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Synthesis and Modification of the Morphology of Zinc Oxide (ZnO) Nano Particles with Induced Biopolymer Chitosan.

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ABSTRACT

Synthesis of ZnO with induced biopolymer chitosan aims to modify the morphology of nanoparticles ZnO/chitosan. Chitosan serves as a template matrix printer pores on the surface of ZnO, so that an increase in the performance of the nanoparticles when used as a catalyst to degrade organic pollutants. Synthesis of ZnO/chitosan done by hydrothermal method using water solvent. Composite ZnO/chitosan to form a more homogeneous and evenly distributed with the addition of surfactant Cetyl Trimethyl Ammonium Bromide at a temperature of 180^0C. From FTIR characterization, showsthe effect of the addition of chitosan to the ZnO with a ratio (1:10, 1:5 and 1:3) gives the intensity changes due to stretching and bending vibrations of OH-, NH, CH, and ZnO in the range of fingerprint region 4000 - 400 cm^{-1}. The XRDanalysis, while the addition of chitosan in ratio greater decline in the intensity of ZnO crystals at 2 theta 36.27^0, due to a modification of ZnO crystal structure, but the effect of the addition of chitosan and CTAB can form a more homogeneous morphology and surface of ZnO and porous see in SEM and can be correlated with PSA. EDX showsthat the composition semi-qualitative of nanocomposite ZnO/chitosan.

Keywords : Hydrothermal , biopolymer chitosan , ZnO , surfactant CTAB ,

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INTRODUCTION

In the 21st century, nanotechnology is the science that is being developed to produce nanometer-sized products, given the very wide application of nanoscale materials in fields such as medical, industrial, textile, and the environment. Nanotechnology is a technique to manipulate a material and create materials in the nanometer structure, in order to obtain a material that has special properties far superior to raw material [1].

Nanomaterial of ZnO is a compound semiconductor that is widely used as a catalyst in photocatalytic activity is quite high, non-toxic, and easy to obtain [2]. To improve the activity of catalityc, it is necessary to modify various synthesis processes such as setting optimization conditions, temperature, pH, the addition of complexing agent, and calcination time [3]. To improve the performance of ZnO is usually used dopant with organic and inorganic compounds. Dopant compound can modify the morphology of ZnO and thus affects the character of the resulting product. The Products ZnO/Chitosan will be applied as an antimicrobial compound. In previous studies, researcher has used precursor for TiO_2 modified with transition metals and SiO_2 matrix inhibition six species of pathogenic microbes to power approximately 85% inhibition with UV light at 385 nm. And The performance of TiO_2 is less efficient when used visible light, so the researcher on the basis of these considerations replacing TiO_2 with ZnO precursor that has a smaller band gab of TiO_2, and si expected to be applied to the visible light region at ≥ 400 nm, the light si Moore dominant Ni nature. (Makara Journal Dissertation).

Some of the Research in the synthesis of ZnO usedDopant type are widely used to improve the conductivity of ZnO is trivalent atoms (atoms that have three valence electrons) as elements of group III A (Al, In, Ga) through cation substitution [4].In this study used a sampel of organic compound that has been used is chitosan[5]. Chitosan is a biopolymer derived from chitin. Chitin is a polymer compound of N-acetyl-D-glucosamine which is a major component of fungal cell walls and the exoskeletons of marine animals such as shrimp intervetebrata (Crustaceae) and crab. Chitosan has a hydroxyl and amine functional groups so easily bind with other compounds through hybridization with hydrogen bonds and covalent[6].

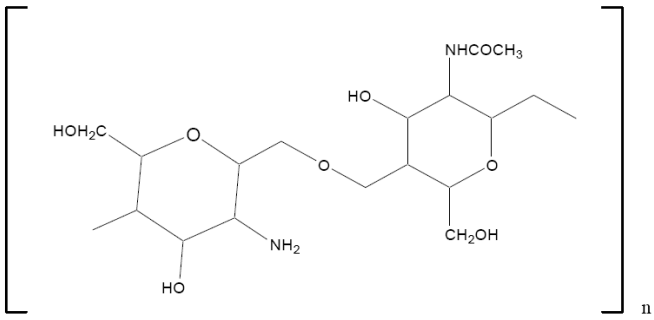

Figure 1

Chitosan also has a positively charged polication able to suppress the growth of bacteria and molds[5]. Chitosan is a polication with a positive charge on the amine group, so it can act as a cation exchanger. Therefore, chitosan is relatively more widely used in various industrial fields of applied and health[7]. Structure of chitosan molecular show at figure 1.YetriaRilda, et al., (2014) Ade reported the results of his Research, the use of chitosan as a template to pores on the surface of TiO_2 synthesized through sol-gel process, where the increasing length of time the process of condensation can multiply the number of pres on the surface of TiO_2(RJPBS,2014).

