

MODE OF DRYING THE NANOPARTICLES AND IT'S STABILITY OF THE FERROFLUIDS

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Abstract: Bare and oleic acid capped magnetite nanoparticles were obtained by coprecipitation method. Ferrofluids were prepared by dispersing bare and oleic acid capped magnetite (dried at room temperature and 80 °C) nanoparticles in H₂O and ethylene glycol (EG). Ferrofluids prepared by non-polar solvent i.e. ethylene glycol is found to be more stable than the one prepared by a polar solvent. Among the ferrofluids prepared in EG, the oleic acid capped nanoparticles dried at 80 °C settles in less interval of time. The interaction of the nanoparticles resulting to agglomeration is discussed in details.

1. Introduction:

1. 1. Magnetic nanoparticles:

Nanoparticles with dimension 0 to 100 nm which possess ordered magnetic moments are categorized into magnetic nanoparticles. Industrial applications of magnetic nanoparticles are of interest with nanoparticles having dimensions from a single domain and below. Magnetic storage devices are generally prepared by single domain magnetic nanoparticles. Ferrofluids and other nanoparticles utilized for catalysis and detection fall in the regime of superparamagnetism. Magnetic nanoparticles are class of nanoparticles that can be manipulated using magnetic fields. Physical and chemical properties of magnetic nanoparticles largely depend on the synthesis method and chemical structure. Magnetite is one of the most popular magnetic materials utilized in modern technology. Magnetite can be represented as $(\text{Fe}^{3+})_{\text{Tet}}[\text{Fe}^{2+}_{(1-3\delta)}\text{Fe}^{3+}_{(1+2\delta)}\square_{\delta}]_{\text{Oct}}$, where δ stands for the amount of oxidation and \square for vacancies formed in the crystal to account for charge balance [1]. The stoichiometry of magnetite and the morphology differs as the ratio of Fe precursor and sodium acetate varies [2]. The size of magnetite cluster increases as the sodium acetate is decreased. Apart from the physical appearance, the Fe vacancies increase as the amount of sodium acetate was reduced. L.H. Singh et al have worked on tuning the size of the precipitated magnetite nanoparticles by zeolite substrate [3]. The magnetic properties of the nucleated magnetite nanoparticles in zeolite template were investigated using SQUID magnetometer and Mössbauer spectroscopy [4]. The magnetization of magnetite nanoparticles in the initial concentration of zeolite (25–180mg) is 53–34.7 emu/g. The magnetization decreases at higher zeolite contents (200–250 mg). At lower zeolite amount, the magnetic interaction between Fe₃O₄ located at the pores and the surface results in the transformation of the superparamagnetic doublet to a sextet in the Mössbauer spectra. The interactions of surface particles decrease as the zeolite content increases and they become isolated.

1.2. Ferrofluids:

Ferrofluid is a liquid that becomes strongly magnetized in the presence of a magnetic field. They are colloidal liquids made of nanoscale ferromagnetic or ferrimagnetic particles suspended in a carrier fluid. Ferrofluids usually do not retain magnetization in the absence of an externally applied field. The magnetic attraction and Van-der Waals force of surfactant capped nanoparticles are weak enough that it is sufficient to prevent magnetic clumping or agglomeration [5]. The nanoparticles of ferrofluids are suspended by Brownian motion and generally will not settle under normal conditions.

1.2.1. Applications of ferrofluids:

Ferrofluids can heat up a localized portion of a living body in the presence of external alternating magnetic field [6]. This property enables the ferrofluids for applications in cancer treatment. Ferrofluids are used in many technological applications such as dynamic sealing; heat dissipation; damping and doping of technological materials [7]. The thermal conductivity of the ferrofluids can also be tuned by external magnetic field [8,9].

1.2.2. Stability of ferrofluids:

When the ferrofluids are prepared in nonpolar carriers, particle aggregation due to Vander Waal's attraction leads to low colloidal stability and a large rate of sedimentation of the aggregates formed in the suspension [10, 11]. To overcome this unwanted behavior we have to coat the particles with certain long-chain molecules particularly those containing a polar group and a tail with dielectric properties matching those of the carrier liquid.

In the present work, bare and oleic acid capped magnetites were synthesized to prepare ferrofluids. The stability of the ferrofluids in the different solvent was investigated to understand the interaction between the particles.

