ISSN: 978-602-71169-7-9

Fabrication of NanoChiSil for Application of Fertilizer

Agus Subagio[1,a], Erma Prihastanti[2,b], Ngadiwiyana[3,c], Khasan Rowi[4,d], Ahmad Gufron[4,e]

[1]Department of Physics, Faculty of Science and Mathematics, Diponegoro University

[2]Department of Biology, Faculty of Science and Mathematics, Diponegoro University

[3]Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University

[4]Division of Research and Development, CV. Dipon Indonesia

[a]agus_fadhil@yahoo.com, [b]ermaprihast@gmail.com, [c]ngadiwiyana@gmail.com, [d]row_kim@yahoo.com, [e]gupron99@yahoo.com,

Abstract. It has conducted research of nanoChiSil material consisting of nanochitosan and nanosilica materials for agricultural fertilizer applications. A total of 10 grams of chitosan powder was weighed and dissolved in 500 ml of 1% solution of acetic acid and stirred for 30 minutes, then filtered to separate the chitosan solution with impurities. Nanochitosan synthesized by using 50 ml liquid chitosan diluted further by adding 200 ml of distilled water while stirring continuously using a magnetic stirrer. The chitosan solution was then added to 20 ml of solution 0.02% STTP drop by drop, stirring constantly with a magnetic stirrer until the chitosan solution changes color to white. The nanoChiSil material is performed by adding 30 ml of colloidal nanochitosan into 70 ml of colloidal nanosilica (Nanosil 99) using a magnetic stirrer until homogenous. The nanoChiSil was then analyzed the shape and particle size by using TEM, while its content was measured by EDX. The observed TEM results clearly indicate that the particles of NanoChiSil material have size of 10-20 nm.

Keywords: NanoChiSil, nanochitosan, nanosilica, FTIR, TEM, EDX

Introduction

Silica is a beneficial element for rice, corn and sugarcane. Silica was mainly derived from irrigation water and the large amount of Si removed through harvest resulted in a deficit of Si in soils. Decreasing of soil available silica in tropical soils mostly was caused by desilication. The loss of silica through harvest was more than double that of the other major nutrients, including N, P and K. This deficit implies that the enormous amount of Si removed during rice harvest cannot be replenished by a natural Si source such as geological fertilization and an additional silicate fertilizer is necessary [1]. Nutrient content derived from fertilizer, irrigation water, and nitrogen fixation, and output parameters were nutrient loss through harvest, drainage water, and denitrification. The results showed a positive balance for N, P, Ca, Mg, and Na; however, K and Si showed a negative balance. The decreasing in Si and K were due to the substantial uptake of these nutrients without adequate replenishment through fertilizer [2].

Silica is an oxide form of silicon. Silica is widely used as a one of the basic raw materials in the field of electronics, ceramic, polymer industry and to enhance the compressive strength of concretes in construction industry. Silica in nanometer size was rarely used as fertilizer. Some silica fertilizer products were in granular form and their size was still micron scale. If nanosilica can be made as fertilizer so it is very effective to be absorbed by plants.

Silica is manufactured in several forms, they are fused quartz, crystal, fumed silica, (or pyrogenic silica, trademarked aerosil or Cab-O-Sil), colloidal silica, silica gel and aerogel [3]. The nanoscale silica materials have been prepared through several methods such as sol–gel process [4-6], vapour-phase [7] and thermal decomposition technique [8]. However, the high cost of preparation has limited their wide application. Nanosilica has received much attention because of their wide range of applications in pharmacy and medicine, desalination optics, and other fields [9].

Colloidal nanosilica denotes small particles consisting of an amorphous SiO_2 core with a hydroxylated surface, which are insoluble in water. The size of the particles can be varied between 1 and 500 nm, hence they are small enough to remain suspended in a fluid medium without settling. Parameters such as specific surface area, size and size distribution can be controlled by the synthesis technique [10]. The nano-scale size of particles can result in dramatically improved properties from conventional grain-size materials of the same chemical composition.

The aim of the present research work was fabrication of nanoChiSil fertilizer made from colloidal nanosilica addition in nanochitosan. Nanochitosan is a biodegradable polymer which is most abundant. The benefit of the nanochitosan as coater is the release rate of fertilizer nutrients is slowly with covering the greater part of the pores so that the water can still enter to dissolve through the pores. Therefore, nanochitosan was able to coat the fertilizer well and have biodegradibel, biocompatible, nontoksit and environmental friendly properties [11].

The Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) tests were conducted to identification of bonding force and particle size of materials.

Experiment method

There are several methods available for the preparation of colloidal nanosilica and nanochitosan. The intension of the work is to optimize the best method for colloidal nanosilica and nanochitosan preparation from synthesis. A total of 10 grams of chitosan powder was weighed and dissolved in 500 ml of 1% solution of acetic acid and stirred for 30 minutes, then iltered to separate the chitosan solution with impurities. Nanochitosan synthesized by using 50 ml liquid chitosan diluted further by adding 200 ml of distilled water while stirring continuously using a magnetic stirrer. This chitosan solution was then added drop by drop to 20 ml of 0.02% STPP (sodium tripolyphosphate) solution, stirring constantly with a magnetic stirrer until it becames white colloidal nanochitosan. The nanoChiSil material is performed by adding 30 ml of colloidal nanochitosan into 70 ml of colloidal nanosilica (Nanosil 99) using a magnetic stirrer. The nanoChiSil was then analyzed the shape and particle size by using TEM, while its content was measured by EDX.

