release of fertilizer N and P with the absorption of the plant, thereby preventing the nutrient losses and avoiding unwanted nutrients interact with microorganisms, water, and air [4]. By utilizing nanofertilizer absorption of nutrients by the plants will be maximal. Nanofertilizer encapsulated nanosilica can form a binary films on the cell wall after absorption of nutrients that can prevent fungal infections, bacteria and nematodes, improving plant growth under the pressure of high temperature and humidity and to improve plant resistance to disease [11]. Silicon-based fertilizers used to increase plant resistance. SiO_2 in nanostructures can improve seedling growth and root development [5]. To further optimize the use of fertilizers to increase food production, TiO_2 or titania that are non-toxic can be used as additives in fertilizers. The addition of additives in fertilizers can increase water retention [4].

Based on the above, this research focuses on increasing the efficiency of pesticide encapsulated urea-based nanofertilizer nanosilica from rice husk with the addition of additives TiO_2 which is expected to regulate the discharge of pesticides into the environment so well that it can save the use of pesticides.

EXPERIMENTAL SECTION

1. Preparation Nanosilica of Abu Rice Husk

Rice husk ash first characterized using XRF (X-Ray fluorescence) to determine the content of silica and other compounds. Rice husk ash in NaOH solution is stirred and boiled for 3 hours. The solution is then filtered and the residue washed with boiling water. While the resulting filtrate was cooled and added H_2SO_4 up to pH 2 and then added NH_4OH to pH 8.5. The filtrate was dried at 120°C for 12 hours. Furthermore, to determine the functional group formed characterization using FTIR (Fourier Transform Infra Red). Refluxed silica extracted using 6 N HCl for 4 hours, then washed repeatedly with deionized water. Repeated washing process aims to eliminate the free acid. Then dissolved in NaOH with stirring continuously for 10 hours. H_2SO_4 was added to adjust the pH in the range 7.5 to 8.5. The precipitated silica is washed repeatedly with deionized water until the filtrate becomes truly free alkali. After the washing process is dried at 50°C for 48 hours in an oven. Nanosilica is then characterized using SAA (Surface Area Analyzer) to determine the pore volume, pore size and surface area. It also carried out the characterization by SEM (Scanning Electron Microscopy) to determine the surface morphology characterization using [6]

2. Preparation of Urea Encapsulated Loading Nanosilica

A total of 1 gram of urea solids are heated until melted, then added to 2 grams nanosilica. Do variations in comparison nanosilica: urea, 2: 1 and 1: 1 (w / w). Urea Encapsulated nanosilica characterized using FTIR (Fourier Transform Infra Red) to determine the functional groups is formed. Urea Encapsulated next nanosilica taken each 1 gram and added 100 ml of deionized water and then stirred at 120 rpm at room temperature. , Filtrate each time (0-120 minutes)% release is then measured using a UV-Vis spektrovotometer at λ 536 nm. Effect on pH also performed with a contact time every time (0-120 min).

3. Preparation of Urea Encapsulated Formula Nanofertilizer Nanosilica with the addition of TiO_2 Additives

Urea Encapsulated nanosilica with variation ratio of 2: 1 and 1: 1 is added TiO_2 by weight variation 10%, 15% and 20% of the weight nanosilica, thus obtained 6 nanosilica formula: urea: TiO_2 .

4. Testing Activity Inhibition of Fungi Nanofertilizer Urea Encapsulated Additives Nanosilica with the addition of TiO_2

Antifungal activity test performed on 6 nanosilica formula: urea: TiO_2 and nanosilica: urea before the addition of TiO_2 . A. flavus spores sterilized by soaking in alcohol 70% for 1 minute. After rinsed with sterile distilled water, then mushrooms grown on PDA in petridish. This test is done to determine the inhibition of the extract to see the formation of a clear zone around the wells extract. 2 ml suspension of fungal spores concentration test 2×10^5 conidia / ml put in a petri dish and then pour 20 ml PDA that is still liquid. The culture is shaken until conidia mixed evenly

to all media. Once frozen prepared hole and subsequent pit filled with samples that have been prepared (Setiasih, et al., 2013).

RESULTS AND DISCUSSION

One type is the most widely used fertilizer in the agricultural sector is urea which is a fertilizer nitrogen the efficiency is still low. One of the efforts to increase the efficiency of nitrogen fertilizer use is by nanosilica encapsulation-based innovation. Encapsulation on pesticides that do will remove pesticides into the environment. Efforts to optimize the use of fertilizers to increase food production is done with the addition of titania that are non-toxic, which acts as additives in fertilizers.

