Stabilization of Magnetite Nano Iron Oxide with a Series of Novel Surfactants

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***Abstract*—** Oleic acid which is one of the palm oil derivatives is known to effectively stabilize dispersions of nanomagnetite in nonpolar solvent. Stabilization occurs because the carboxylic acid group covalently reacts with the surface of the magnetite and the aliphatic chain extends out into the nonpolar solvent, preventing aggregation of the particles by a steric (entropic) mechanism. One goal of this work has been to develop a generalized methodology for stabilizing nanomagnetite dispersions using a series of novel surfactants which had been synthesized from palm oil derivatives so that the resultant modified magnetite nanoparticles can be used in a range of applications.These nanoparticles have been characterized by FT-SEM, DLS, FTIR and XRD. The FTIR results showed that the surfactants had been successfully coated with the magnetite nano iron oxide and it exhibited a particle size in the range of 25-30 nm as shown on the FT-SEM. In addition to that, the X-ray diffraction pattern showed that the the modified nanoparticles is corresponded to the spinal phase of the bare magnetite iron oxide.

***Keywords*:** Stabilization, magnetite iron oxide, surfactants synthesis.

I. INTRODUCTION

Nanoparticles (particles with diameters on the order of 10^{-9} m) has been attracting much attention in the literature because of their unique optical, magnetic, and electrical properties. They are used in a variety of applications including biodiagnostics, gas sensing, and catalysis [2-5]. Nanoparticles, especially those of the coinage elements (i.e. gold and silver), express striking colors in the visible region of the electromagnetic spectrum. These color changes lend to many applications in the optical and optoelectrical fields [3]. Changes in color are caused by the oscillation of the conductive electrons in response to the alternating electric field generated by the electromagnetic radiation. Even more interesting is the ability to modulate the color of the nanoparticles based on interparticle interaction, separation, and size [3-5].

Particles in the nanometer-size range have a strong tendency to agglomerate due to van der Waals interactions. It is therefore important to develop synthetic methods by which the particles can be stabilized, that is, where repulsive forces between the particles can be provided to balance this attraction (Fig. 1(A)) [6]. Generally two types of stabilization are used to prevent agglomeration of nanoparticles, namely, electrostatic stabilization and steric stabilization by adsorbed molecules or steric hindrance [7-8]. Electrostatic stabilization involves the creation of an electrical double layer arising from ions adsorbed on the surface and associated counterions that surround the particle. Thus, if the electric potential associated with the double layer is sufficiently high, the Coulombic repulsion between the particles will prevent their agglomeration (Fig. 1(B) and Fig. 2) [9-10]. Nanomagnetite is particularly desirable because it displays strong ferrimagnetic behavior, and is less sensitive to oxidation than magnetic transition metals such as cobalt, iron, and nickel.

In this study, the steric stabilization method was applied by using a series of novel surfactants which synthesized from palm oil derivatives which can be obtained easily in Malaysia. These surfactants are special because they can be synthesized cheaply, easily and exhibited excellent properties which can be applied in nanochemistry.

II. EXPERIMENTAL PROCEDURE

a. Materials

Oleic acid was purchased from Sigma Aldrich and hydrogen bromide in 33% acetic acid from Merck was used for bromination. $FeCl_3$, $FeSO_4$, thioglycolic acid, thiomalic acid, thiosalicylic acid and DBU of analytical grade purity, which obtained from Merck, Germany were used as starting materials without further purification. Tetrahydrofuran and hexane of analytical grade from Fisher Scientific were used without further purification.

b. Synthesis

Synthesis of Brominated Oleic Acid

Brominated oleic acid was synthesized by bromination of 90 % oleic acid with hydrogen bromide in 33 % acetic acid in the presence of hexane for 6 hours. The end product is washed with diethyl ether and deionized water for a few times and then purified with column chromatography with isopropanol/hexane as the eluent in

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the ratio of 4:6. The purified product is used for further reaction.

10-Carboxymethylsulfanyl-octadecanoic acid (T6)

10-Carboxymethylsulfanyl-octadecanoic acid was synthesized by reacting purified brominated oleic acid and thioglycolic acid in the molar ratio of 1:1 under inert atmosphere at ambient temperature in the presence of DBU and tetrahydrofuran for 24 hours. The resulting product was then acidified with 0.5 N acid hydrochloric and extracted with diethyl ether and deionized water. The product was recovered from diethyl ether layer by rotary evaporation and purified with column chromatography with Chloroform/Methanol in the ratio of 6:4.

