

Effect of FeCl₂ Concentration on the Properties of Magnetic Nanoparticles by Using Massart's Procedure

(Kesan Kepekatan FeCl₂ terhadap Sifat Nanozarah Magnet dengan Menggunakan Prosedur Massart)

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ABSTRACT

The effect of variation of FeCl₂ concentration on the properties of magnetic nanoparticles produced by Massart's procedure was investigated. Samples with different FeCl₂ concentration of 0.1, 0.8, 1.0, 1.2 and 1.5 M were produced. In this technique, an aqueous mixture of ferrous and ferric chloride was co-precipitated under controlled conditions to yield magnetic iron oxide nanoparticles. Thermogravimetric analysis (up to 700°C) showed a continuous weight loss from room temperature to 200°C that was mainly due to evaporation of water from the sample. Above 230°C, no more weight loss was observed indicating the stability of the maghemite nanoparticles. The lattice parameter of the samples obtained from X-ray diffraction analysis showed that the nanoparticles formed were maghemite (γ -Fe₂O₃). The crystallite sizes calculated from the broadening of XRD peaks were 6.79, 6.56, 6.15, 6.72 and 7.24 nm for FeCl₂ concentration of 0.1, 0.8, 1.0, 1.2 and 1.5 M, respectively. The magnetization curves showed no hysteresis indicating that the particles were superparamagnetic. The least upper bound of the 'magnetic' sizes calculated were 7.53, 6.29, 5.92, 6.41 and 8.04 nm and the physical sizes measured from TEM images were 5.97, 6.02, 4.98, 5.35 and 5.98 nm, respectively. The crystallite, magnetic and physical sizes were similar, indicating that the particles are monocrystals.

Keywords: Maghemite; magnetic nanoparticles; Massart's procedure

ABSTRAK

Kesan kepekatan FeCl₂ yang berlainan ke atas sifat nanozarah magnet yang dihasilkan oleh prosedur Massart telah dikaji. Lima sampel telah dihasilkan dengan kepekatan FeCl₂ yang berlainan iaitu 0.1, 0.8, 1.0, 1.2 dan 1.5 M. Dalam teknik ini, campuran akueus ferus dan ferik klorida akan mendak di bawah dalam keadaan terkawal untuk menghasilkan nanozarah ferrum oksida. Analisis termogravimetri menunjukkan kehilangan berat sampel yang turun berterusan daripada suhu bilik ke 200°C yang disebabkan oleh penyejatan air daripada sampel. Pada suhu melebihi 230°C, tiada kehilangan berat sampel diperhatikan, menunjukkan kestabilan nanozarah maghemit. Parameter kekisi sampel yang diperolehi daripada analisis belauan sinar-X menunjukkan nanozarah yang terhasil adalah maghemit. Saiz hablur yang dikira dari pelebaran puncak XRD adalah 6.79, 6.56, 6.15, 6.72 dan 7.24 nm untuk kepekatan FeCl₂ 0.1, 0.8, 1.0, 1.2 dan 1.5 M, masing-masing. Lengkung pemagnetan yang tidak menunjukkan histerisis menunjukkan bahawa nanozarah adalah superparamagnet. Saiz AGM ialah 7.53, 6.29, 5.92, 6.41 dan 8.04 nm manakala saiz TEM yang diperolehi dari TEM adalah 5.97, 6.02, 4.98, 5.35 dan 5.98 nm untuk sampel 0.1, 0.8, 1.0, 1.2 dan 1.5 M masing-masing. Saiz XRD, AGM dan TEM di atas menunjukkan keputusan yang agak sama dan menunjukkan nanozarah ini adalah terdiri daripada monokrystal.

Kata kunci: Maghemit; nanozarah magnet; prosedur Massart

INTRODUCTION

Magnetic nanoparticles are the focus of many researchers because they often exhibit unique properties, which cannot be achieved by their bulk counterparts, such as their thermal stability (Gleiter 1989), unique magnetic properties (Cannas et al. 1999) and surface properties (Galina et al. 2009). Due to its unique magnetic properties, magnetic nanoparticles especially maghemite nanoparticles are increasingly required for potential application. Maghemite nanoparticles are used as matrices for magneto-optical devices (Cannas et al. 1999), magnetic refrigeration (McMichael et al. 1992) and as controlled drug delivery systems (Bhatnagar & Rosensweig 1995).