Result and discussion

In order to improve the stability of chitosan biopolymer in acid medium and also to improve its adsorption capacities, certain chemical and physical modifications have been commonly done. Among the various chemical modifications, the cross-linking process is the one which is used to produce a great effect. The adsorption capacity of chitosan was found to be increased with the addition of crosslinking agent. The sodium tripolyphosphate (TPP), a crosslinking agent is a non-toxic polyanion is suitable. The ionic cross linked networks were created by the electrostatic interaction between the protonated amine groups in chitosan and the negatively charged counterion STPP [12]. The structure of nanochitosan prepared from chitosan using STPP as a cross linking agent was represented below (Fig. 1).

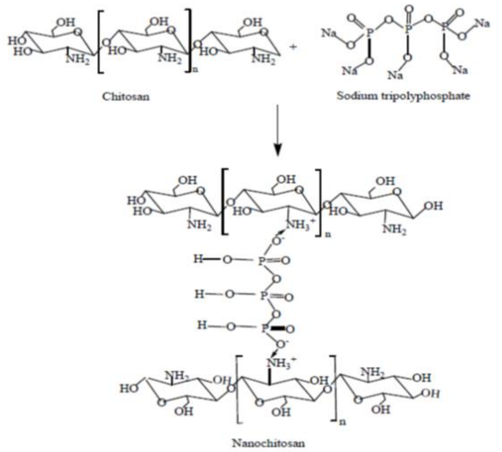


Fig. 1. Structure of nanochitosan [13]

Fig. 2 showed the FTIR spectra of nanochitosan (0.02% STPP), a strong peak was obtained at 3490 cm^{-1}, 3386 cm^{-1}, 2950 cm^{-1} and 1050 cm^{-1} which indicates the presence of the NH stretching vibration, the OH stretching vibration, the CH stretching vibration in NH_3^+, and C-O stretching vibration, respectively. The peak observed at 3386 cm^{-1} corresponding to the presence of OH in nanochitosan samples may indicate

ISSN: 978-602-71169-7-9

an interaction of the sodium tripolyphosphate with the pure chitosan [13].

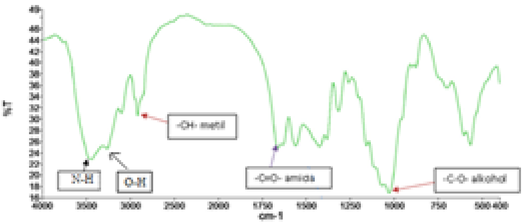
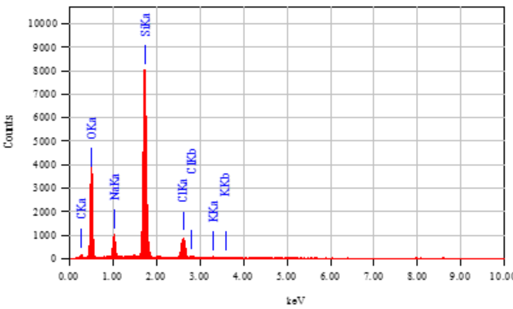


Fig. 2. FTIR spectra of nanochitosan

The colloidal nanoChiSil is a blend of nanosilika and nanochitosan as a fertilizer that can be applied to food crops. The aim of utilization of nanochitosan is to increase fungsionalization of fertilizer of nanosilica, which in addition to healthy plants also keep the plant from bacteria or fungi. However, nanochitosan also can control the release of nanosilica particles to be effective in its use as a fertilizer.

Fig. 3 shows the EDX profile of colloidal nanoChiSil evidences predominantly with elements. The colloidal nanoChiSil has the carbon (C), natrium (Na), chlor (Cl), potassium (K) and calcium (Ca) with contains 24.02 wt.% of Si and 55.39 wt.% of O as shown at the table in the Fig. 3. Both Si and O peaks represent the presence of silica.



Element	(keV)	Mass%
C	0.277	12.14
O	0.525	55.39
Na	1.041	4.56
Si	1.739	24.02
Cl	2.621	3.71
K	3.312	0.18
Total		100.00

Figure 3. Energy dispersion X-ray (EDX) of NanoChiSil.

Transmission electron microscopy (TEM) images of colloidal nanochitosan, nanosilica and nanoChiSil were shown in Fig. 4. The shape of nanochitosan particles were a circle with a hollow in the middle and verify the absence of aggregation (Fig 4a). The nanosilica particles were almost spherical in shape and nano sizes (Fig. 4b). Fig 4c showed the shape of nanoChiSil particles with a smaller size than nanochitosan and nanosilica. There was the surface modification of nanoChiSil particles. The homogenous dispersion of nanochitosan and nanosilica particles without any agglomeration and their thermal stability were confirmed by TEM. The observed TEM results clearly indicate that the particles of NanoChiSil material have size of 10-20 nm.

a.
b.
c.

