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Synthesis and Characterization of Superparamagnetic Iron Oxide Nanoparticles Prepared With Tween-80

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Abstract – In this study attempt was made to develop a simple low temperature procedure for the synthesis of stable, surface modified superparamagnetic iron oxide nanoparticles (SPIONs) in different phases. Tween-80 was used for surface modification of the SPIONs and as prepared samples were air annealed to study the effect on the phase development. Characterization of the samples was carried out using various techniques such as powder XRD, SEM, EDS, FTIR and UV/Vis spectroscopy; and thermal stability was checked by TGA. From PXRD data of the synthesized NPs, crystallite size came out to be approximately 60 nm and samples were polydispersed in nature. FT-IR spectra confirmed the presence organic surfactant used for surface functionalization of SPIONs. At room temperature, these SPIONs attracted towards the external applied magnet. For the evaluation of thermal stability, TGA curves displayed excellent stability due to role of surfactant used in the synthesis of SPIONs at higher temperatures i.e. up to 1000 ºC.

Keywords – SPIONs; Tween-80; Thermal Annealing; magnetization

1. Introduction

Iron oxides are commonly found widespread in nature i.e. atmosphere, pedosphere, biosphere, hydrosphere and lithosphere [1]. At the nanoscale, SPIONs like magnetite and its oxidized form maghemite are of great interest for physicists, chemists and biologists due to their biodegradability and non-cytotoxic nature to humans [2]. Important applications of SPIONs include magnetic resonance imaging for contrast enhancement at nanomolar concentration range for studying tumors, in drug delivery for nanoscale anticancer drugs, magnetic data storage, nanowires, plastics, coatings, nanofibers and textiles, alloy and as catalyst [3-6]. More recently, SPIONs have been employed for the removal of biological and abiological contaminants in water and food related applications like enzyme immobilization, protein purification and food analyses etc. [7, 8].

Several techniques are used for the synthesis of SPIONs including liquid phase methods, two-phase methods, sol-gel methods, gas/aerosol-phase methods, polyols methods, hydrothermal routes, sonolysis, microwave irradiation and biological routes [9]. Liquid phase method is a well-established and probably the simplest approach offering a better yield of magnetic nanoparticles and surface treatments [10]; further, water solubility and biocompatibility of nanoparticles are required for biological and biomedical applications [11]. Organic molecules like cetyltriammonium bromide, dodecylethylene tetraammonium bromide are used to control and modify the size, shape and surface of SPIONs. Polyethylene sorbitan monooleate (Tween-80) is a non-ionic surfactant and has been recently reported by our group for the synthesis of ZnO nanoparticles [12]; based on these facts, we decided to carry out liquid phase synthesis of SPIONs using Tween-80 as surfactant.

2. Materials and Methods

2.1. General

Analytical grade iron(II) nitrate hexahydrate (Sigma Aldrich), commercially available Tween-80™, sodium hydroxide, ethanol and double distilled water were used during synthetic manipulations.

2.2 Physical Measurements

UV/visible spectra were recorded in the range of 200 to 800 nm on UV/visible spectrophotometer SP-1103. FT IR spectra were recorded on Brüker Spectrum-100 FT IR spectrophotometer using KBr pellet method in the range of 4000-400 cm^{-1}. TG analysis was conducted on Q500 V20.13 Build 39 thermal analyzer in platinum pan at a temperature rate of 10 ºC/min under flowing nitrogen environment to from ambient to 1000 ºC. SEM was recorded on JEOL (JSM-7600F, Japan). For PXRD, JDX-3532 JEOL JAPAN X-ray Diffractometer (40 kV, 30 mA, monochromatic) using a Cu K alpha source (1.5418 Å). The scanning range used for the sample analysis was $20º \leq 2\theta \geq 70º$ with a scanning rate of 0.5 seconds per step and a step size of 0.05º.