Some of the factors that influence the properties of maghemite nanoparticles are of particle size, shape and surface chemistry (Kroll et al. 1996; Vollath et al. 1995). If the particles size is sufficiently small, the magnetic properties of nanoparticles transforms from ferromagnetic to superparamagnetic. Among these, maghemite nanoparticles with size range of 2-10 nm are of particular significance.

To produce a single phase of the maghemite nanoparticles and to stabilize it is the main concern of current researchers. Some authors report the evolution from the γ to the α -Fe₂O₃ phases as a size dependent transition, a decrease in particle size seems to provide better stability

of γ -Fe₂O₃ (Ayyub et al. 1988; Cannas et al. 2001). Hence, the particles size of maghemite nanoparticles need to be further reduced.

A very classic method used to produce maghemite and magnetite nanoparticles is Massart's procedure. Several attempts have been done by researchers to improve the size, shape and size distribution of the particles (Liu et al. 2004; Tao et al. 2008), however most of the study are focus on the formation pure magnetite and additional of precursor materials are needed.

In this research, the effects of variation of FeCl₂ concentration on physical and magnetic properties of the nanoparticles were investigated. FeCl₂ was chosen because it is the main magnetic contributor to the samples produced. Even though, Massart and Cabuil (Tao et al. 2008) reported that the concentration of the iron species in classical coprecipitation has a significant effect on the overall nanoparticles size and mentioned that the increase of the concentration of the iron salts will result into larger magnetite/maghemite particles with wider size distribution but in this study we have different finding which has not been mentioned in previous references.

EXPERIMENTAL DETAILS

The chemicals used in this research were ferrous chloride hexahydrate from SIGMA, ammonium hydroxide and ferric chloride from Fisher Chemicals, ferric nitrate and hydrochloric acid from AJAX Chemicals and nitric acid from Merck. Deionised water with resistivity of approximately 16-18 M Ω /cm was obtained using ELGA ultra analytic deionizer. It was used for preparation of solutions. All reagents were of analytical grade and were used without any further purification.

Maghemite nanoparticles were synthesized by chemical coprecipitation (Massart's procedure) of ferric and ferrous ions in alkaline solution. Aqueous solutions of FeCl₂.4H₂O (stabilized with addition of a few drops of HCl) and FeCl₃.6H₂O were mixed at molar ratio of Fe³⁺: Fe²⁺ of 2:1. Excess amount of ammonium hydroxide (NH₄OH) was then added to the solution to ensure the precipitation process was complete. The addition of NH₄OH caused instantaneous formation of black precipitates. After the precipitate settled to the bottom, the clear supernatant liquid was decanted. The precipitate was then washed with deionised water. This process was repeated several times to remove the excess NH₄OH. The precipitate was then stirred in nitric acid solution (HNO₃). Nitric acid was used as an oxidation agent to oxidize the remaining iron oxide into maghemite. The particles were then recovered by centrifugation at 6000 rpm for 15 min. They were then completely oxidized to maghemite at 90°C in ferric nitrate solution. The particles were isolated again and then peptized in deionized water (Bee et al. 1995). Powder specimens were obtained by drying the suspension in an oven at slightly elevated temperature.

Three samples were produced using different FeCl₂ concentration of 0.1, 0.8, 1.0, 1.2 and 1.5 M. These samples

were named as M01 for 0.1 M, M08 for 0.8 M, M10 for 1.0 M, M12 for 1.2 M and M15 for 1.5 M. The concentration of the FeCl₃ was changed accordingly, maintaining the molar ratio of Fe³⁺: Fe²⁺ of 2:1.

CHARACTERIZATION

Transmission electron microscopy (TEM) images were recorded on a Leo LIBRA 120 microscopes. A drop of the suspension was then placed on a conventional carbon-coated copper grid for observation. The average physical size and size distribution histogram were determined by counting about 100 particles. A Mettler Toledo TGA/SDTA 851 was used to analyze the thermal stability of the nanoparticles. The structure and phase of the nanoparticles were examined by X-ray Diffractometer (XRD) using Cu K α radiation (Philips X-Pert MPD PW 3040). The mean crystallite size was deduced from the full width at half maximum (FWHM) of 3 main peaks of the X-ray diffraction pattern using Scherrer's equation. The magnetic properties of the samples were measured using an Alternating Gradient Magnetometer (MicroMag, model 2900), with maximum applied fields of \pm 10kOe at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the TGA curves of the samples. All the curves show similar behavior. Weight loss of about 18-25% is observed upon heating over the range of room temperature to 700°C. Most of the weight loss occurs below 230°C, which is mainly due to solvent removal and dehydration process. At the range of 230 - 700°C, no obvious weight loss is observed which indicates that the samples are completely oxidized into maghemite. Otherwise a sudden weight loss should occur at about 450°C due to the transformation of hematite and magnetite into maghemite.