Figure 1. The molecular structure of the compound chitosan Surface-active agent substance called urfactant is also an active compound, is lowering the surface tension and has a bipolar structure. The head is hydrophilic and a hydrophobic tail, so that surfactants tend to be at the interface between two phases of different polarity. Usefulness of surfactant among others to lower the surface tension, interfacial tension, increasing the stability of the dispersed particles and controls the type of formation emulsion[10].One example is the CTAB surfactant. CTAB in the solution will be ionized into CTA^+ and Br^-.

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Hydrophilic head is often referred to as the ammonium group and the hydrophobic as the tail is composed of a hydrocarbon chain cetyl group as in Figure 2[11].

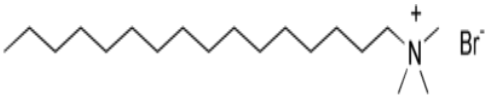

Figure 2: moleculesof CTAB surfactant

ZnO is reacted with CTAB where Zn ions in the form of $[Zn(OH)_4]^{2-}$ is negatively charged , while the positively charged CTA^+ with tetrahedral heads and hydrophobic tails. Through the ion pair formed hydrothermal process, CTA^+ - $[Zn(OH)_4]^{2-}$ is formed by electrostatic interactions initially. CTAB molecules could accelerate ionization $[Zn(OH)_4]^2$.Ion pair formed a combination and ZnO CTAB, CTAB collected between ZnO crystallites during the hydrothermal crystallization and washed with distilled water to form ZnO powder[11]. The following illustration ZnO bond with CTAB surfactant in Figure 3.

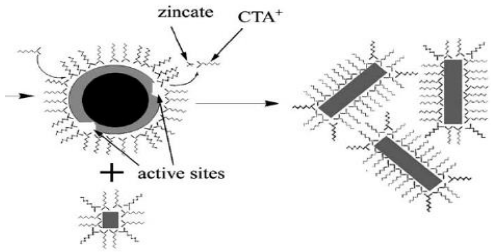

Figure 3:Ilustration of ZnO bond with CTAB surfactant

Given two compounds both chitosan and ZnO each has advantages in this study synthesized ZnO/chitosan with the addition of CTAB which serves as an additive compounds in order to homogenize the particle distribution is spread evenly so as to improve the performance of ZnO as catalyst by hydrothermal method[12]. In this study, the methods used in the synthesis of ZnO nanoparticles is hydrothermal method because can produced a fairly high surface area and fewer impurities generated so that a more pure product obtained[13].The resulting products were characterized by FT-IR, XRD, SEM-EDX, PSA .

MATERIAL AND METHODS

Materials

The material used is a commercial chitosan $(C_6H_{11}NO_4)_n$, ZnO (Merck), NaOH (Merck), acetic acid (Merck), Cetyl trimethylammonium bromide (CTAB) (Merck), distilled water.

Apparatus

The instrumentation used is some glassware, pH meter, magnetic stirrer, centrifuge, analytical balance. The instrument used was an oven, The resulting products were characterized by Fourier Transform Infrared Spectrocopy (FT-IR) (Spectrophotometer Infrared FT-IR Perkin Elmer 1600 series), X-ray diffraction (XRD) (X′ Port PAN Analytical), Nano Laser Particle Size Analyzer (PSA) (FrittschAnalysette 22 Wet Dispersion Unit, Nano Tec plus), Spectroscopy Electron Microscopy and - Energy Dispersive X-ray (SEM-EDX) (Leosupra 50 VP Field Emission SEM Oxford INCA 400 Energy Disspersive X-Ray Micro analysis System).