***2.3** Synthesis of IONPs*

In a typical reaction, to 100 mL aqueous solution of $Fe(NO_3)_2.6H_2O$ (0.25 M), different volumes of the non-ionic surfactant Tween-80 (3 mL, 5 mL and 7 mL) were added gradually and stirred for 30 minutes. To this mixture, 3M NaOH solution was added dropwise to get a suspension and this mixture was further stirred vigorously for four hours at 90 ºC under ambient pressure. Dark brown precipitates were filtered by suction filtration over a Membrane filter paper and washed copiously with distilled

water and ethanol to remove any unreacted materials and impurities. As-obtained powders were air dried at 100 ºC overnight; parts of the dried powder samples were subsequently annealed in air at 200, 300, 400 and 500 ºC for 1 hour each.

3. Results and Discussion

The UV/Visible absorption spectra of SPIONs are given in Figure 1; all samples showed a broad peak located at about 400 nm, which is similar to previous reports. Peak broadening was attributed to the amorphous nature of the sample where the absorption band edge is diffused compared to the very sharp band edges of crystalline samples. Importantly, all of the samples displayed appreciable absorbance in the visible region a property that proved synthesized SPIONs to be very useful in bio-imaging

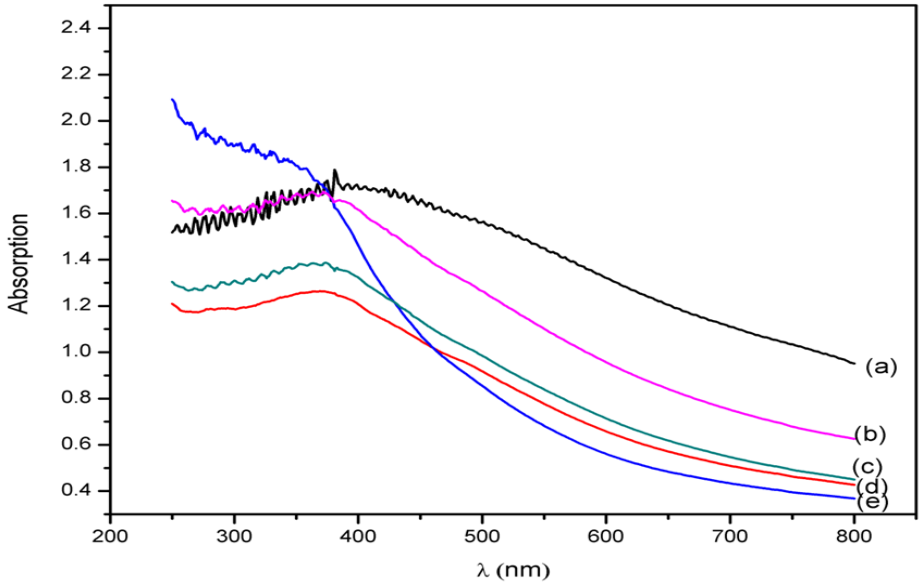