2-(9-Carboxy-1-octyl-nonylsulfanyl)-malonic acid (T7)

2-(9-Carboxy-1-octyl-nonylsulfanyl)-malonic acid was synthesized by reacting purified brominated oleic acid and thiomalic acid in the molar ratio of 1:1 under inert atmosphere at ambient temperature in the presence of DBU and tetrahydrofuran for 24 hours. The resulting product was then acidified with 0.5 N acid hydrochloric and extracted with diethyl ether and deionized water. The product was recovered from diethyl ether layer by rotary evaporation and purified with column chromatography with Chloroform/Methanol in the ratio of 6:4.

2-(9-Carboxy-1-octyl-nonylsulfanyl)-benzoic acid (T8)

2-(9-Carboxy-1-octyl-nonylsulfanyl)-benzoic acid was synthesized by reacting purified brominated oleic acid and thiosalicylic acid in the molar ratio of 1:1 under inert atmosphere at ambient temperature in the presence of DBU and tetrahydrofuran for 24 hours. The resulting product was then acidified with 0.5 N acid hydrochloric and extracted with diethyl ether and deionized water. The product was recovered from diethyl ether layer by rotary evaporation and purified with column chromatography with Chloroform/Methanol in the ratio of 6:4.

Saponification of T6, T7 and T8

T6, T7 and T8 are saponified with 0.5 N ethnolic potassium hydroxide under reflux for 8 hours. After saponification, the product is purified with absolute ethanol and recrystallized to get the pure compounds.

Method for Preparation of Magnetite Nano Iron Oxide

Magnetite, Fe_3O_4, nanoparticles were prepared by coprecipitation as reported previously by Bee and Massart, [11] but with a little modification.[12] Superparamagnetic nanosized magnetite was prepared by controlled chemical co-precipitation of Fe^{2+} and Fe^{3+} (1:2 ratio) from ammoniacal medium at room temperature under argon atmosphere. In a typical experiment, 1 mmol of ferrous sulfate and 2 mmol of $FeCl_3$ were dissolved in 30 ml of de-ionized and de-oxygenated water. The resulting solution was vigorously stirred at room temperature under an argon atmosphere. Subsequently about 10 ml of 25 % ammonia solution was injected into the flask and stirring was continued for another 30 minutes to allow the growth of the nanoparticles. The solution was then cooled to room temperature and the resulting particles were subjected to magnetic decantation followed by repeated washing with distilled water. The pH of the suspension was brought to neutral by washing with distilled water.

Stabilization of Potassium salt of T6, T7 and T8 with Magnetite Nano Iron Oxide

For stabilization, a 5 mL solution of Potassium salt of T6. T7 and T8 in ethanol was added to 20 mg of colloidal suspension of magnetite nanoparticles at pH 3,7 and 9 with sonication using a high intensity ultrasonic probe (Misonix Ultrasonics-2210) operated at 20 kHz with 100 W power for 30 minutes. The particles were then isolated with a rare earth magnet, washed three times with de-ionized water and sent for FTIR analysis. The colloidal dispersion is sent for DLS, Zeta potential analysis and SEM.

III. CHARACTERISATIONS

a. *Analysis of Chemical Structures.*

The chemical structure of all compounds were analyzed by 1H NMR (Bruker, 400MHz) and mass spectrometry.

10-bromo-octadecanoic acid

H-NMR: 0.9 (t,3H, C**H**$_3$-CH$_2$-), 1.4-1.5 (m,2H, CH$_3$-C**H**$_2$-CH-), 2.1-2.2 (m,2H, -C**H**$_2$-), 2.3 (m, 2H, -C**H**$_2$COOH), 4.0 (m,1H,-C**H**Br).

10-Carboxymethylsulfanyl-octadecanoic acid

H-NMR: 0.9 (t,3H, C**H**$_3$-CH$_2$), 1.4-1.5 (m,2H, CH$_3$-C**H**$_2$-CH-), 2.1-2.2 (m,2H, -C**H**$_2$-), 2.3 (m, 2H, -C**H**$_2$COOH), 4.8 (m,1H, C**H**-S).

2-(9-Carboxy-1-octyl-nonylsulfanyl)-malonic acid

H-NMR: 0.9 (t,3H, C**H**$_3$-CH$_2$), 1.4-1.5 (m,2H, CH$_3$-C**H**$_2$-CH-), 2.1-2.2 (m,2H, -C**H**$_2$-), 2.3 (m, 2H, -C**H**$_2$COOH), 4.8 (m,1H, C**H**-S).