Procedure

Activation of the precursor of ZnO

The first treatment was performed on ZnO smoothing using nano-miling for 1 hour so as expected to obtain a homogeneous ZnO. After nano-milling, ZnO is activated at a temperature of 200 ºC for 5 hours, with the goal of eliminating fisisorbtion attached to the ZnO surface and to open the pores so that the surface of

ZnO is more active and not a lot of impurities. At the time of activated ZnO should be stirred using a magnetic stirrer and stirring assisted manually by using a stir bar that aim to speed up the release process fisisorbtion.

Synthesis of ZnO / chitosan

ZnO powder and weighed as much as 1 g dissolved in 25 mL of distilled water. Distirr until homogeneous and then added to the CTAB surfactant concentration variation (0.05, 0.1 dan 0.01)mol of the ZnO. Homogenized for 20 minutes, was added a solution of chitosan that has been dissolved in 5 % acetic acid with various concentration (1 : 5, 1 : 4 dan 1 : 3). Distirer for 30 minutes and the pH was adjusted with 1M NaOH up to pH 10. The mixture was autoclaved at a temperature of 180°C for 3 hours. Furthermore, the mixture centrifuged and the precipitate was washed with distilled water and dried in an oven for 1 day at 60°C temperature. Then powder ZnO/chitosan were characterized by FT-IR, XRD, PSA, and SEM -EDX

RESULTS AND DISCUSSION

FT – IRAnalysis

FTIR analysis can be used to determine the functional groups in an organic compound or polymer compounds in the fingerprint region 400-4000 cm^{-1}.Chitosan-ZnO powders were characterized by FT-IR to identify the functional groups present in chitosan-ZnO powder and determine the spectrum of Zn-O. The functional groups are shown in table 1 is described that chitosan substituted in ZnO.

Table 1: Wave absorption of Zn-O clusters with various concentration of chitosan and CTAB

Precursor	Concentration Variation	Wave Number (cm^{-1})				
	Chitosan	CTAB	OH	CN	NH_2	ZnO
ZnO	-	-	-	-	-	447,4
ZnO	20%	5%	3428,8	1024,9	1637,2	448,3
		10%	3438,4	1025,9	1637,2	434,8
		15%	3435,5	1029	1631,4	443,3
ZnO	25%	5%	3436,5	1031,7	1637,2	440,6
		10%	3432,6	1064,5	1642	425,2
		15%	3443,2	1032,6	1638,2	443,5
ZnO	30%	5%	3430,7	1027,8	1565,9	445,4
		10%	3423,9	1027,8	1563,3	451,2
		15%	3410,4	1027,8	1561,1	471,5

It can be seen from the spectra of ZnO/chitosan namely the C=O group at wave numbers around 1658 cm^{-1} to 1630 cm^{-1} for chitosan and contained Zn-O group at wave numbers around 408.835 cm^{-1} to 471.151 $cm^{-1}$for zinc oxide . OH group, CH, NH, and NH amide amine of chitosan and CTAB also still be found in the spectra of ZnO/chitosan for all variations of the concentration of CTAB but only shifted wave number and intensity of the absorption changes due to interactions between chitosan and CTAB with zinc on nanocomposite ZnO /Chitosan .

Interpretation of the results of the infrared spectra of functional groups can be seen that in all the powders of ZnO-chitosan appeared uptake in the surrounding area (3000-3750) cm^{-1}, this indicates that there is a hydroxyl group (-OH) and NH_2 (primary amines) which is an active group on chitosan. In the region 2900-2930 cm^{-1} absorption appears indicating the presence of vibration absorption range of -CH (methylene). In the catchment area around 1375-1450 cm^{-1} absorption appears which indicates a methyl group ($-CH_3$). In the catchment area around 1600-1655 cm^{-1} appear indicate amide -NH bending vibration. Based on the above data, it can also be seen of Zn-O. In ZnO/chitosan Zn-O absorption variations appear in absorption around 420 cm^{-1}.

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XRDAnalysis

XRD analysis provides information about the crystallinity of the samples, a kind of crystalline phase, crystals quality and size of the crystals in the sample. Information about the crystallinity is necessary given the photocatalytic reaction is very dependent on the quality and quantity of type ZnO crystal phase. Figure 4 shows the intensity of ZnO- chitosan.