Figure 1. UV/Visible spectra of surface modified iron oxide nanoparticles

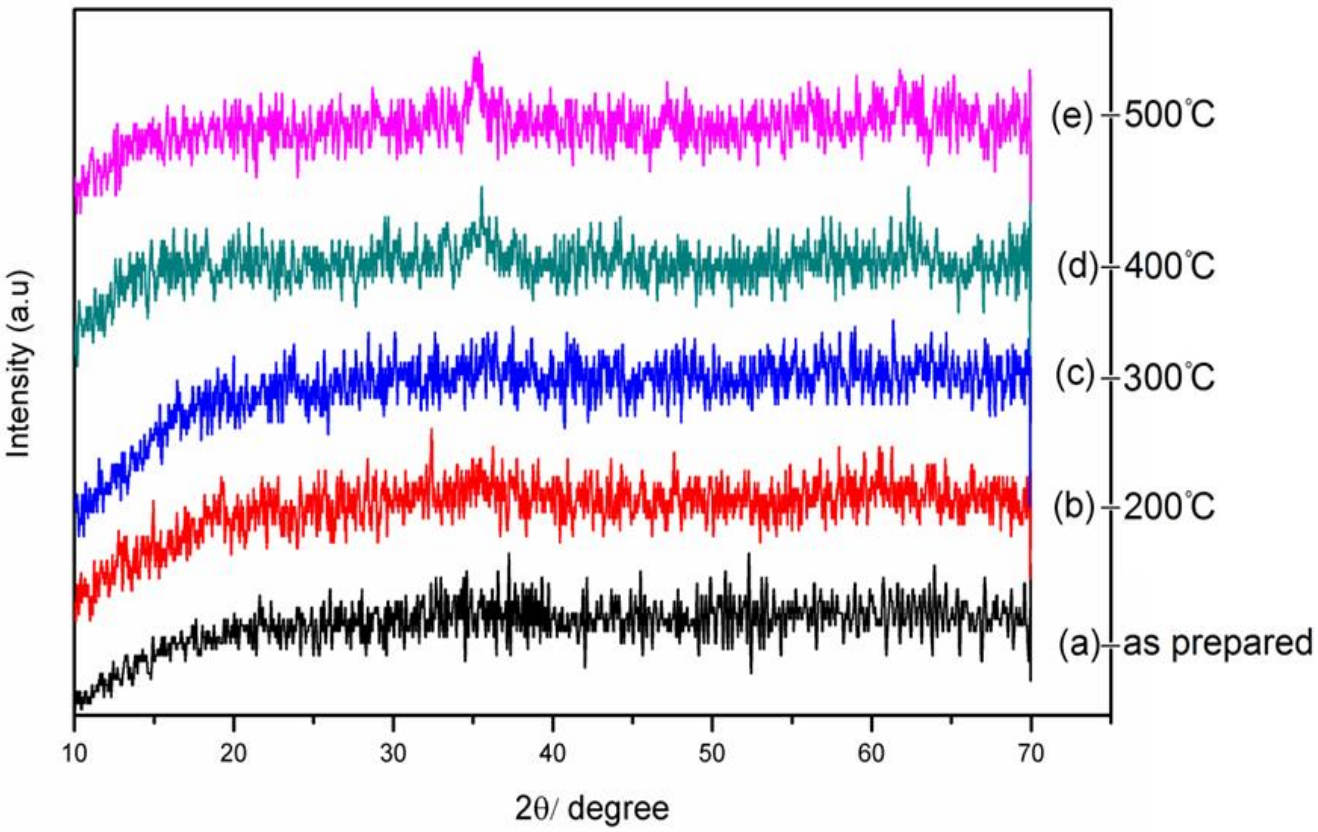

Figure 2 PXRD patterns of iron oxide nanoparticles prepared at (a) 90 ºC and annealed at (b) 200 ºC (c) 300 ºC (d) 400 ºC (e) 500 ºC.

PXRD patterns of as-synthesized and annealed samples are given in Figure 2. The XRD pattern indicated no clear diffraction peaks for all the samples dried at 100 ºC indicating the amorphous nature of synthesized nanoparticles. The crystallinity of the samples remained low even when annealed up to 500 ºC in air for 30 minutes at 20 ºC per minute for all the samples. Only a weak reflection at 2θ value around 36.2º was observed to gradually develop at 500ºC. Low crystalline nature of these samples is because of several factors like faster heating rate and short annealing time and very fast Fe^{2+} ions precipitation upon addition of strongly basic NaOH solution. Another reason for the amorphous nature of the Fe_2O_3 is the very low synthesis temperature for all the samples (90 ºC). However when the samples were annealed for 2 hours, well crystalline reflections was observed even at 400 ºC as shown in Figure 3. The sizes of crystallites can be calculated from (104) and (110) reflections applying Scherrer's equation, which were found to be 20 nm for samples annealed at 400 ºC [13].

