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Crystal-growth kinetics of magnetite (Fe_3O_4) nanoparticles with Ostwald Ripening Model approach

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Abstract. Magnetite (Fe_3O_4) nanoparticles is a magnetic nanomaterial that have potential properties to be applied as drug delivery The purpose of this study was to determine the influence of time and temperature synthesis of magnetie characteristics and determine its crystal growth kinetics model with Ostwald ripening model approach. Magnetite nanoparticles synthesized from $FeCl_3$, citrate, urea and polyethylene glycol with hydrothermal method at 180, 200 and 220 ^oC for 1,3,5,7,9 and 12 hours. Characterization by *X-ray Diffraction* (XRD) indicated that magnetite formed at temperatures of 200 and 220 ^oC. Magnetite crystallite diameter obtained was 10-29 nm. Characterization by *Transmission Electron Mycroscope* (TEM) shows that magnetite nanoparticles have uniform size and non-agglomerated. Core-shell shaped particles formed at 200 ^oC and 220 ^oC for 3 hours. Irregular shape obtained at 220 ^oC for 12 hour synthesis with particle diameter about 120 nm. Characterization using *Vibrating Sample Magnetometer* (VSM) shown that magnetite has super paramagnetism behaviour with the highest saturation magnetization (Ms) was 70.27 emu/g. magnetite crystal growth data at temperature of 220 ^oC can be fitted by Ostwald ripening growth model with growth controlled by the dissolution of surface reaction ($n \approx 4$) with the percent error of 2.53%.

1. Introduction

Recently, nanoparticles technology have been used in various biological applications such as drug delivery or nano drug delivery. Nano drug delivery is a direct transfer method to the target (the pain part). The crucial issues showed that the importance of development nano drug delivery technology, it is because a cancer is a second of death cause in the world. WHO said if we don't controll it, they predict that 26 million people will get cancer and 17 million will die because of cancer in 2030. The chemotherapy method is less effective because not only kill cancer cells but also make the quality of patientlife will be down. Nano drug delivery is a method that will provide a good solution of the negative effects of chemotherapy.

Nanomagnetite (Fe_3O_4) is a nanomaterial which recently got more attention in various studied. In last decade, nanomagetite synthesis which has a superparamagnetism is always did for many various applications especially in biological application such as MRI contrast agent and cancer therapy via hyperthermia [1] and recently develop as drug delivery [2]. This is because nanomagnetite has the appropriate properties for medical applications that are superparamagnetic and have high biocompatibility [3].

Nanomagnetite was synthesized as a drug delivery from $FeCl_3$, citrate, urea and polyethylene glycol (PEG) with hydrothermal method at 200 ^oC [4]. The resulting magnetite particles are shaped *hollow* and *core shel l*has the behavior of super paramagnetism, having high water solubility which is claimed to be

the most ideal for drug delivery application. With this advantages, it would be better if particles size and morphology could be controlled because it is an important factor in drug delivery system [5] [6].

This study was to determine the magnetite (Fe_3O_4) crystal growth kinetics model with Ostwald Ripening model approach followed with the magnetite synthesis by Cheng et al. [4]. In this study, results of nanoparticle biocompatibility also improved by using polyethylene glycol (PEG) as capping agent. The study of crystalline growth kinetics modeling is needed to investigate factors that affected to the crystal growth more systematically and as the basis of planning in the synthesis process. This modeling is also required in the tailoring process.

2. Experimental

In this study, all chemicals used was Ferric (III) Chloride ,Aquadest, Urea, Sodium Citrate ($C_6H_5O_7Na_3.2H_2O$) Polyethylene Glykol (PEG), dan Ethanol 99%. Synthesis process for hydrothermal method have been done with mixtures $FeCl_3$, Sodium Citrate, urea dan aquadest into *Teflon Lined Autoclave*. Then 0.3 gr PEG added and hydrothermal method was started at 180, 200 and 220 ºC. The liquid samples is taken from reaction container in various time intervals such as 1, 2, 3, 5, 7, 9 and 12 hours, and liquid and solid was decanted. The solid was washed using ethanol and let it dried during the nighttime at 60 ºC. Next the solid will characterization with XRD, TEM and Magnometer.