2. Synthesis and characterizations:

Fe_3O_4 was synthesized using coprecipitation method. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1M) and FeCl_3 (2M) were mixed in a beaker and stir it using magnetic stirrer for about 45-50 minutes at 70°C . To maintain a pH of 10, 25 % NH_3 solution is added to the solution and continue stirring for about 45-50 minutes. The precipitate was then divided into two equal halves. Then in one halve oleic acid was added and continue to stir for 30 min. The precipitates are separated from the solution by centrifugation method. Structural investigations were performed using XRD and FTIR. For checking the stability of the ferrofluids prepared with H_2O and ethylene glycol (EG), the samples were fixed on a steady wall after ultrasonication for 1 hrs/day for 60 days and observed the sedimentation.

3. Results and discussions:

3.1. Structural studies:

The XRD pattern of the bare Fe_3O_4 and oleic acid capped Fe_3O_4 ($\text{Fe}_3\text{O}_4\text{-OA}$) as shown in Figure 3.1 can be indexed only with cubic spinel ferrites (JCPDS No. 01-087-0244).

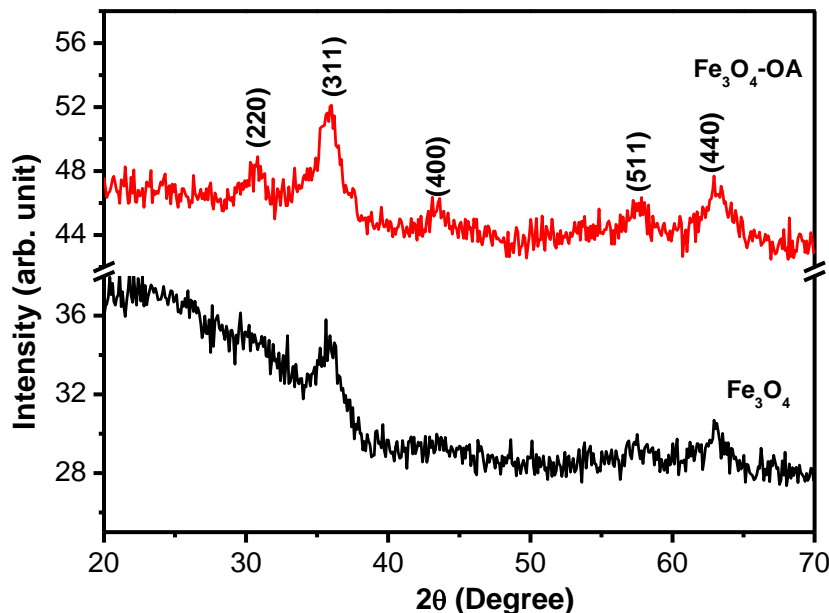


Figure 3.1: XRD spectra of bare Fe_3O_4 and oleic acid capped Fe_3O_4 ($\text{Fe}_3\text{O}_4\text{-OA}$).

The spectra have broad peaks which indicate the particles have very low dimension. The peaks of the $\text{Fe}_3\text{O}_4\text{-OA}$ are more intense than the Fe_3O_4 . During the synthesis, the precipitate was separated into two equal half and oleic acid was added in one halve. Therefore, the higher intense may be contributed to the higher crystalline nature of the particles.

The Fourier transform infrared spectroscopy confirmed the surface functionalization of magnetic nanoparticles. In relation to the peaks present in the spectra, the 558cm^{-1} corresponded to vibration of Fe-O tetrahedral site and

625 cm^{-1} corresponded to the Fe-O octahedral site. The peak around 1710 cm^{-1} is contributed by C=O stretching bond from oleic acid.