Figure 2 shows XRD patterns of the samples. All the patterns are similar. Analysis of the XRD patterns showed that the particles are maghemite (ICDD PDF Card No. 39-1346). Further confirmation is obtained by calculating the lattice parameter of these samples. The lattice parameter calculated is in the range of 8.32 - 8.34 Å which confirms that the particles are more similar to maghemite than magnetite (lattice parameter of bulk maghemite is 8.33 Å and magnetite is 8.396 Å). The line broadening indicates that the crystallite sizes of the maghemite nanoparticles are a few nanometers for all samples, which is in agreement with TEM result. M10 shows the broadest XRD peaks compared with others. This indicates that the crystallite size for M10 is the smallest. The average crystallite sizes of the samples calculated from two major peaks (311) and (440) by Scherrer's equation are 6.79, 6.56, 6.14, 6.72 and 7.24 nm for M01, M08, M10, M12 and M15, respectively.

Figure 3(a) and 3(b) are TEM micrographs of M10 and M15. The particles are almost spherical in shape. About 100 particles are selected for physical size distribution measurement and the distribution histograms are shown in Figure 4. A slightly narrower size distribution for sample

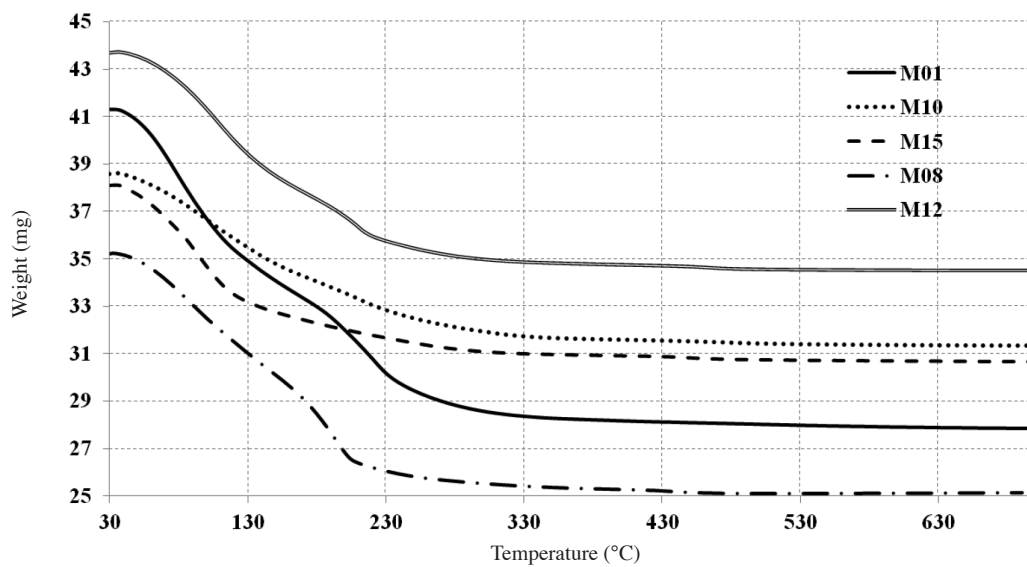


FIGURE 1. TGA curves for samples

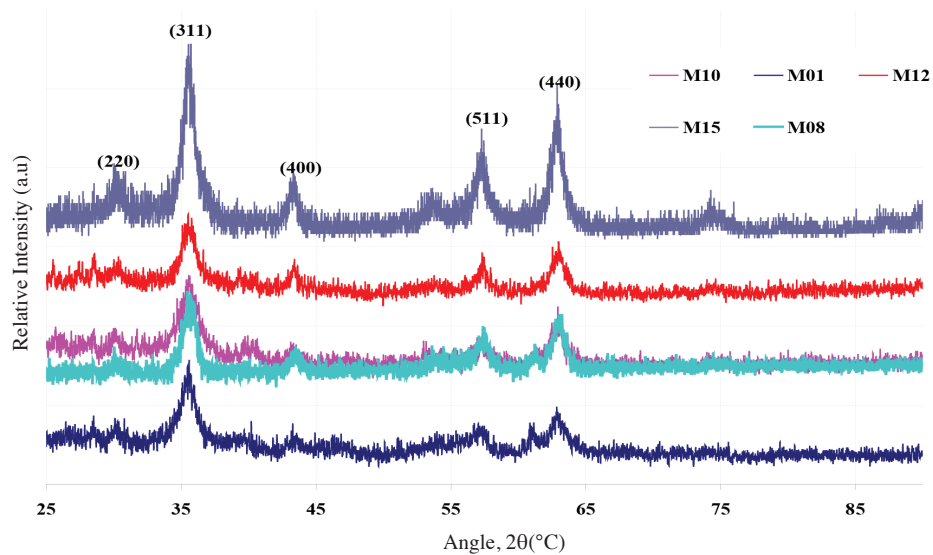


FIGURE 2. XRD pattern for M01, M08, M10, M12 and M15

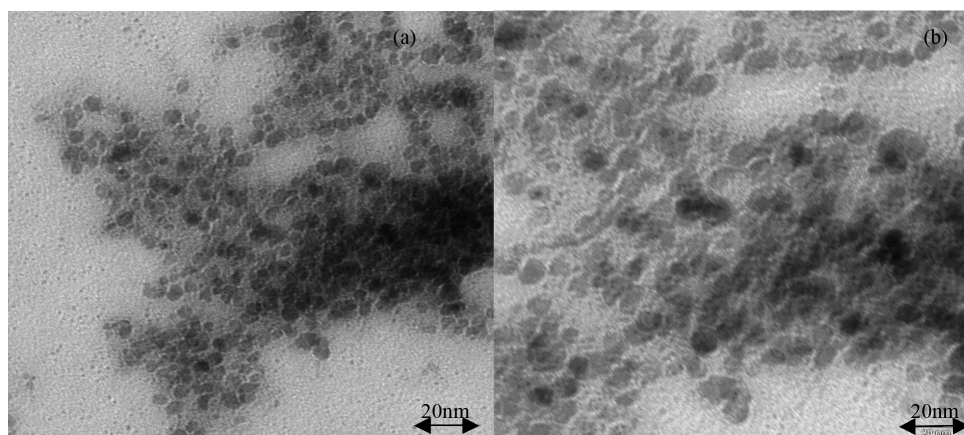


FIGURE 3. TEM micrograph of (a) M10 and (b) M15

M10 is observed. The average physical sizes for M01, M08, M10, M12 and M15 are 5.97 nm, 6.02 nm, 4.98 nm, 5.35 nm and 5.98 nm, respectively.