3. Result and discussion

3.1. The Effect of temperature and reaction time of hydrothermal method for yield and composition

The variation of temperature of 180, 200 and 220 ºC were used in this study. This variable was selected because the response of the kinetic reaction when the temperature decreases from 20 ºC from the temperature reference (200 ºC). At 180 ºC, the precipitate was formed after synthesized for 5 hours. The precipitate was obtained from 5 hour synthesis reddish brown colored and drawn weak by magnet. Synthesis nanomagnetite at 200 ºC, precipitate was formed after 3 hours with brown colored, while the precipitate for long time synthesis have a black color and drawn by magnet. Synthesis at 220 ºC, gived a precipitate in black colored since 3 hours synthesized. The color of precipitated was more dark if the synthesis time was more. If the synthesis time is longer, the precipitate is getting more (see Figure 1) that is 33.33% at 3 hour synthesis, 36.67% at 5 hour synthesis, and then increasing to 80% at 7 hours and become 100% at 9 hour and 12 hour synthesis.

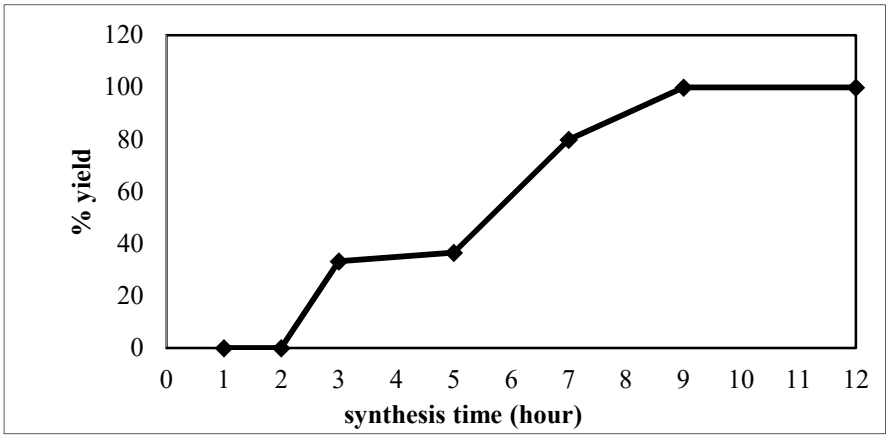

Figure 1. A relation between synthesis time and percentage of yield.

3.2 Effect of temperature and reaction time of hydrothermal method to cristal size

The size modification of the crystal particles was determined using Scherre Equation (1). At the application of Scherrer was a sistimatic error. This error can be reduced with modification of Scherrer equation into logarithmic Equation [7].

$$\beta = \frac{K\lambda}{D.\cos\theta} = \frac{K\lambda}{D}.\frac{1}{\cos\theta} \quad (1)$$

$$ln\beta = ln\frac{K\lambda}{D.\cos\theta} = ln\frac{K\lambda}{D} + ln\frac{1}{\cos\theta} \quad (2)$$

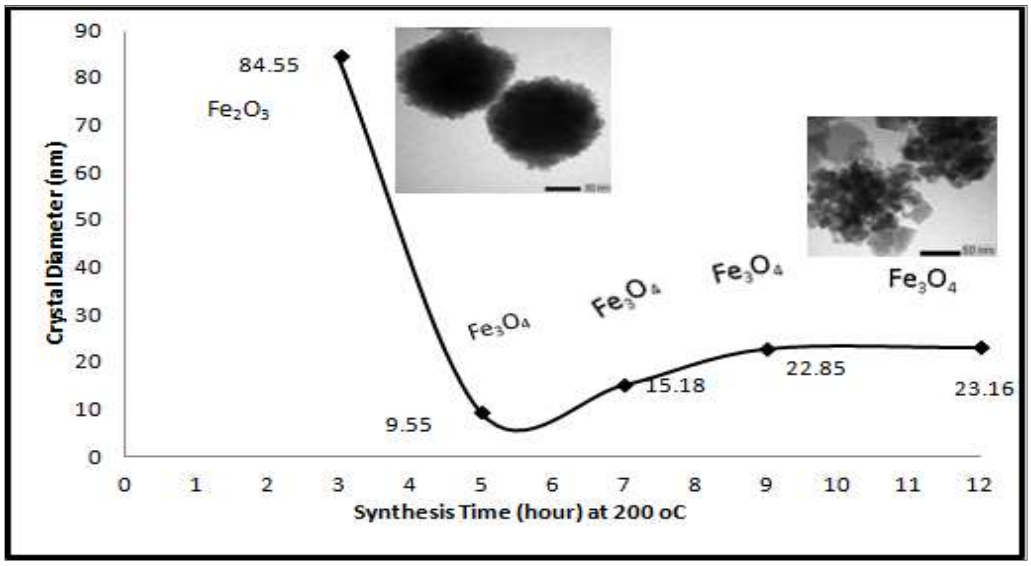

Figure 2. A Relation between synthesis time with crystal diameter at 200 °C.

