The Effect of pH and Time on The Stability of Superparamagnetic Maghemite Nanoparticle Suspensions

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Abstract. Maghemite (γ-Fe_2O_3) nanoparticles have been synthesized using a chemical co-precipitation method. The morphology and particle size is characterized using Transmission Electron Microscopy (TEM), and magnetic characterization using Alternating Gradient Magnetometry (AGM). The stability of the maghemite nanoparticles suspension were studied at different pH and time of storage. Dynamic Light Scattering (DLS) and Zeta Potential were conducted to determine the stability of the suspensions. TEM observation showed that the particles size is 9.6 nm and have spherical morphology. The particles showed superparamagnetic behavior with saturation magnetization 25.5 emu/g. The suspensions are stable in the acidic condition at pH 4 and alkaline condition at pH 10. The suspensions remain stable after 4 weeks of storage.

1 Introduction

Maghemite nanoparticles is a magnetic materials which have been widely interest of researchers due to their unique characteristics. They generate a new class of liquids called "magnetic fluids" in the solvent. The unique of these smart materials is because they have superparamagnetic behavior and biocompability.

They used in wide range application including electronic, mechanical engineering, aerospace, environmental, and bioengineering [1-3]. The flow and energy transport of magnetic fluids can be controlled using external magnetic fields. Therefore, the magnetic fluids can be used effectively in thermal engineering applications [4].

Many attemps have been carried out to synthesize stable magnetic nanoparticles suspension in various methods in order to achieve proper control of particle size, shape, crystallinity and the magnetic properties [5]. Various methods are available for synthesis of magnetic nanoparticles such as co-precipitation [[6-8], sol-gel synthesis [9, 10], and microemulsion [11-13]. The most common is the co-precipitation method [14]. This method is reproducible, simple and cheap and it gives high yields result.

Although attemps have been made towards the synthesis of stable magnetic nanoparticles suspension, it still presents a big challenge. The most important parameter is the stability of the magnetic nanoparticles suspension. Due to the particle in nanosize, the particles have high surface energy hence tend to aglomeration and aggregation that become sedimentation. For magnetic nanoparticles, this issue is worsened because of magnetic attraction. These two effects reduce the stability of maghemite nanoparticle suspensions. This issue will be constraint of the application of maghemite nanoparticles suspensions. To overcome this issue,

In this paper, the stability of maghemite nanoparticles suspensions were studied by monitoring their particle size distribution using DLS on the effect of pHs and time of storage.

2 Experimental Methods

Maghemite nanoparticle with 0.1 % volume fraction used in this experiment has been synthesized using a chemical co-precipitation method and characterized using several characterization techniques. The samples were separated in different bottles and tubes for pHs and time of storage studies.

The effect of pHs were studied by variated the pH of suspension by hydrochloric acid to ajust the pH in acidic condition and sodium hydroxide for alkaline condition adjustment. The stability of the suspensions were characterized by measurement of DLS and zeta potential at particular pHs.

The effect of time of storage were conducted at 0.1 % volume fraction of maghemite nanoparticles suspensions. The measurements were conducted for as-prepared maghemite nanoparticles suspensions and at 1, 2, 3, and 4 weeks time of storage. Zeta potential and particle size were measured at each time using Malvern Zetasizer equipment.

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3 Results and Discussion

The shape and particle size distribution of maghemite nanoparticles were examined by transmission electron microscopy (TEM) as shown in Fig.1. It is clearly observed that the maghemite particles have spherical shape with the average particle size of 9.6 nm. It is also shown that the particles are in narrow size distribution. There are a few larger 'particles' which are found to be aggregates, which may be due to long-range magnetic dipole-dipole interaction between the particles.
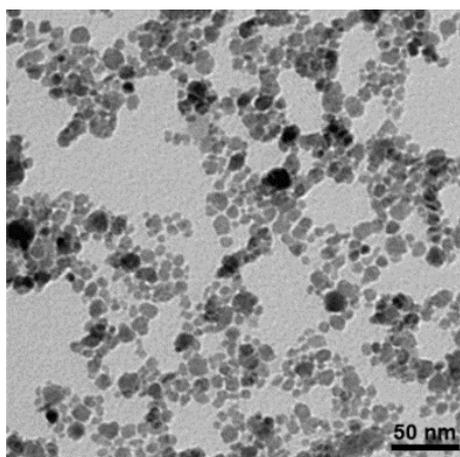
Figure 1. TEM images of maghemite nanoparticles for stability experiment