2-(9-Carboxy-1-octyl-nonylsulfanyl)-benzoic acid

-NMR: 0.9 (t,3H, C**H**$_3$-CH$_2$), 1.4-1.5 (m,2H, CH$_3$-C**H**$_2$-CH-), 2.1-2.2 (m,2H, -C**H**$_2$-), 2.3 (m, 2H, -C**H**$_2$COOH), 3.26 (m,1H, C**H**-S), 7.2-8.0 (phenyl), 9.5-10.5 (-COO**H**)

b. *Nanoparticle size and surface charge.*

The hydrodynamic (HD) size of the particle aggregates was measured by laser light scattering using a Brookhaven 90 Plus particle size analyzer. The surface charge of the nanoparticles was investigated through ξ potential measurements (Zetasizer 4, Malvern Instruments) after dilution of the samples in 0.01 M phosphate buffers at pH between 3 and 9.

c. *Characterization of particle structure and morphology*

The phase analysis of the synthesized magnetite nanopowder was performed on an X'pert Pro Phillips x-ray diffractometer. High-resolution transmission electron microscopy (JEOL 3010, Japan) was employed to characterize the microstructure of the different nanoparticle preparations.

IV. RESULTS AND DISCUSSION

a. *Crystal structure, size and morphology of nanoparticles*

The high-resolution x-ray diffraction pattern of bare magnetic iron oxide nanoparticles and modified magnetite nanoparticles with modified moagnetite iron oxide with T6, T7 and T8 was shown in Figure 1. The *d* values correspond to those of spinel phase magnetite [Fe_3O_4] (JCPDS card no. 77-1545). The broadening of XRD peaks indicates the nanocrystalline nature of the synthesized magnetite nanopowder. Taking into account the broadening of each peak in XRD mean crystallite size was calculated by applying Scherrer's equation: $D = 0.9\lambda/\beta \cos \theta$, where D is the average diameter in A° , β is the broadening of the diffraction line measured at half of its maximum intensity in radians, λ is the wavelength of the x rays and θ is the Bragg diffraction angle. The mean crystallite size for modified magnetite nanoparticles was found to be around 11.6 nm.

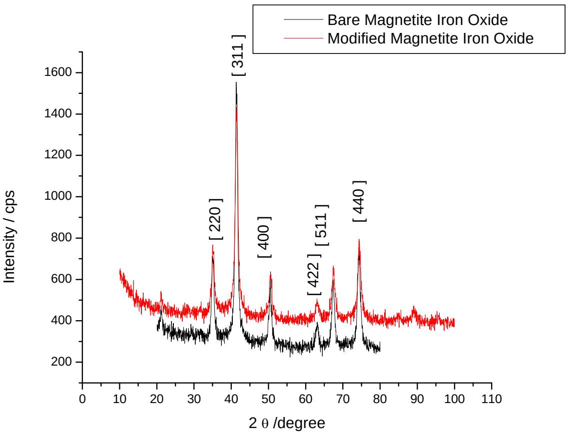

Figure 1: X-ray diffraction pattern of bare superparamagnetic magnetite nanopowder and modified magnetite nanopowder with T6, T7 and T8.

b. *Surface chemistry: FTIR Spectra Study*

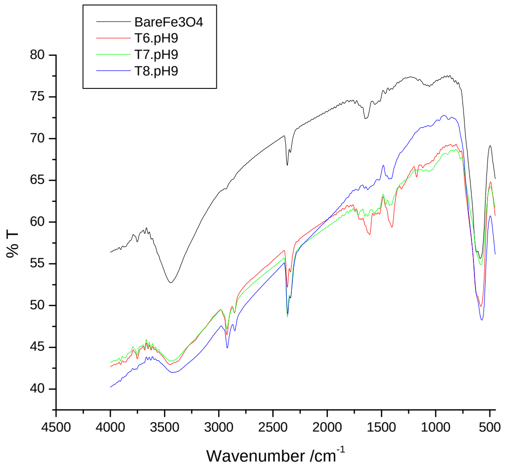

Figure 2 FTIR spectra of bare magnetite iron oxide, T6, T7 and T8.

The transmission infrared spectra of bare magnetite iron oxide and modified magnetite iron oxide nanoparticles for the range 400–4500 cm^{-1} have been depicted in Figure 2. The unmodified iron-oxide nanoparticles show a broad band around 3300 cm^{-1}, indicative of the presence of –OH groups on the nanoparticle surface. The IR spectrum of bare magnetite shows a strong band around 580 cm^{-1}, characteristic of the Fe–O vibration related to the magnetite core

Peaks at 2856 and 2926 cm^{-1} presents –CH_2 stretching of the oleic acid moieties adsorbed onto a metaloxide surface. The typical vibration of a –CO_2H group (1710 cm^{-1}) appear in the corresponding FTIR spectrum, which shows the successful derivatization of the surface-thiol group with Fe_3O_4. The FTIR spectra showed that the characteristic peaks of the functionalized nanoparticles, indicating successful tailoring of the nanoparticle surface with the surfactants.