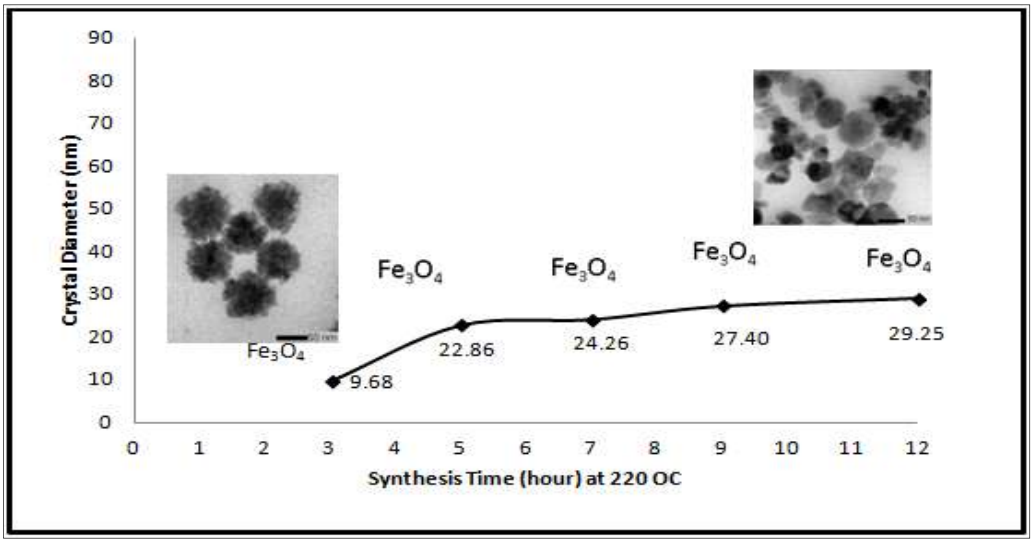

Figure 3. A Relation between synthesis time with diameter crystal at 220 °C.

The last crystal size (12 hour synthesis) at 200 °C more small like 23.16 nm if compare between at 220 °C with crystal diameter like 29.25 nm. The rate grow of crystal diameter size at the two temperature was different too. At 200 °C the rate grow of crystal diameter was more than at 220 °C was 5:2. This is

would be different from mecanism growth of crystal at the two temperatures that will be prove by modeling.

3.3 Effect of adding PEG to nanoparticle morfology

PEG was selected as a *capping agent* because its prove has a high biocompatibility [8-10]. With this adding gave a hope that the result of nanoparticles size was uniform and can avoid agglomeration between particle. Nanoparticles morphology was shown by TEM at Figure 4 and Figure 5. Based on TEM in 80.000 time, in general shown that the formed particle has a nano size with size distribution was enough uniform and not agglomerated.

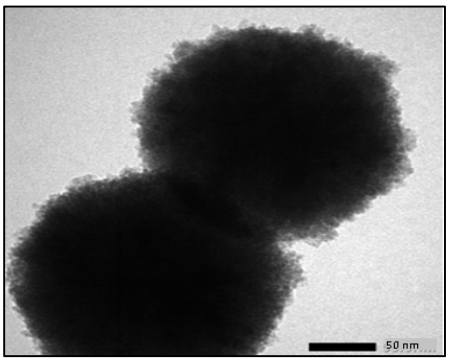

Figure 4.TEM images of sample at 200 ˚C for 3 hours.

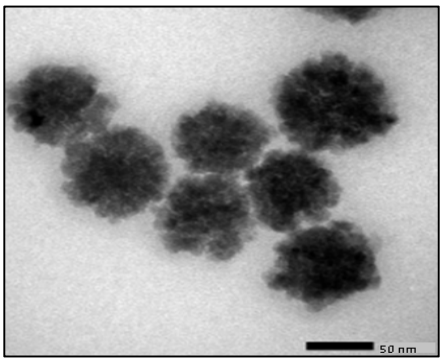

Figure 5. TEM images of sample at 220 ˚C for 3 hours.

The result at 200 ºC for 3 hour was a particle formed like a ball with 100 nm diameter and on the other side at the same time at 220 ºC the form was close to *core-shell* with *black* core and *shell* which was more light with diameter 100 nm less. This different shape and size was affected by the temperature of reaction and crystal composition.