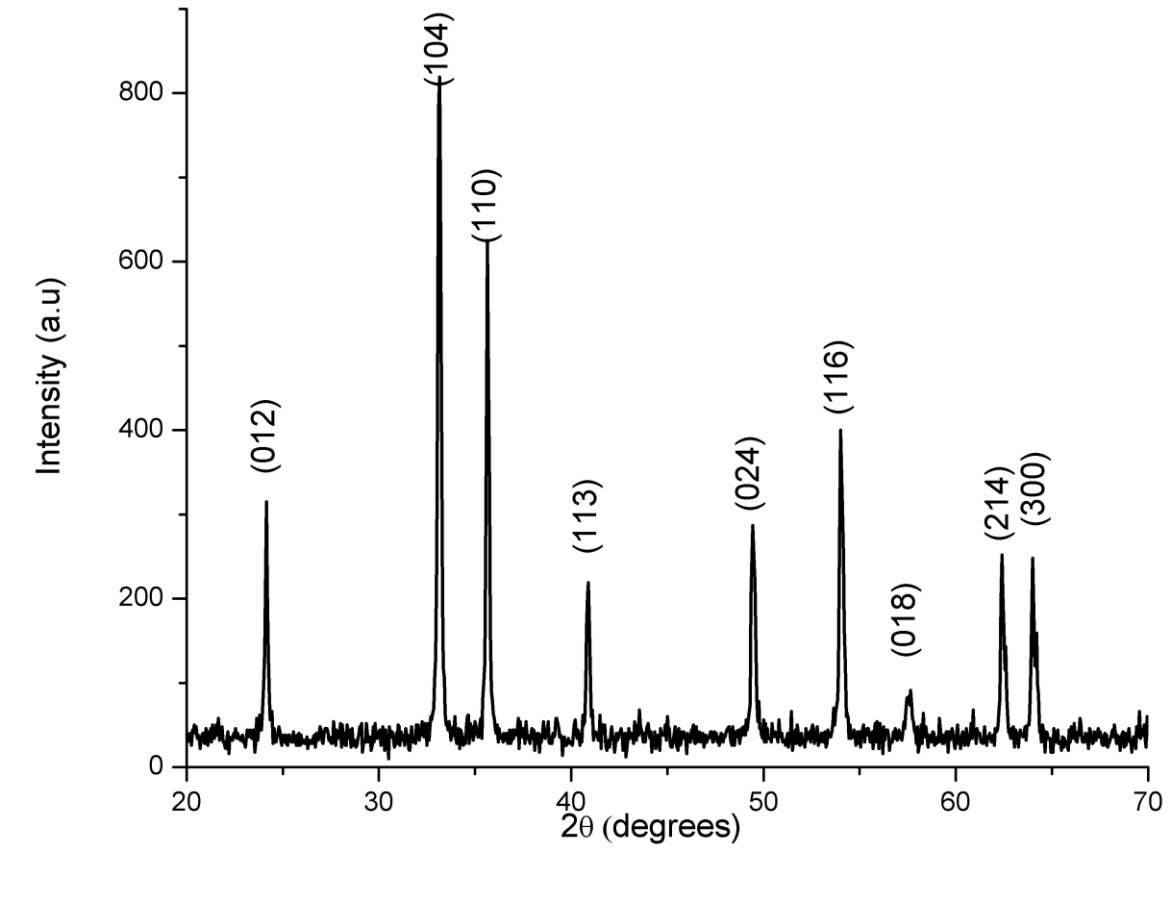

Figure 3 PXRD patterns of iron oxide nanoparticles prepared at 90 ºC and annealed at 400 ºC for 2 hours.

The low and high resolution SEM images of the SPIONs are shown in Figure 4. As-synthesized sample consisted of very fine particles in the low resolution image but from the high magnification it was observed that these fine particles consisted of still smaller particles which were heavily agglomerated together ranging in sizes 60-100 nm. But when the samples were annealed, nanoparticles appeared to get shrunk in sizes and their outer appearance became rough as shown in Figure 4b-4e. This shrinkage in size can be attributed to evaporation of chemisorbed water from the surface of the nanoparticles on annealing. As sample is annealed at further higher temperatures, a slight increase in particles size is evident from high magnified SEM image as shown in Figure 4d and 4e [14].