The magnetization curve of sample is shown in Fig.2. It is clear that the curves do not exhibit hysteresis and passes through the origin, which indicates that the samples is superparamagnetic. The saturation magnetization value of maghemite nanoparticles at room temperature is 25.5 emu/g. These values are lower than that of bulk maghemite (74 emu/g). This is related to the crystallite size of maghemite particles which are in nanosize range. This phenomenon is usually observed in nanoparticle interacting systems. Such a reduction of maximum magnetization can be ascribed to surface effects arising from broken symmetry and reduced coordination of atoms lying at the surface of maghemite nanoparticles and also to a high degree of interparticle interactions [15].
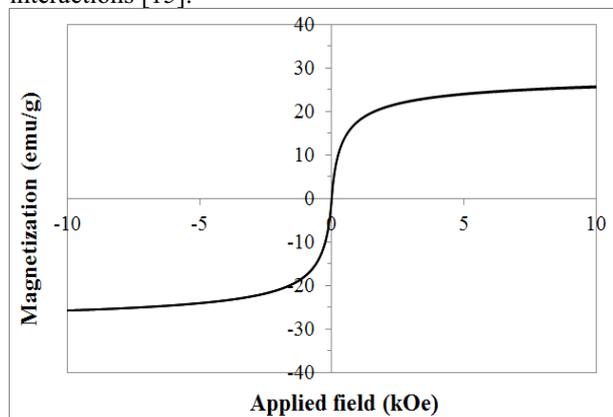
Figure 2. Magnetization curves of superparamagnetic maghemite nanoparticle.

Electrostatic stabilization is a simple way for imparting high stability to maghemite suspensions, which are sensitive to the changes in the pH. The response of the maghemite nanoparticles suspensions to different pHs values were determined by measuring electrophoretic mobility (zeta potential) as a function of pHs.

The pH control as an important role in stability control, determines the iso electric point (IEP) of suspension in order to avoid coagulation and instability. A repulsion force between suspended particles is caused by zeta potential which increases with the increase of surface charge of the particles suspended in the solution [16].

The isoelectric point (IEP) is the concentration of potential controlling ions at which the zeta potential is zero [17]. Zeta potential is an indicator of dispersion stability. The zeta potential of any dispersion is influenced by the surface chemistry.

The zeta potential of any dispersion is influenced by the surface chemistry. The surface chemistry can be changed by different methods such as the variation of pH value. At the isoelectric point, the repulsive forces among metal oxides are zero and nanoparticles close together at this pH value. Pursuant to the Derjaguin–Landau–Verwey–Overbeek theory [18], when the pH is equal to or close to the IEP, nanoparticles tend to be unstable, form clusters, and precipitate. As the pH of a solution departs from the IEP of particles, the colloidal particles get more stable [19].

The zeta potential value of maghemite nanofluids at different pH is shown in Fig. 3. It can be seen that the value of zeta potential is zero when the pH of maghemite nanofluids is 6.6, which is the iso electric point (iep). When the pH greater than 6.6, the particle surface begin to have a negative charge, on the other hand if suspension's pH lower than 6.6, the particle surface have a positive charge. The value of zeta potential is higher when the pH of the suspension is far from the IEP.

It is shown that the highest value of zeta potential is 41.7 mV at pH 4.0 at the acidic condition and -40.4 mV at pH 10.0 at the alkaline condition. It is related to the particle size at any pH that is smaller at a higher zeta potential values. The particle size is 58.2 nm at zeta potential of 41.7 mV while, at the iso electric point, the particle size is 4670 nm.

This phenomenon can be explained by at the IEP, the particles surface charge is lower hence the particles are become greater because of the agglomeration and aggregation of the particles in fluids. On the other hand, as the pH of the fluids far from IEP, the particles surface charge become higher. Hence, there is a resistance of the particles to agglomerate that give the particles in suspension is become smaller.

The suspension has electrostatic stability due to the strong repulsive force between charged particles. At the lower pH (acidic condition) and higher pH (alkaline condition), the particles create high surface charge that result in higher zeta potential values. This condition provides enough electrostatic repulsion force between particles to prevent attraction and collision caused by Brownian motion.
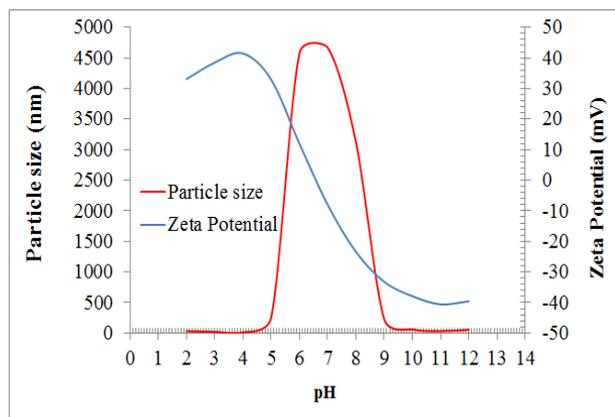
Figure 3. Effect of pH on particle size and zeta potential