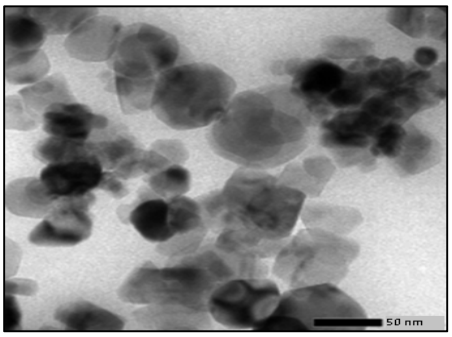

Figure 6. TEM images of sample at 200 ˚C for 12 hours.

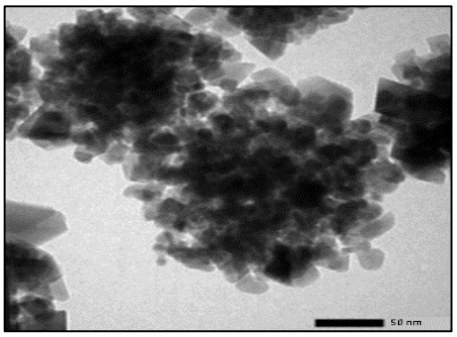

Figure 7. TEM images of sample at 220 ˚C for 12 hours.

The nanomagnetite with capping agent PEG has a morphology shape like core shell about 120 nm. So that, with this adding PEG did prevent the agglomeration and reduce nanoparticles size. The size of the nanomagnetite is suitable with drug delivery criteria that 10nm - 200 nm [11]. Core shell structure has a majority as a carrier drug delivery. The shell was role as a part of core protector from oxidation by the air and has a function as a attachment place with ligands or drug [12].

3.4 The Effect of Temperature and Synthesis Time to Magnetism Properties of Nanomagnetite

The magnetism properties was investigated using *vibrating sample magnetometer* (VSM) at 300K with magnet at range -1 T to 1 T.

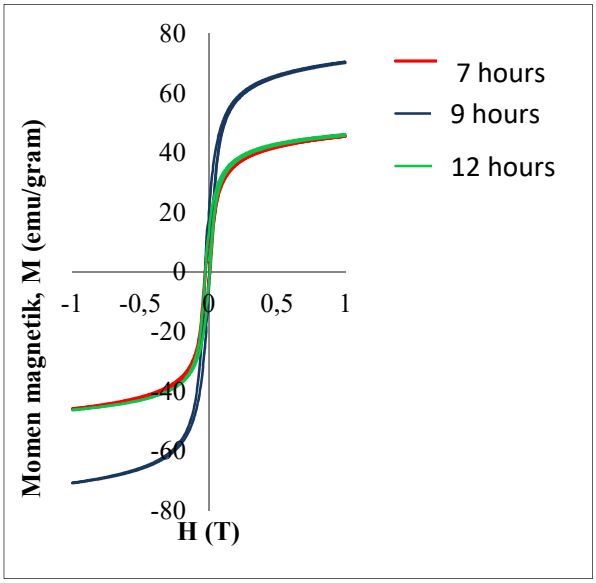

Figure 8. Hysteresis curve nanomagnetite at 200 ˚C for 7, 9 and 12 hours.

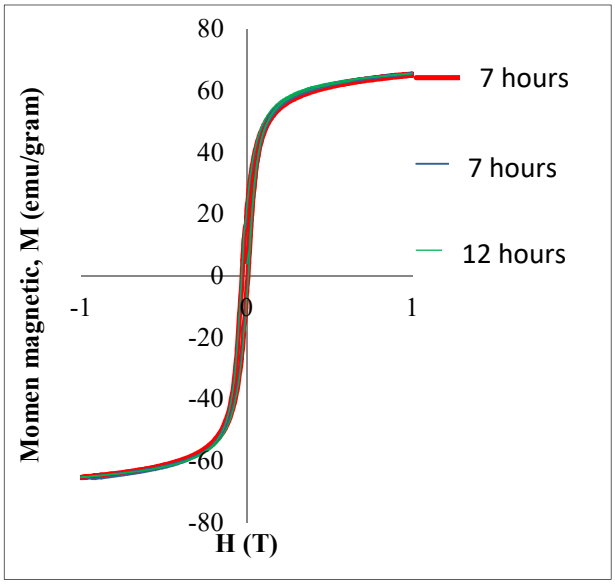

Figure 9. Hysteresis curve nanomagnetite at 220 ˚C for 7, 9 and 12 hours.