FTIR spectra confirmed the presence of Tween-80 on the surface of iron oxide nanoparticles as shown in Figure 5. A characteristic broad band was observed in range of 3340 cm^{-1} which was assigned to the presence of moisture or active groups coming from Tween-80. The observed broadening of absorption band in this region occurred due to the introduction of three OH groups of Tween-80. Another characteristic peak was observed in range of 550-430 cm^{-1} which indicated the presence of synthesized Fe_2O_3 nanoparticles; this was assigned to vibration mode of hematite phase (Fe—O) present in all the samples. In addition, some prominent peaks were observed for C-O-Fe, C-O-C and CH_2 at 1660 cm^{-1}, 1080 cm^{-1} and 2830 cm^{-1} respectively, which were assignable to the active groups coming from Tween-80, functionalizing the surface of iron oxide nanoparticles. Peak at 1710 cm^{-1} was recorded due to stretching mode of carbonyl functionality from Tween-80 [15].

Thermogravimetric analysis (TGA) was carried in air at a rate of 5 ºC per minute up to 1000 ºC. TGA curve for surface modified iron oxide nanoparticles as shown in

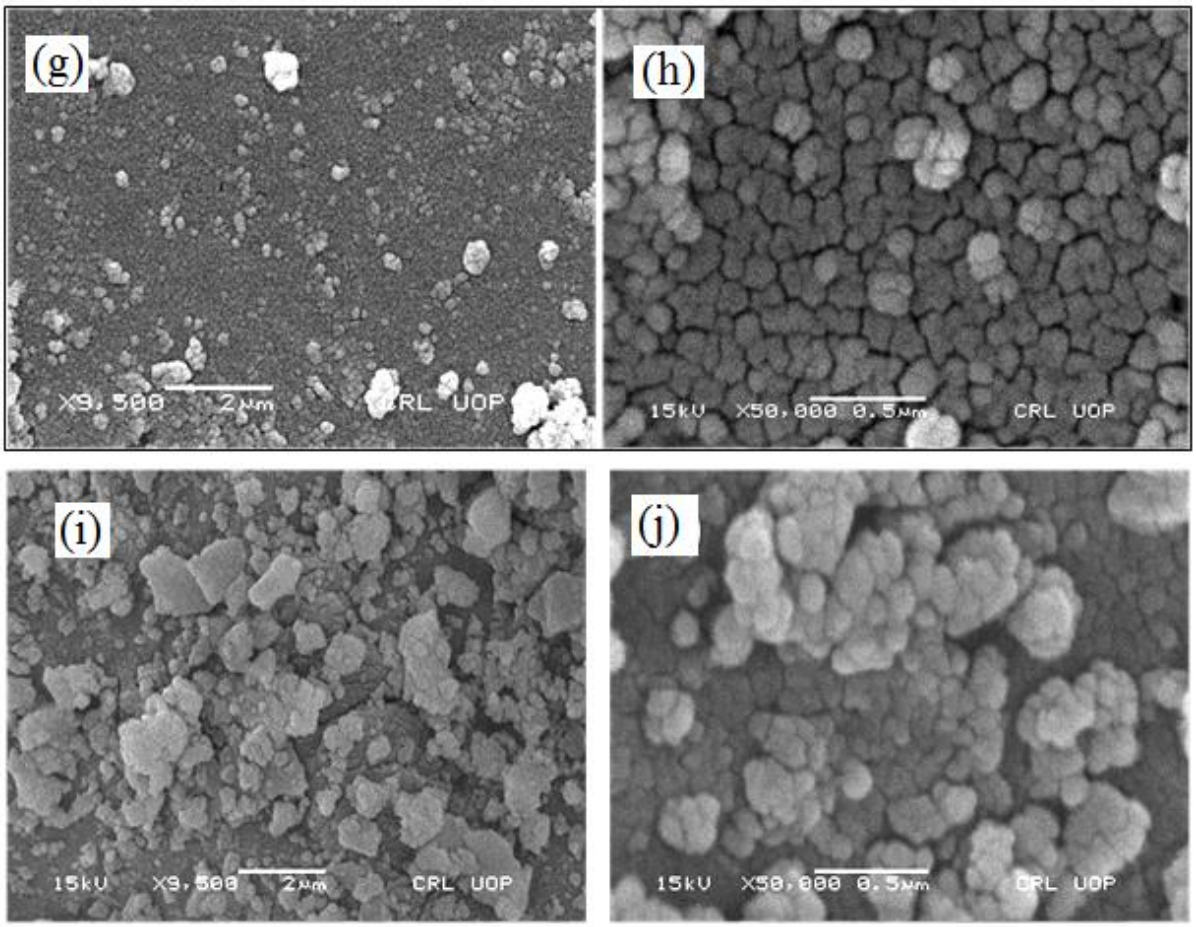

Figure 4. Low and high resolution SEM image of the as-prepared sample (a,b); samples annealed at 200 ºC for 2 hours in air (c,d); 300 ºC (e,f), 400 ºC (g,h), 500 ºC (i,j).

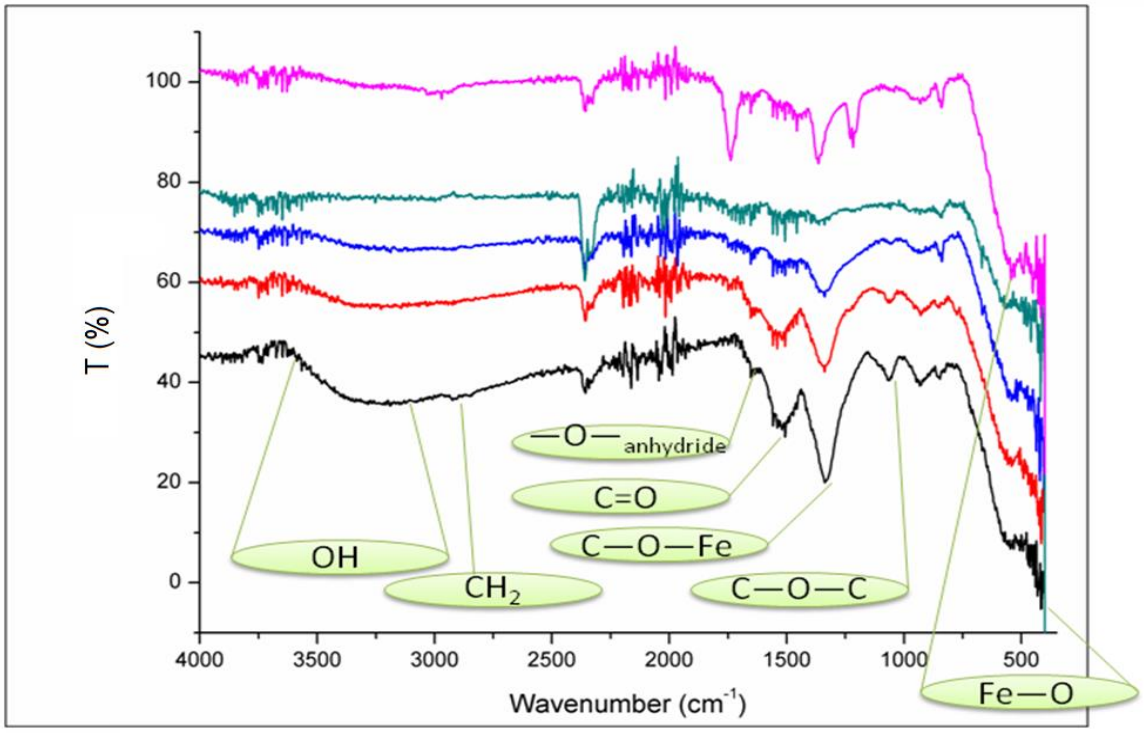

Figure 5. FTIR spectra of iron oxide nanoparticles surface modified using Tween-80.