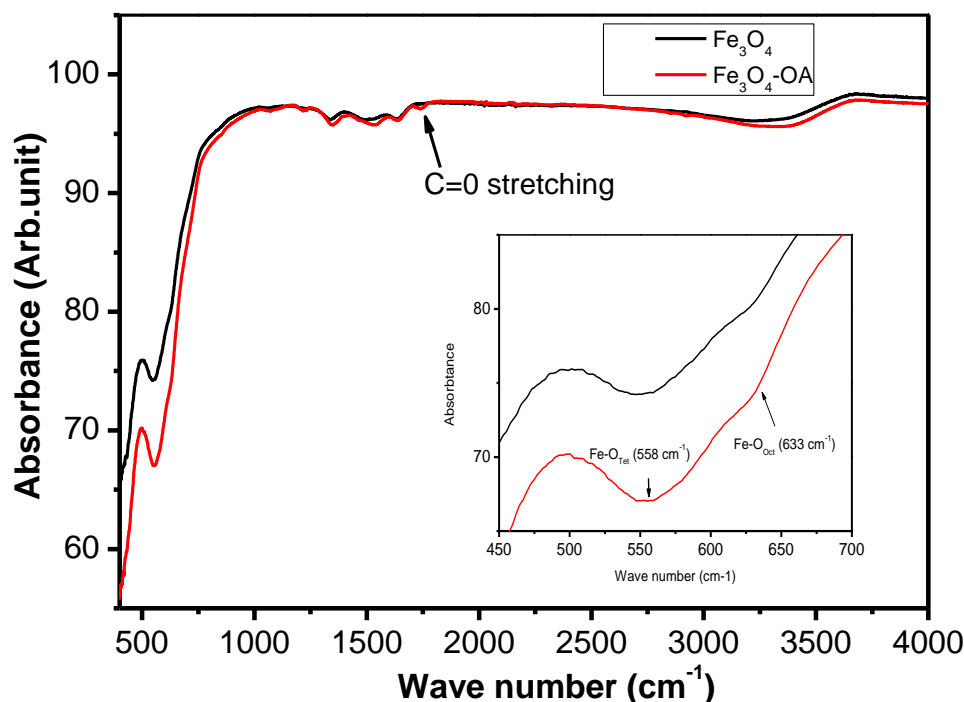


Figure 3.2: FTIR spectra of Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{-OA}$. Extended spectra from 450 to 700 cm^{-1} (Insert).

3.2. Physical observation of the ferrofluids:

The Ferrofluids prepared by magnetite nanoparticles treated differently. The details of the treatments are listed in Table 3.1.

Table 3.1: Treatment of the nanoparticles for synthesizing ferrofluids.

Sl No.	Modification	Drying conditions	Weight of the particles	Solvent/Vol
1	No surfactant	Room temperature in air	50 mg	Water/2 ml
2	Oleic acid capped	Room temperature in air	50 mg	Water/2 ml
3	No surfactant	80 °C in air	50 mg	Water/2 ml
4	Oleic acid capped	80 °C in air	50 mg	Water/2 ml
5	No surfactant	Room temperature in air	50 mg	Ethylene glycol/2 ml
6	Oleic acid capped	Room temperature in air	50 mg	Ethylene glycol/2 ml
7	No surfactant	80 °C in air	50 mg	Ethylene glycol/2 ml
8	Oleic acid capped	80 °C in air	50 mg	Ethylene glycol/2 ml

The nanoparticles were dispersed in the specified solvent and then ultrasonicated for 1 h each for 60 days. The ultrasonicated ferrofluids are then fixed to a static wall and observed the stability.