Figure 5 shows the typical hysteresis curves of the samples at room temperature. The magnetization versus applied field curves show no hysteresis and they pass through the origin. There is no observable remanent magnetization and coercivity. These indicate that all the samples are superparamagnetic. Superparamagnetic phenomena occur only when the particle size is below a certain critical dimension. In fact, below the critical size thermal energy becomes comparable to the anisotropy energy. The latter is proportional to the particle size. In this case, the magnetic moment of the particles relaxes between the easy directions and the averaged magnetization becomes weaker than bulk (Cannas et al. 2001). The magnetization values at 10kOe applied field, $M_{S_{10kOe}}$, for M01, M08, M10, M12 and M15 are 17.83, 13.29, 9.53, 12.65 and 23.49 emu g^{-1} , respectively. The $M_{S_{10kOe}}$ values are about 30-40% of the bulk material.

By assuming the M_s of bulk maghemite is 74 emu g^{-1} and its bulk density (ρ) is $5.07 \times 10^6 \text{ gm}^{-3}$, the least upper bound 'magnetic' size can be calculated from the formula shown (Ang & Yaacob 2007), where k is the Boltzmann constant, T is the room temperature, $\frac{dM}{dH}_{H=0}$ is the slope of the magnetization curve near zero field, ρ is the density of maghemite and M_s is the saturation magnetization.

$$d_{mag} = \left(\frac{18kT \left(\frac{dM}{dH} \right)_{H=0}}{\pi \rho M_s^2} \right)^{1/3}$$

The least upper bound of the 'magnetic' sizes is 7.53, 6.29, 5.92, 6.41 and 8.04 nm for M01, M08, M10, M12 and M15, respectively. This result is comparable with the TEM and XRD results. It shows that the magnetization of maghemite nanoparticles is very sensitive to the size of the sample. When the size decreases, its magnetization decreases when compared to the bulk (Santra & Tapeç 2001).