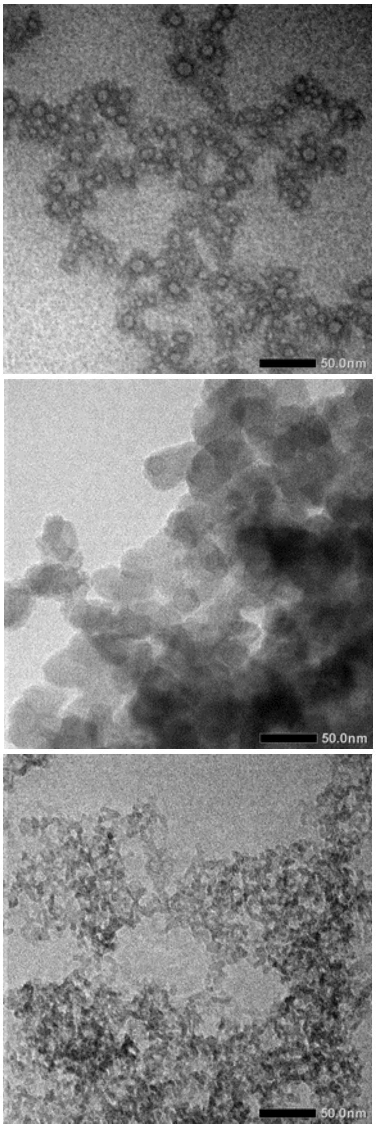


Fig. 4. TEM image of (a) nanochitosan, (b) nanosilica and (c) nanoChiSil

Conclusions

Colloidal nanoChiSil fertilizer has made by mixing between colloidal nanosilica and colloidal nanochitosan. All of the process steps were carried out to get materials with nano size, which simplified the material synthesis. The homogenous dispersion of nanochitosan and nanosilica particles without any agglomeration and their thermal stability were confirmed by TEM. The observed TEM results clearly indicate that the particles of NanoChiSil material have size of 10-20 nm.

References

[1] T. Wakatsuki, T. Masunaga, Ecological engineering for sustainable food production and the restoration of degraded watersheds in tropics of low pH soils: focus on west, Soil Sci. Plant Nutr. 51 (2005) 629–636.

[2] Husnain, T. Wakatsuki, T. Masunaga, Field assessment of nutrient balance under intensive rice-farming systems, and its effects on the sustainability of rice production in Java Island, Indonesia, Journal of Agricultural, Food and Environmental Sciences, Volume 4, Issue 1, (2010) 1-11.

[3] M. Balamurugan, S. Saravanan, Producing nanosilica from Sorghum vulgare seed heads, Powder Technology 224 (2012) 345–350.

[4] M. Tomozawa, D.L. Kim, V. Lou, **Preparation of high purity, low water content fused silica glass**, Journal of Non-Crystalline Solids 296 (2001) 102–106.

[5] P.A. Tanner, B. Yan, H. Zhang, Preparation and luminescence properties of sol-gel hybrid materials incorporated with europium complexes, Journal of Materials Science 35 (2000) 4325–4328.

[6] G. Wu, J. Wang, J. Shen, T. Yang, Q. Zhang, B. Zhou, Z. Deng, F. Bin, D. Zhou, F. Zhang, Properties of sol-gel derived scratch-resistant nano-porous silica, Journal of Non-Crystalline Solids 275 (2000) 169–174.

[7] S. Sadasivan, D.H. Rasmussen, F.P. Chen, R.K. Kannabiran, Preparation and characterization of ultrafine silica, Colloids and Surfaces A: Physicochemical and Engineering Aspects 132 (1998) 45–52.

[8] G.H. Bogush, M.A. Tracy, C.F. Zukoski IV, Preparation of monodisperse silica particles: Control of size and mass fraction, Journal of Non-Crystalline Solids 104 (1988) 95–106.

[9] T.K. Barik, B. Sahu, V. Swain, Nanosilica-from medicine to pest control. Parasitol. Res. 103 (2008) 253–258.

[10] J. Björnström, A. Martinelli, A. Matic, L. Börjesson, I. Panas, Accelerating effects of colloidal nano-silica for beneficial calcium–silicate–hydrate formation in cement. Chem Phys Lett 392(1–3) (2004) 242–248.

[11] Mingzhu, Liu, Preparation and Properties of Chitosan-coated NPK Compound fertilizer with controlled released and water-retention, Polymer 55 (2014) 1964-1976.

[12] F.L. Mi, H.W. Sung, S.S. Shyu, C.C. Su, C.K. Peng, Synthesis and characterization of biodegradable TPP/genepin crosslinked chitosan gel beads, Polymer 44 (2003) 6521–6530.

[13] K. Vijayalakshmi, T. Gomathi. P. N. Sudha, Preparation and characterization of nanochitosan/sodium alginate/ microcrystalline cellulose beads, Der Pharmacia Lettre 6 (4) (2014) 65-77.