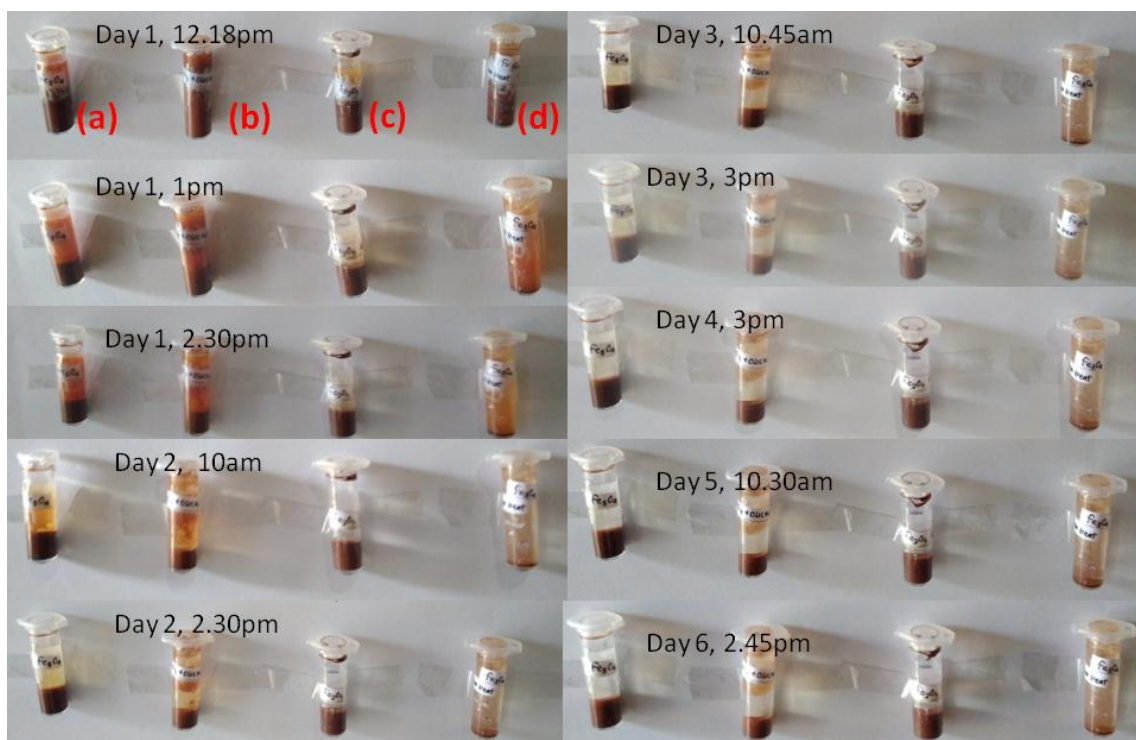


Figure 3.3: Snapshots of the ferrofluids with H₂O as solvent after 1 h sonication/day for 60 days for the bare nanoparticles (BN) dried at room temperature (a), oleic acid coated nanoparticles (OAN) dried in room temperature (b), BN dried at 80 °C, OAC dried at 80 °C.