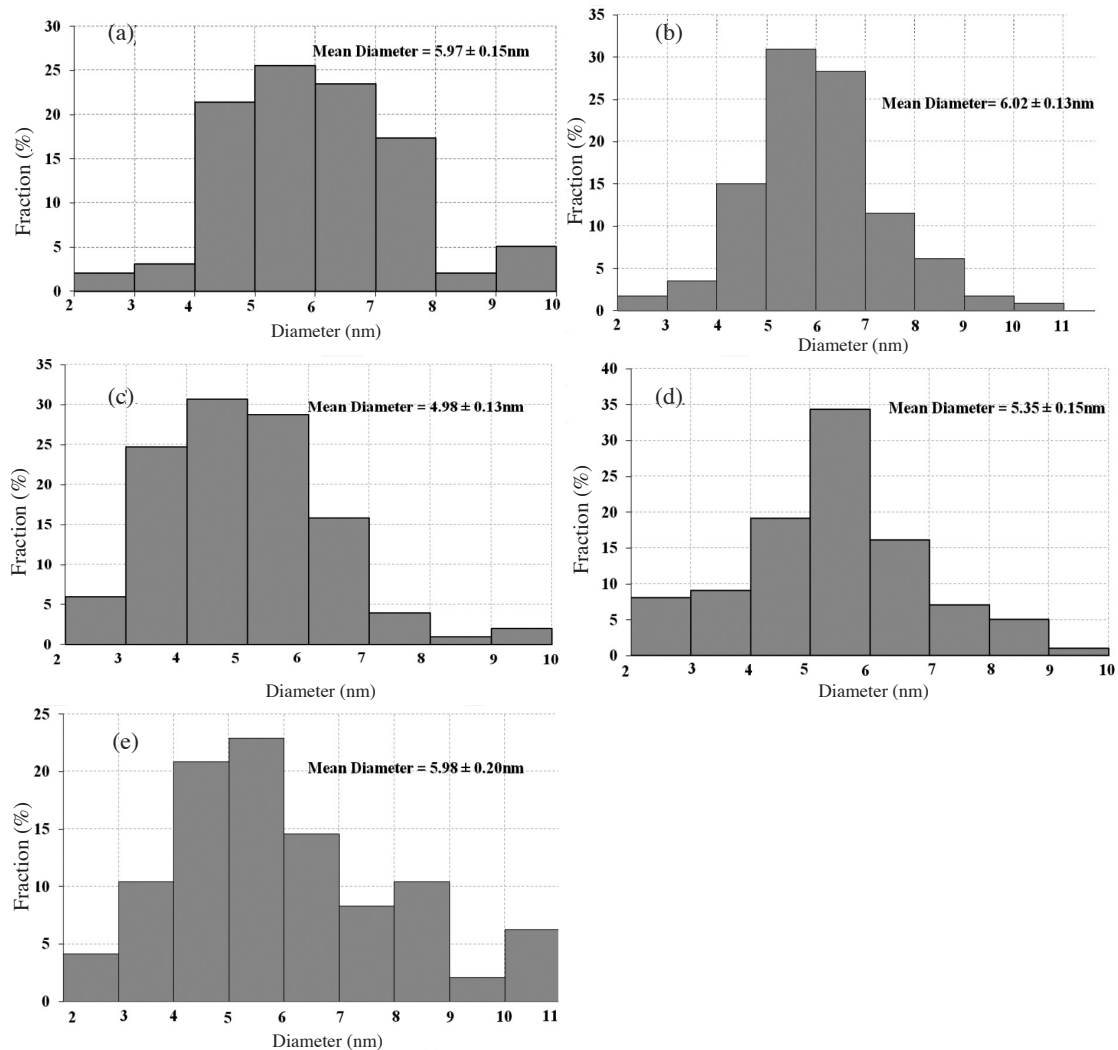


FIGURE 4. Physical Size Distribution Histogram of (a) M01, (b) M08, (c) M10, (d) M12 and (e) M15

All these results do not show the trend of increasing the precursor concentration will increase the synthesized nanoparticles as reported. However when we plot sizes versus concentration (Figure 6), it will show a V-shape, which means when the concentration is too low or too high, it will also lead to formation of larger particles. This is because of high concentration of FeCl_2 , double layer of ions around the particle will be enhanced, suppressing diffusion speed and resulting in larger size. Whereas by low concentration of FeCl_2 , the particles are not stable and tend to form aggregation and agglomeration. Hence, larger particles size are observed.