V. ZETA POTENTIAL MAG IRON OXIDE, HYDRODYNAMIC DIAMETER AND POLYDISPERSITY INDEX OF MODIFIED MAG IRON OXIDE

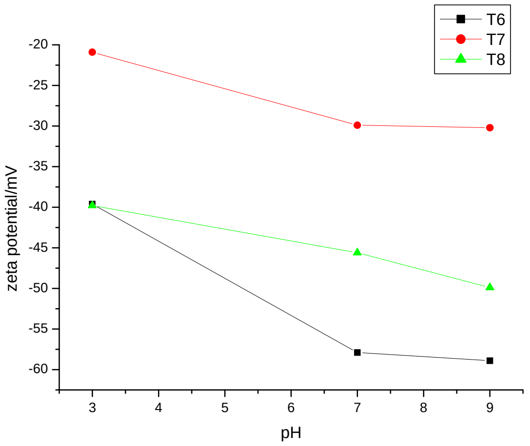

Figure 3 Variation of zeta potential of modified Fe_3O_4 against pH.

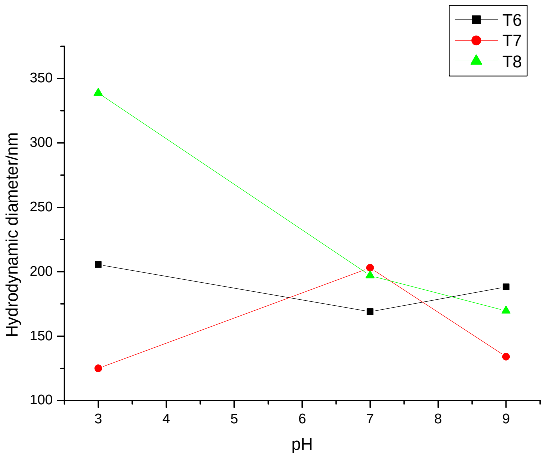

Figure 4 Variation of particle size of modified Fe_3O_4 against pH.

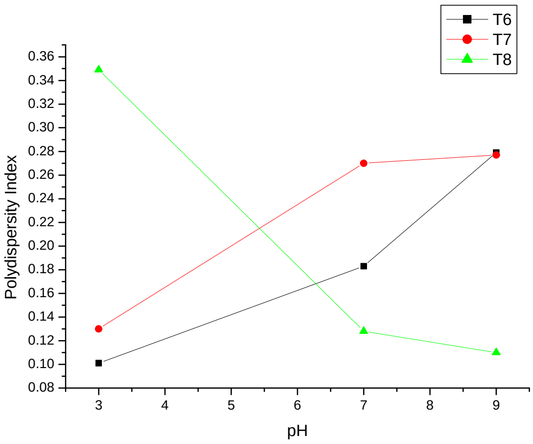

Figure 5 Variation of polydispersity index of modified Fe_3O_4 against pH.

The hydrodynamic (HD) sizes of modified magnetite iron oxide, zeta potential and polydispersity index were measured against pH as shown on Figure 3-5. The modified magnetite iron oxide colloidal dispersion showed a mean HD size of 107.6 nm with a polydispersity index (PDI) less than 0.3. Change of pH (3–9) of the medium had significantly changed the hydrodynamic size of the samples. Measurement of hydrodynamic diameter against pH shows there is no increase in the size of modified particles in slightly alkaline medium, but the particles become comparatively less stable at pH 3 and slight agglomeration takes place with lower pH. The stabilization of Fe_3O_4 nanoparticles with potassium salt of T6, T7 and T8 were due to both steric and electric repulsions because of functionalization with the hydrophilic linker and carboxylic acid groups.

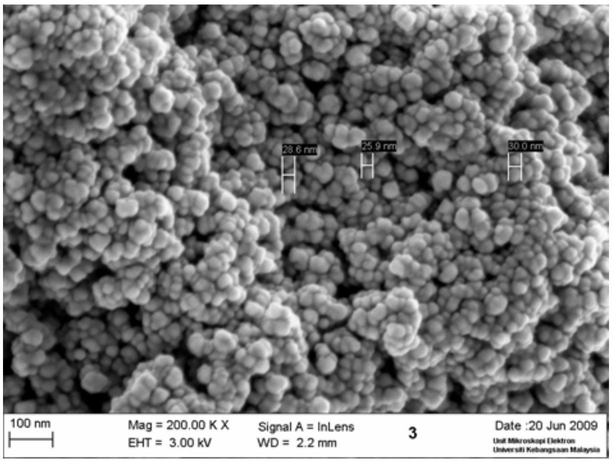

Figure 6 FT-SEM analysis of modified magnetite nano ron oxide

VI. CONCLUSIONS

In this paper, a novel technique has been developed to stabilize superparamagnetic magnetite iron oxide nanoparticles using a novel surfactant which is synthesized from the palm oil derivatives. The stabilized colloidal dispersion impart excellent stability to the magnetic nanosystem in an aqueous medium over a wide range of physiological conditions with reasonably good hydrodynamic size.

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