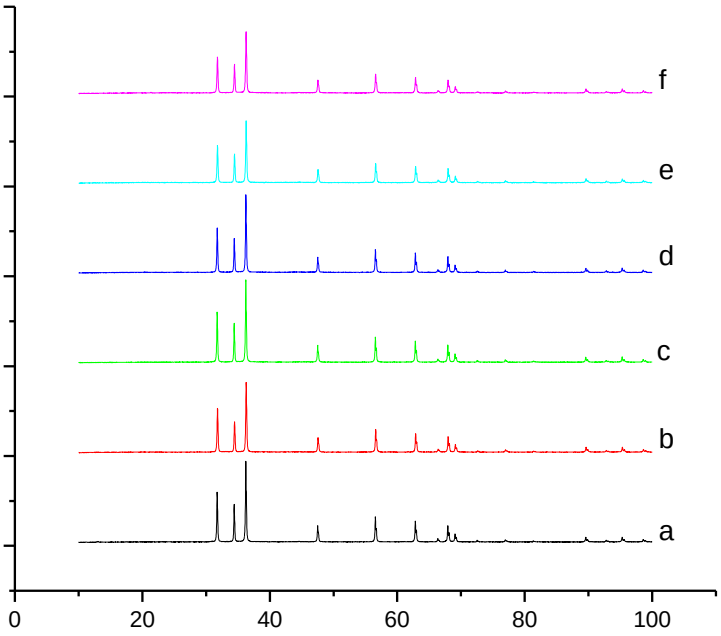

Figure 4: XRD spectrum with the variation of chitosan. (a) ZnO (b) ZnO-chitosan, (c) ZnO-CTAB, (d) ZnO-CTAB 15%-Chitosan 20%, (e)ZnO-CTAB 15%-chitosan 25%, f) ZnO-CTAB 15% –Chitosan 30%

XRD test results indicate that ZnO has a wurtzite structure and if the modification with the addition of chitosan concentration decreased intensity generated and produced more amorphous structure. XRD patterns of ZnO/chitosan showed peaks of ZnO are compared with data JCPDS No. 01-073-8765 . The pattern of peaks that appear to show the variation of chitosan intensias different so it can be concluded that the addition of CTAB increased crystallinity of ZnO, however, when the addition of chitosan concentration reduced the crystallinity of ZnO.

X-ray diffraction patterns can also provide information on the size of the crystal. Crystal size is usually determined by using the Scherrer method, in which a sharp peak with a narrow peak width indicates that the large crystal size , while experiencing peak dilation indicating small crystal size. Table 2 below shows the particle size of each nanoparticle to the highest peak.

Table 2: Crystallite size of ZnO-chitosan based Scherrer formula

Precursor Variation	Crystal Size
ZnO	53,91 nm
ZnO-CTAB 10%	53,87 nm
ZnO-Chitosan 25%	46,03 nm
ZnO-CTAB 15%-Chitosan 30%	46,18nm
ZnO-CTAB 15%-Chitosan 25%	46,18 nm
ZnO-CTAB 15%-Chitosan 20%	46,66 nm

From table 2 we can see that the addition of CTAB obtained crystal size gets smaller . The addition of chitosan obtained crystal size is getting smaller. With the variation of the concentration of CTAB and chitosan can be concluded that there was no significant difference in the crystal size.