CONCLUSION

Maghemite nanoparticles were successfully produced using Massart's procedure. In this research, the effects of varying the FeCl_2 concentration toward the physical properties and magnetic size were studied. XRD patterns of the samples showed peak broadening effect indicating that the crystallite sizes of the particle were in nanometer range. The calculated crystallite sizes were 6.79, 6.56, 6.14, 6.72 and 7.24 nm for sample M01, M08, M10, M12 and M15, respectively. The physical sizes measured from TEM micrograph were 55.97, 6.02, 4.98, 5.35 and 5.98 nm and the least upper bound of 'magnetic' sizes were 7.53, 6.29,

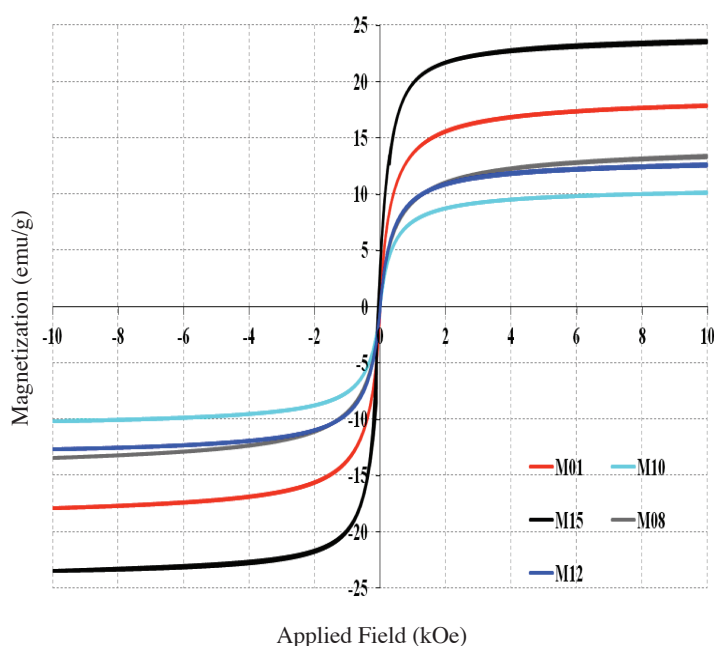


FIGURE 5. Magnetization curves of the samples

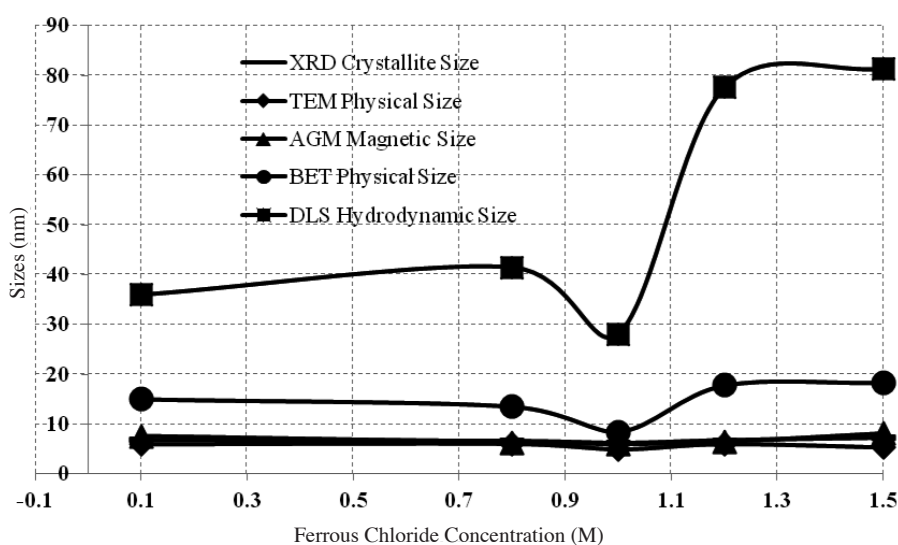


FIGURE 6. Sizes versus FeCl_2 concentration

5.92, 6.41 and 8.04 for sample M01, M08, M10, M12 and M15, respectively. The TEM micrograph showed that the maghemite nanoparticles were roughly spherical in shape. All the samples showed lower saturation magnetization value at 10 kOe applied field as compared to bulk. This could be caused by the small particle size that leads to higher surface area. From the result, it can be concluded that the product from Massart's procedure was highly dependent on the concentration of the precursor and from this study we can also conclude that decreasing the iron salt concentration will not necessary reduce the size of maghemite nanoparticles.

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