The first achievement of this research is nanosilica preparation of rice husk ash carried by precipitation or deposition method. Rice husk ash is known to have a silica content of about 87-97% for certain abortion analyzed by XRF spectrometer. Rice husk ash beforehand sieved using a 150 mesh sieve, with the size of the product is expected to be obtained strong and not brittle. Results of the analysis of the ash straw by using XRF, data showed that the chemical composition shown in Table 1. The content of silica (SiO_2) of rice husk ash used were obtained by 82.12%. XRF analysis results indicate that the main composition of rice husk ash is silica, while the number of 17, .88% is oxide compounds other than major elements K, Ca, Al, P, Cl, Mn Fe and SiO_2 content of 82 S., 12% of the rice husk ash has shown the decomposition of organic matter content is very high.

Table 1. Test Results Composition of Chemical Ingredients Abu Rice Straw

Chemical Composition	content (%)	Chemical Composition	content (%)
SiO_2	82,12	Fe_2O_3	0,82
K_2O	9,72	SO_3	0,73
CaO	2,52	TiO_2	0,09
Al_2O_3	1,00	Rb_2O	0,06
P_2O_5	0,99	ZnO	0,05
Cl	0,98	SrO	0,01
MnO	0,87		

Figure 1 shows the FTIR spectra to determine the functional group. Figure 1a, the spectra for commercial silica as a comparison to the spectra of silica synthesized from rice husk ash. Both spectra show the same characteristics. Uptake widened at 3418.01 and 1634.74 cm^{-1} is an OH absorption of hydrophilic silanol groups which can hydrogen bond with water vapor[8]. Uptake of these characteristics is very strong, widened sharply if the H_2O content more and more. The dominant absorption peaks showing the presence of siloxane groups (Si-O-Si) are at 1110.08 cm^{-1} , 796.64 cm^{-1} , 465.83 cm^{-1} [9]

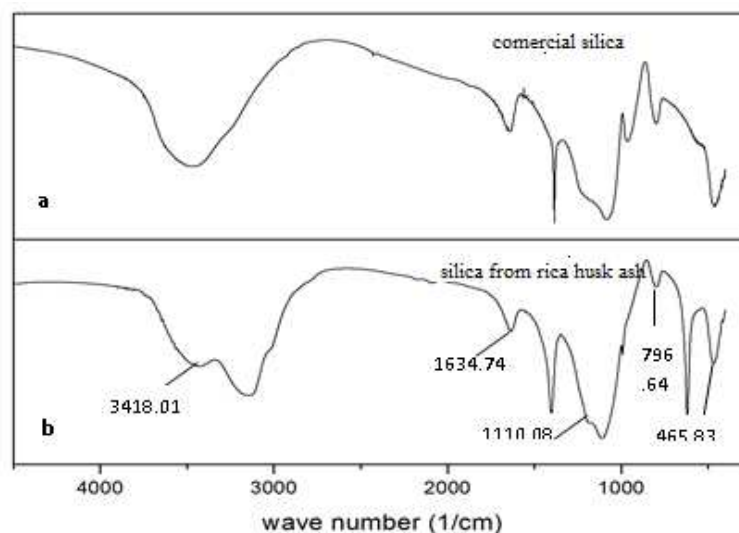


Figure 1. IR Spectra of a) the commercial silica and (b) the results of the synthesis of silica rice husk as

Silica from rice husk ash preparasi results with solvent refluxing 6 N HCl for 4 hours to resolve the inorganic oxide still containing oxide impurities. NaOH concentration is very influential in the process of separating the silica from rice husk and to eliminate some of the impurities that do not participate dissolved from the main product [10].

Silica pore characteristics of rice husk ash and nanosilica the SAA obtained by measuring the surface area, total pore volume and average pore size, as shown in Table 2. The rice husk ash has character 10-3 pore pore volume 5.34 cm³ / g, more nanosilica smaller than the pore volume of 9.919 10-2 cc / g. An average pore size of rice husk ash of 5.996 nm, whereas the average pore size nanosilica obtained 7.752 nm. Both have a range of mesoporous material pore size (2 nm-50 nm). Nanosilica increased surface area which is 25.591 m² / g compared with rice husk ash before bernilai structural modifications which only 1,780 m² / g.

Tabel 2. Rice husk ash characterization

	Total volume of porous	Average size of porous	Surface Area
Rice husk ash	5,337 10-3 cc/g	5,996 nm	1,780 m ² /g
Nanosilica	9,919 10-2 cc/g	7,752 nm	25,591 m ² /g

The second achievement of this research was the encapsulation process by nanosilica urea and urea release test done with a variety of contact time and temperature variations. To confirm the formation of urea has been encapsulated nanosilica can be seen in Figure 2 of the FTIR spectra to determine the amine functional groups on urea.