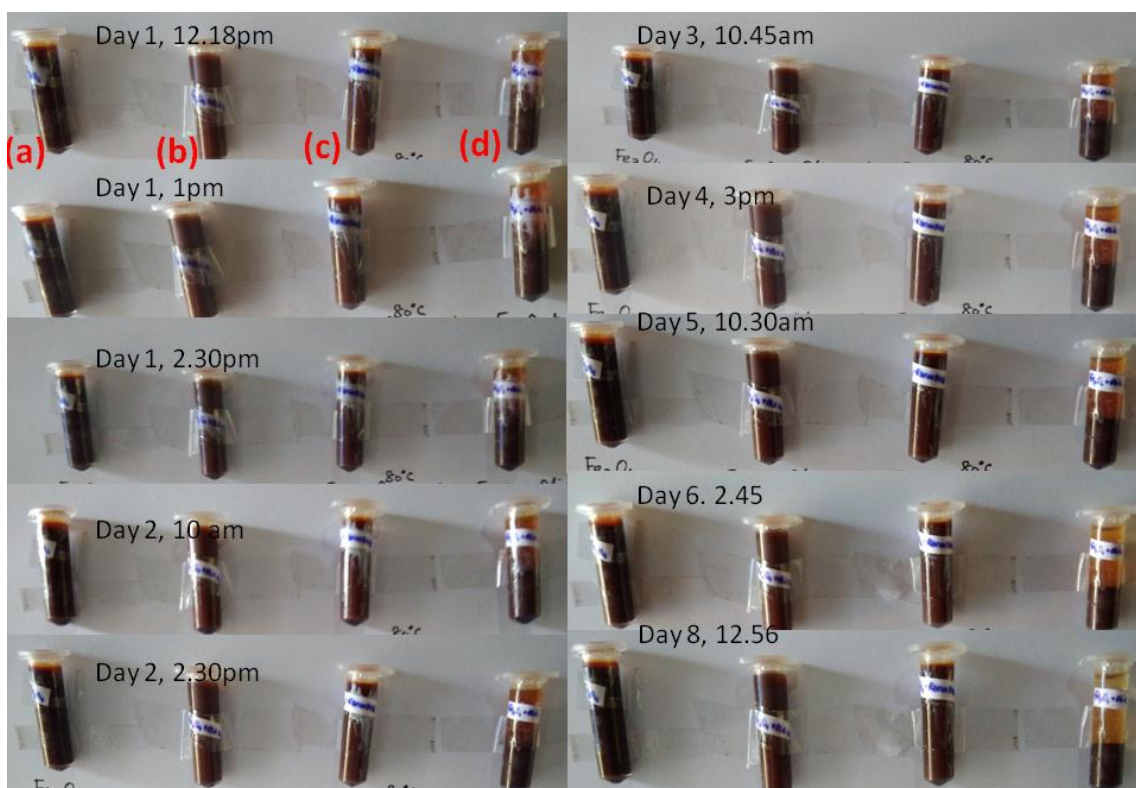


Figure 3.4: Snap shots of the ferrofluids with EG as solvent after 1 h sonication/day for 60 days for the bare nanoparticles (BN) dried at room temperature (a), oleic acid coated nanoparticles (OAN) dried in room temperature (b), BN dried at 80 °C, OAC dried at 80 °C.

From figure 3.3, the ferrofluids prepared in the polar solvent is unstable. The particles settle in few minutes. The rate of settlement is highest in the sample no. d i.e. oleic acid capped Fe_3O_4 dried at 80°C . Second highest is found to be oleic acid capped Fe_3O_4 dried at room temperature. However, the rate of settlement in the bare Fe_3O_4 dried at room temperature and 80°C is almost same.

In figure 3.4, the most unstable ferrofluids prepared in ethylene glycol is the oleic acid capped Fe_3O_4 nanoparticles dried at 80°C . Remaining fluids are still stable until the eight days. The plausible reason behind the anomaly observed in the ethylene glycol based ferrofluids is graphically represented below.

3.3. Graphical representation of the particles in the ethylene glycol based ferrofluids:

The capping agent consists of a head and a long chain as a tail. In the case of oleic acid, the head consists of COO^- and is attached to the nanoparticles. The long tail expands when dispersed in a solvent. As the solvent dries, the tail bends and lies on the surface of the nanoparticles.

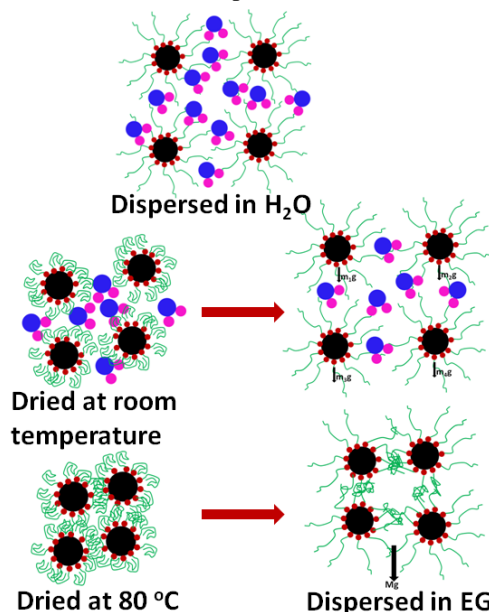


Figure 3.5: Schematics of the oleic acid capped nanoparticles dispersed in H_2O , Dried at room temperature and 80°C and dispersed in ethylene glycol (EG).

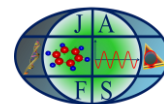
In the room dried samples of oleic acid capped nanoparticles, the H_2O molecules exist in between the particles which prevent from intercrossing the tails. However, for the case of 80°C the H_2O molecules escaped leaving the space for the intercrossing of the tails. The tails most possibly intercrossed resulting in agglomeration. These intercrossed tails could not release from one another when dispersed in the solvent. Therefore the gravity of the cumulative mass overcomes the Brownian agitation and settles down.

4. Conclusions:

Magnetite was successfully synthesized using coprecipitation method. These nanoparticles were treated for preparation of ferrofluids. The functionalization of the nanoparticles with oleic acid was confirmed by FTIR. The stability of the nanoparticles was observed to be high in the case EG solvent compared to H_2O . Among the ferrofluids prepared using EG, the sample no. 8 (Table 1) i.e. the oleic acid capped nanoparticles dried at 80°C settle faster than the others. This is plausibly due to intercrossing of the tails while drying as the H_2O molecules escaped. As the H_2O molecules escaped the cumulative weight due to agglomeration overcomes the Brownian agitation.

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