Generally, both of those figure shown there is loop hysteresis that so narrow with coercivity value close to zero. This shown that nanomagnetite has a superparamagnetism behavior at room temperature. Magnetite with size less than 30 nm have a super paramagnetism behavior [4]. The particle of crystal nanomagnetite in this experiment have a size about 20 nm so that it has a super paramagnetism behavior.

Table 1. The saturation of magnetization value (saturated), intensity peak, and crystal diameter from nanomagnetite sampleat temperature and different synthesis time

Temperature (˚C)	Synthesis time	Ms (Emu/g)	Intensity peak XRD high (count)	Crystal diameter (nm)
200	7	45.78	604.707	15.18
	9	70.27	873.271	22.85
	12	45.78	776.103	23.16
220	7	65.04	1330.228	24.26
	9	65.29	1384.059	27.40
	12	65.41	1490.334	29.25

The saturation of Magnetization (Ms) is equal to the level crystalinity of nanoparticles. If the crystalization is high, so the saturation of magnetic is high too. This is because at high crystallization the structure is close to the structure of material bulk crystal.

3.5 Model of crystal growth of nanomagnetite

Model of crystal growth of nanomagnetite at this experiment was based on Ostwald Ripening Model approach with commonly equation $r - r_0 = Kt^{1/n}$. The suitable model is did by two approach, was (1) suitable method to determine n and k with logaritmic curve and (2) suitable curvetime versus diameter crystal in practice and theoretical.

Table 2. Result of determining n and K withlogaritmic curve method

Temperature (^{O}C)	R^2	ln K	1/n	k	n
200	0.8229	1.76	0.37	5.80	2.72
220	0.947	1.67	0.27	5.31	3.66

Based on calculation, the value of n was obtained like 2,72 ≈ 3, on the other hand at 220 ^{o}C the value of n was 3,66 ≈ 4. n = 4 indicates that the rate of crystal growth is controlled by the rate of dilution at the interface of particle-matriks. If n=3, it shows that rate of crystal growth controlled by diffusion [13]. But, this result can not be suitable, especially for data at 200 ^{o}C because it has a low linearity and it showed by R^2value less than 0,9 which R^2=0.8229.

To increasing a confidence, approve with model curve that shows like in Figure 10 was did. Errors percentage shows at Table 3.

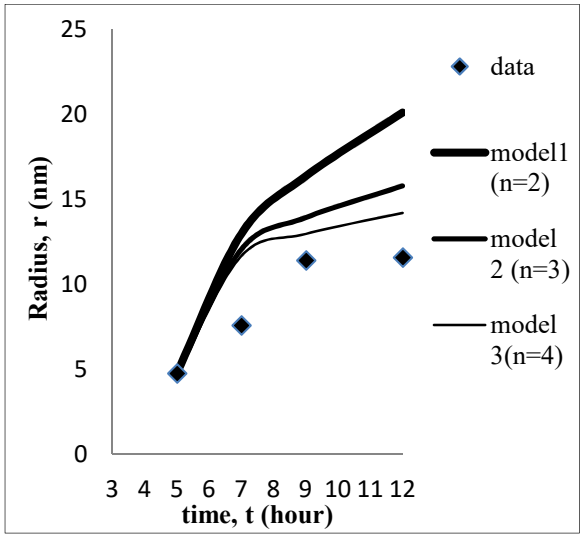

Figure 10. Curve synthesis time(t) vs crystal radius (r) at 200 ^{o}C.

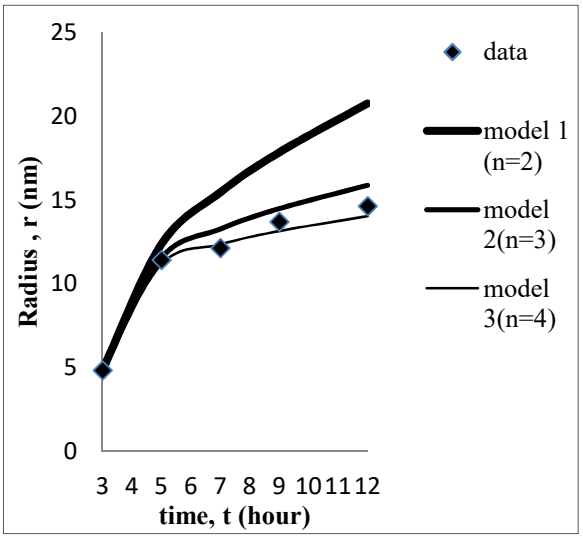

Figure 11. Curve synthesis time (t) vs crystal radius (r) at 220 ^{o}C.