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SEM Analysis

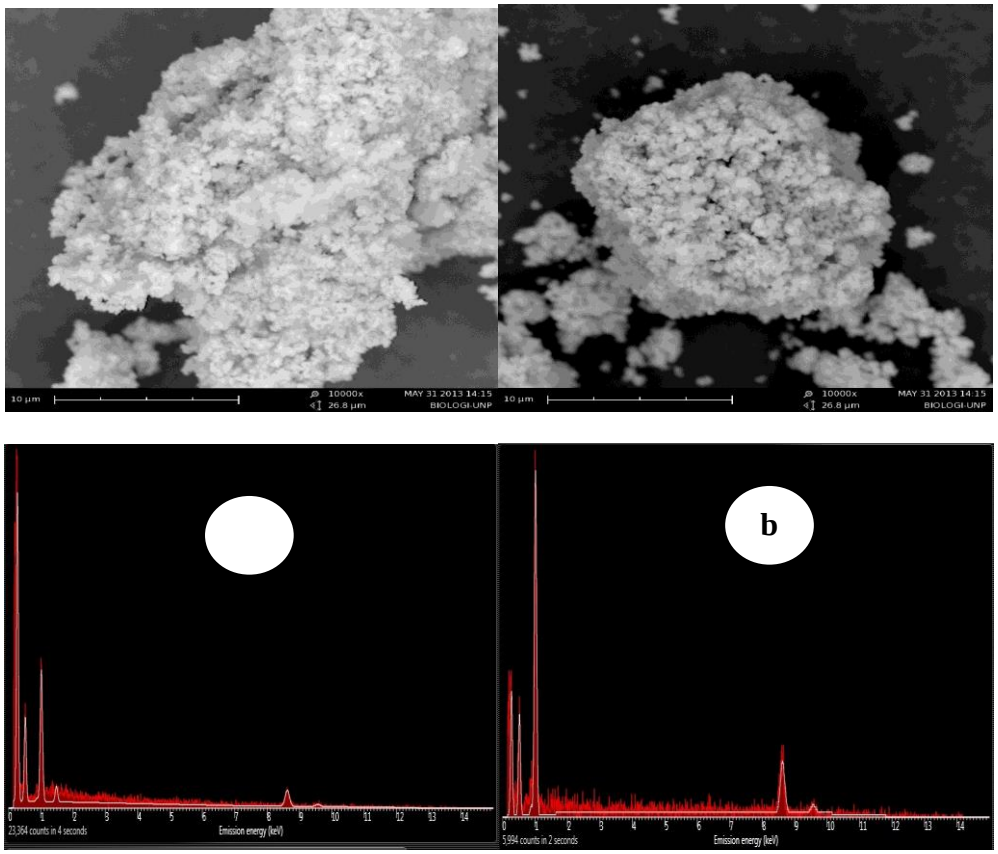

Figure 5: SEM-EDX results of sample ZnO / chitosan a. ZnO-chitosan, b. ZnO-CTAB15%-chitosan30%.

SEM patterns can provide information on the surface morphology analysis. The morphology of ZnO-chitosan can be seen in Figure 5.

In general, the morphology of ZnO-chitosan has a porous surface. The pattern of ZnO-chitosan composite distribution more evenly and homogeneously with the surfactant CTAB. In Figure 5 seen surface differences, that the addition of chitosan produced larger chunks and chunks of porous rock formed and agglomeration occurs between ZnO with chitosan.

Role of CTAB with the ZnO/chitosan in Figure 5 show that the more homogeneous surface with more uniform particle distribution. This is because the CTAB serves as a useful additive compound as a distributor so that the particles evenly dispersed and homogeneous so as do prevent aglomeration. With ZnO covered by chitosan molecules can be said to be The successful reaction . The addition of chitosan with dopant concentration greater yield chitosan porous structures where more attached to the surface of ZnO.

Table 3: The composition and the percentage of the elements making up the compound ZnO/chitosan

Sample	The Composition of The Constituent (%)			
	C	O	N	Zn
ZnO-Chitosan 25%	14,1	30,3	3,9	51,7
ZnO-CTAB 15%-Chitosan 30%	21,6	21,6	5,2	51,5

EDX analysis gives a semi-quantitative composition of constituent information in a matrix of ZnO/chitosan. Table 3 above shows the percentage composition and the constituent elements of the compound ZnO/chitosan nanoparticles. ZnO-chitosan samples containing Zn. This proves that the process pendopingan successfully. However, the percentage composition of the two different samples.

This is caused by the formation of more organic oxide on the addition of 30 % compared to 20 % addition of chitosan .

PSAAnalysis

SEM pattern when correlated with the pattern of PSA can provide information that there are differences in particle size distribution with the addition of CTAB surfactant and chitosan. Effect of addition of CTAB surfactant can provide the sized is distribution pattern at two different regions (50-130 µm),it can give you an idea that there are effects of the addition of CTAB surfactant in modifying the morphology of nano compositeZnO / chitosan in figure 6.CTAB cam distributor nanoparticles in the size of 50-125 micrometers.