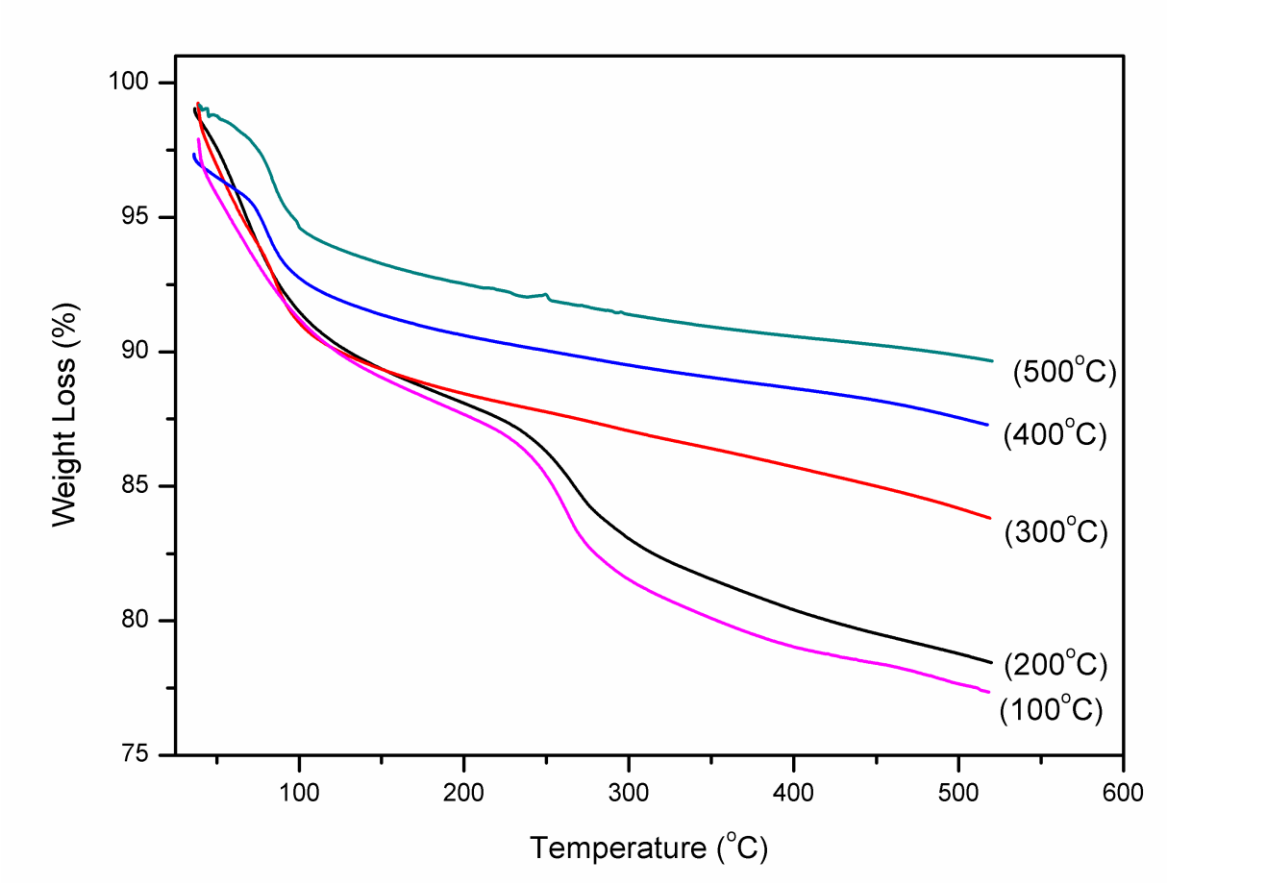

Figure 6 TG curves of the iron oxide nanoparticles annealed at different temperatures