The particle size distributions of maghemite nanoparticles suspension at different time of storage obtained from dynamic light scattering (DLS) measurement are shown in Fig. 4. It is presented that the intensity averaged particle size of maghemite nanoparticles for all samples. The initial hydrodynamic size of the particles is are 58.2 nm. The average sizes of the same suspension after one week, two weeks, 3 weeks, and four weeks are 59.7, 62.1, 63.5, and 66.5 nm, respectively.

The rise in the average particle size after prolonged storage indicates that a small degree of aglomeration occurred. However, there is no significant agglomeration and sedimentation visually observed on the maghemite nanofluids even after four weeks of storage. It is also shown that the particle sizes obtained from DLS measurements are larger than the TEM results. It can be explained that the size measured from DLS measurement are the hydrodynamic size that are the size of particles and their surrounding diffuse layer while from TEM is the size of maghemite nanoparticles itself.
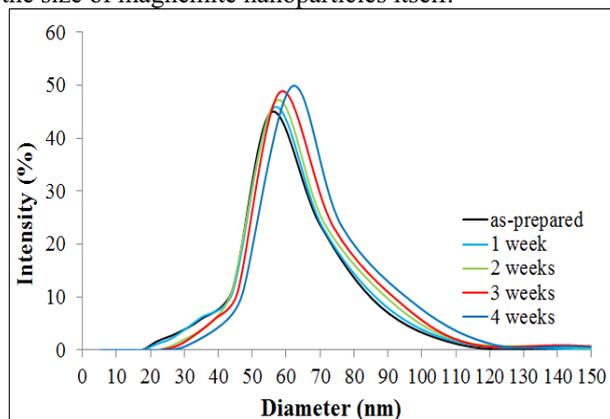

Figure 4. DLS measurement of maghemite nanoparticle suspensions with the effect of time.

To further understand the stability of the suspension, the study of electrophoretic behavior through measurement of zeta potential is crucial [20]. It is well known that suspensions become stable with zeta potential value higher than ± 30 mV. The zeta potential values depend on the pH of the suspensions.

The zeta potential of maghemite nanoparticles suspension are shown in Fig. 5. The values of zeta potential as prepared maghemite nano particle suspension is 41.7 mV. The values of zeta potential at the same suspension after 1, 2, 3, and 4 weeks of storage are 40.8, 39.6, 38.3 and 36.0 mV, respectively. These values offer enough electrostatic repulsion force between particles to avoid attraction and collision caused by Brownian motion.

There is a gradually decrease of zeta potential values with lapse of time of storage. It indicate that particle aglomeration and aggregation occur in the suspension with time. However, the zeta potential values indicate that the maghemite nanoparticles suspension are stable even after 4 weeks of storage.
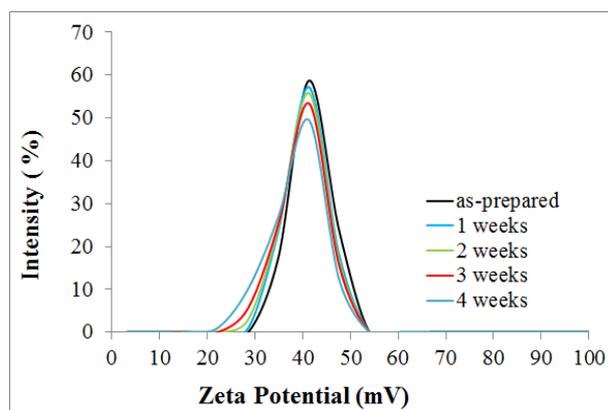
Figure 5. Effect of time on zeta potential of maghemite nanoparticle suspensions.

4 Conclusions

Stable maghemite nanoparticles suspensions have been successfully synthesized by co-precipitation method. TEM observations and image analysis show that the maghemite nanoparticles have spherical morphology and 9.6 nm particle size. Magnetization curve show that maghemite nanoparticles exhibit superparamagnetic behavior. The maghemite nanoparticle suspensions are more stable in acidic and also in alkaline conditions. Maghemite nanoparticle suspensions remain stable after 4 weeks of storage.

Acknowledgements

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