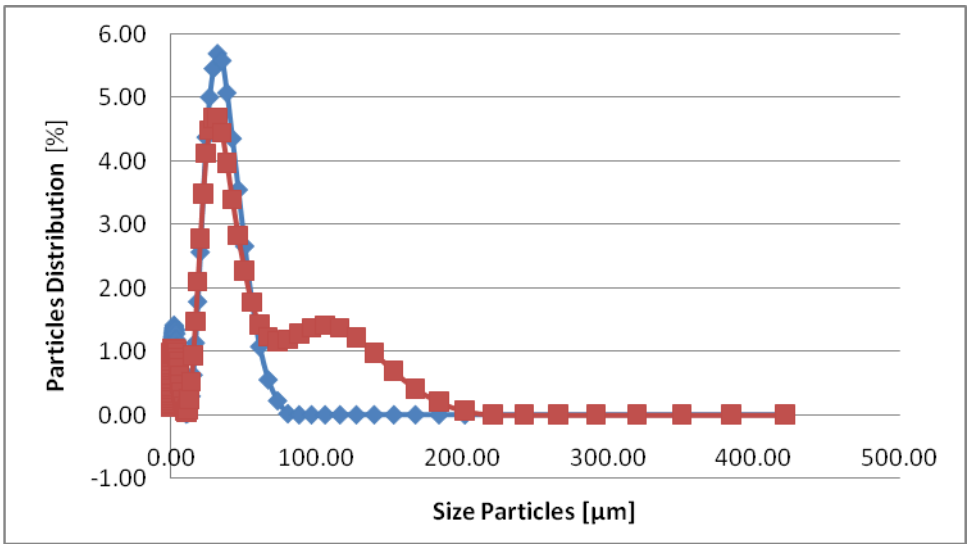

Figure 6: PSA patterns of ZnO samples / Chitosan a. ZnO-chitosan (blue), b. ZnO-CTAB15%-kitosan30% (red)

CONCLUSION

Based on the results of research on the synthesis of ZnO/chitosan nanoparticles can be concluded that the hydrothermal method can be used as a method for the synthesis of compound chitosan/ZnO, the results obtained in crystalline form with wurtzite structure after characterized by FT-IR, XRD, SEM-EDX, PSA.With this method of synthesis, a more equitable distribution of the particle on the surface.

From the characterization results obtained information that the addition of chitosan to the printer pore but does not significantly affect the crystal size. CTAB surfactant can affect the distribution of the particles so that a more homogeneous, porous, and evenly.

REFERENCES

[1] Behera O. 2010. Synthesis and Characterization of ZnO Nanoparticles of Various Sizes and Applications in Biological Systems. Thesis.Department of Biotechnology and Medical Engineering National Institute of Technology Rourkela.
[2] Abdelhady MM. International Journal of Carbohydrate Chemistry 2012;10:1-6.
[3] Song D. 2005. Zinc Oxide TCOs (transparent Conductive Oxides) and Polycrystalline Silicon Thin-films for Photovoltaic Applications. University of New South Wales.
[4] Hong RY, JH Li, LL Chen. Chem Eng J 2009;189:426-432.
[5] Al – Sagher FMuslim. J Nanomater 2009;10:1-7.
[6] Arik, Buket, Necdet Seventekin. J Biochem 2011;21:1-9.
[7] Ramadhan LOAN, et al. Indonesia J Chem 2011;5:17 – 21.
[8] Wiyarsi, Antuni and Erfan Priyambodo. Pengaruh Konsentrasi Kitosan dari Cangkang Udang Terhadap Efisiensi Penyerapan Logam Berat. Skripsi Jurusan Pendidikan Kimia FMIPA UNY, 2010.
[9] Rilda Yetria. Chem J 1995;14:50-51.

[10] Salarian M, M Solati Hashjin, S Sara Shafiei. J Mater Sci 2009;27:961-971.
[11] Febiana ND, R Saleh. Mater Sci App 2012;3:245-252.
[12] B Liu and HC. Zeng. J American Chem Soc 2003;125:4430-4431.
[13] Gosh PK and KK Chattopadhyay. J Nanopart 2005;7:219-225
[14] Rilda Y, A Alif, E Munaf and A Agustien. Res J Pharm Biol Chem Sci 2014;5(2):1417 – 1427.