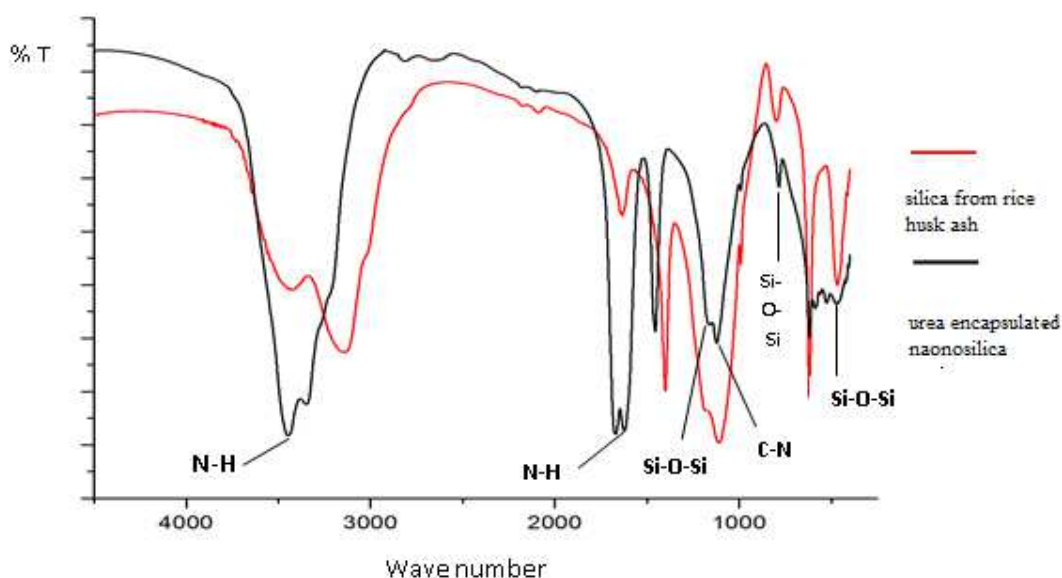


Figure 2. FTIR spectra to determine the amine functional groups on urea

Black line in Figure 2. The FTIR spectra showed absorption of urea encapsulated nanosilica. The dominant absorption peaks indicating siloxane groups (Si-O-Si) contained in 1121.65 cm⁻¹, 784.10 cm⁻¹ and 461,01cm⁻¹. Their sharp absorption at 3445.98 cm⁻¹ and 1623.17 cm⁻¹ showed absorption NH for primary amines (R-NH₂). While at 1158.30 cm⁻¹ is the uptake for CN. From the results of FTIR spectra concluded that the encapsulation of urea by silica successful.

the encapsulated urea loading nanosilica to measure the% release using UV-Vis spektrovotometer at λ 536 nm. Process carried out by variation of contact time every time (0-120 min). Tests conducted on urea without the presence of silica and urea that has been encapsulated by the silica. Results of the analysis are shown in Figure 3 shows that the release urea without silica has almost reached 100% in the early minutes, 15 minutes, while the release of urea with the addition nanosilica on variations of 2: 1 or 1: 1 up to 100% in minutes ke- 120. Effect on pH also performed with a contact time every time (0-120 min). From the graph shown in Figure 4. the longer the contact time, the more alkaline pH indicating that the release of fertilizer occurs.

Last achievement is the end of the encapsulated urea manufacture nanosilica formula with a variation ratio of 2: 1 and 1: 1 is added TiO₂ by weight variation 10%, 15% and 20% of the weight nanosilica, thus obtained 6 nanosilica formula: urea: TiO₂.

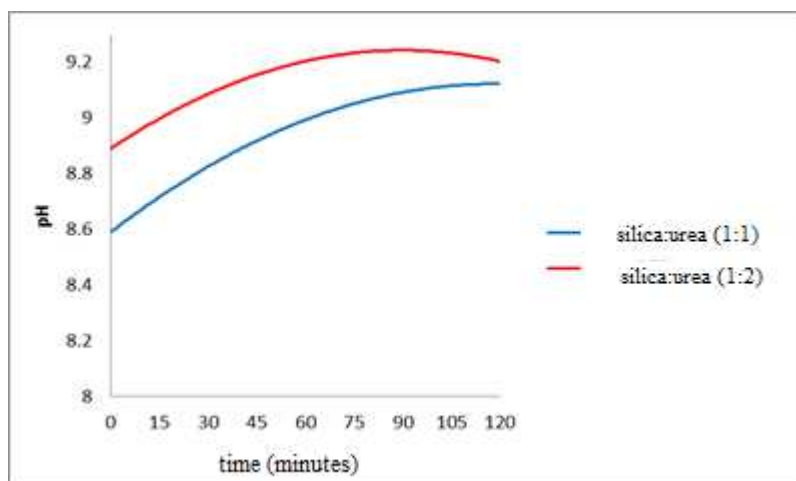


Figure 3. PH Vs time

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