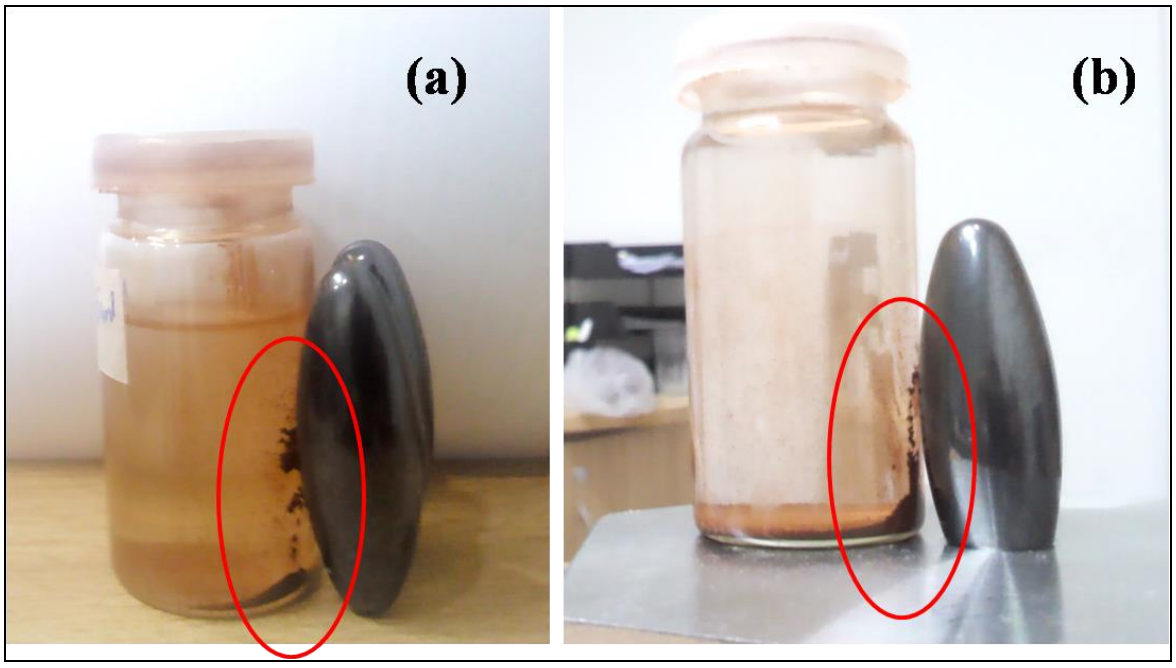

Figure 7 Images showing magnetic behavior of surface modified SPIONs.

Figure 6. Presence of Tween-80 was confirmed by TGA data, characterized by two step weight losses. First step weight loss was observed because of evaporated chemisorbed water over a temperature range of 150-200 ºC. This weight loss was attributed to desorption of chemisorbed water from the surface of iron oxide nanoparticles. With the gradual increase in temperature, gradual weight loss was seen in TGA curve because of the fact that Tween-80 is an organic surfactant and decomposes readily from the surface of iron oxide nanoparticles, even at 500 ºC whole of the organic compound Tween-80 might be evaporated [16].

Figure 6 shows optical images of the magnetic behavior of synthesized SPIONs. The sample were suspended in distilled water and placed beside a tinny magnet. The nanoparticles prepared without Tween-80 showed no affinity to external magnetic field and settle down after 2-3 hours. The nanoparticles prepared with Tween-80 made stable suspensions for at least 5 days and would not settle down. However when placed beside an ordinary magnet, the suspension attracted the SPIONs and settled down making a peculiar curvature with the side walls. All the nanoparticles settle beside the magnetic field that showed their strong paramagnetic behavior [17].

4. Conclusions

Amorphous iron oxide nanoparticles were prepared and rapidly annealed to preserve the magnetization in these nanoparticles. Absorption studies confirmed the visible absorption in these nanoparticles. Although the nanoparticles appear aggregative under SEM, fine dispersions of the nanoparticles stable for over a week. The ready disperssibility and magnetization in these nanoparticles makes them a potential candidate for use in bio-imaging and photo catalysis.

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