Table 3. The error percentage of experiment data to model

Temperature (^{o}C)	model	%error
200	model1 (n=2)	28.54
	model 2 (n=3)	20.45
	model 3 (n=4)	16.34
220	model1 (n=2)	20.44
	model 2 (n=3)	5.69
	model 3 (n=4)	2.53

Based on Figure 10, every model gives a ralat that too close different for the others model with one certain trend to exsperiment data. Error decline with increasing n. The large Error percentage to the three of those model (Table 3) indicates that at 200 ^{o}C the crystal growth not following the Ostwald Ripening model. In other hand at the Figure 11, model 3 with n=4 was the most close to exsperiment data with less % errorwhich 2,53% (Table 3). This is indicate that at 220 ^{o}C, the crystal grow of nanomagnetite following the Ostwald ripening model that controlled by dissolution interface of particle-matrix.

4. Conclusion

The process of nanomagnetite particles synthesis using the hydrothermal method was affected by temperature and synthesis time. If the increasing of the temperature it will made the reaction time become longer so that the reaction of magnetite formation and yield also become faster. The morphology of particles was affected by temperature and reaction time. At 200 ºC 12 hour synthesis and 220 ºC 3 hour synthesis gave a magnetite nanoparticle at core shell shape. Nanoparticles have a super paramagnetism behavior with coersivity value (Hc) and remenensi (Mr) hysteresist curve close to zero. Growth of nanomagnetite crystal following Oswald Ripening model at 220 ºC which controlled by velocity of dissolution rate (n≈4) and K=5,3with % error 2,53%.

References

[1] Qiao R, Yang C and Gao M 2009 Superparamagnetic iron oxide nanoparticles: from preparations to in vivo MRI applications *J. Mater. Chem.* **19** 6274-6293
[2] Mahmoudi A, Simchi M, Imani U O and Hafeli J 2009 Optimal design and characterization of superparamagnetic iron oxide nanoparticles coated with polyvinyl alcohol for targeted delivery and imaging *Phys. Chem. C* **113** 8124-8131
[3] Mohapatra M and Anand S 2010 Synthesis and applications of nano-structured iron oxides/hydroxides – A review *J. Sci and Tech* **8** 127-146
[4] Cheng W, Tang K, Qi Y, Sheng J and Liu Z 2010 One-step synthesis of superparamagnetic monodisperse porous Fe3O4 hollow *J. Mater. Chem.* **2** 1799-1805
[5] Bae H Y and Park K 2011 Targeted drug delivery to tumors: Myths, reality and possibility *J. Cont. Rel.* **153** 198-205
[6] Yu M, Huang S, Yu K J and Clyne A M 2012 Dextran and polymer polyethylene glycol (PEG) coating reduce both 5 and 30 nm iron oxide nanoparticle cytotoxicity in 2D and 3D cell culture *J. Mol Sci* **13** 5554-5570
[7] Monshi A, Foroughi M R and Monshi M R 2012 Modified scherrer equation to estimate more accurately nano-crystallite size using XRD *J. Nano Sci. Eng.* **2** 154-160
[8] Cholan S, Shanmugam N, Kannadasan N, Sathishkumar K and Deivam K. 2014 Effect of poly ethylene glycol (PEG) as surfactant on cerium doped ZnS nanoparticles *J. Mater. Technol.* **3** 222–227
[9] Manson J, Kumar D, Meenan B J and Dixon D 2011 Polyethylene glycol functionalized gold nanoparticles: the influence of capping density on stability in various media *Gold. Bull.* **44** 99-105
[10] Shameli K, Ahmad M B, Jazayeri S D, Sedaghat S, Shabanzadeh P, Jahangirian H, Mahdavi M and Abdollahi Y 2012 Synthesis and characterization of polyethylene glycol mediated silver nanoparticles by the green method *Int. J. Mol. Sci.* **13** 6639-6650
[11] Winarti L 2013 Sistem penghantaran obat tertarget, macam, jenis-jenis sistem penghantaran, dan aplikasinya *Stomatognatic* **10** 75-81
[12] Luszczyk K, Kaleta J and Mech R 2014 Magnetic core-shell structures as potential carriers in drug delivery system *Int J. of Eng Sci*. **1** 1-4
[13] Huang F, Zhang H and Banfield F J 2003 Two-stage crystal-growth kinetics observed during hydhrothermal coarsening of nanocrystalline ZnS *Nano Lett* **3** 373-378