Study the Effect of Ultrasonic Irradiation and Surfactant/Fe ions Weight Ratio on Morphology and Particle Size of Magnetite Nanoparticles Synthesised by co-precipitation for Medical Application

S.Saloomeh Azimipour Meibod, Peyman Pourafshary, Hamid Reza Madaah Hosseini

Abstract—A biocompatible ferrofluid have been prepared by co-precipitation of $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ under ultrasonic irradiation and with NaOH as alkaline agent. Cystein was also used as capping agent in the solution. Magnetic properties of the produced ferrofluid were then determined by VSM test and magnetite nanoparticles were characterized by XRD and TEM techniques. The effect of surfactant to Fe ion weight ratio was also studied during this project by using two different amount of Dextran. Results showed the presence of a biocompatible superparamagnetic ferrofluid including magnetite nanoparticles with particle size ranging under 20 nm. The increase in the surfactant content results in the narrowing of the size distribution and reduction of the particle size and more solution stability.

Keywords—Biocompatibility, Ferrofluid, Nanoparticle, Size distribution, Ultrasonic irradiation

I. INTRODUCTION

THE magnetic solutions are suspension of ferromagnetic or ferrimagnetic nanoparticles which are single domain and show superparamagnetic behavior. Duo to the unique combination of solid state magnetic properties and liquid state mobility and rehology, ferrofluids have different engineering and medical applications such as hyperthermia [1], drug delivery [2], and the improvement of MRI images contrasts [3]. Using bio-compatible magnetic nanoparticles with special morphology and particle size distribution which cause a stable ferrofluid leads to the lowest therapeutic side effects. In medical applications the optimum particle size is reported to be less than 10nm [4]. The most usual particle which takes place in ferrofluids production is 5-15nm magnetite. In this

dimension range the particle starts to take single domain action and each particle will be a permanent magnet in the medium solution. In such a solution the particles will not deposit easily but they can aggregate to each other by van der Waals force simply which disturb the magnetic properties of solution. To prevent agglomeration, the surface of the particles must be coated by a surfactant layer with the average thickness of 2-3 nm duos to needed properties or application. Up to the type of solvent, ferrofluids divided in to two groups: Alkaline and Aqueous. Alkaline solutions usually have more viscosity and stability but aqueous solutions are more biocompatible and better for medical function [4]. There are different methods to produce ferrofluids such as milling [5], inert gas condensation [6,7], sol-gel [8-11], co-precipitation [12,17], and other ones [18-20]. Ferrofluids can be directly produced in one step in liquid phase with cheaper and common equipments by co-precipitation methods with the flaw of wide particle size range which makes them inappropriate for medical application. By optimizing process parameters such as temperature, mixing strategy, alkaline part concentration, and pH, it is possible to control the particle size distribution [21].

Equation 1 shows the chemical reaction to produce magnetic particle by co-precipitation of Fe^{2+} and Fe^{3+} ions [5].

$$2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \qquad (1)$$
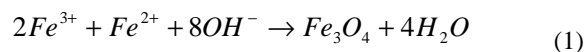
Normally, surfactant will be added to the solution after the reaction is done to avoid agglomeration [5]. To prevent magnetite surface from oxidation it is better to add surfactant during the nanoparticles' creation. If not, Nitrogen (or novel gases) flue can be used to minimize the oxygen potential [22]. By stirring thoroughly, there could be a homogenous turbulence in any part of the reaction bath which causes a narrow particle size distribution. Also ultrasonic irradiation can be used instead of mechanical stirring.

II. METHODS

To produce sample 1U, the salt solution consists of 0.42 gr

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FeCl$_2$.4H$_2$O plus 1.14 gr FeCl$_3$.6H$_2$O in 100 cc pure water was prepared. As mentioned in previous part, in many studies surfactant will be added after the reaction to prevent agglomeration. Here Cystein as a surfactant was added during the production reaction to increase its effect on nanoparticles growing and achieve a sharp particle size distribution. The blowing of the nitrogen was applied to the produced solution under ultrasonic irradiation for 10 minutes. Another solution of 3.56gr NaOH in 100cc pure water was degasified for 10 minutes and added to first one instantly. In past researches, alkalic factor had been added to salt solution slowly and continuously, causes a pH gradient which leads to wide particle size distribution.

The resulted dark solution was introduced to the ultrasonic nitrogen flow for 20 minutes and then separated and dried using magnetic field and centrifuge, respectively. The VSM (Vibrating Sample Magnetometer) test was used to verify magnetic properties and the XRD test was applied on the produced nanopowders for characterization. TEM imaging was also used to define particle size and distribution. To compare the effect of ultrasonic irradiation in particle size distribution, sample 1S was prepared in absence of ultrasonic and characterized by XRD method.

To study the effect of surfactant to Fe ions weight ratio on the size and distribution of nanoparticles, two samples (2L and 2H) were produced with weight ratio equal to 1:3 and 1:1 with Dextran under above condition and characterized by the mentioned methods.

III. RESULTS AND DISCUSSION

Fig. 1(a) shows XRD pattern of Fe$_3$O$_4$ nanoparticles for sample 1U. Six characteristic peaks for $2\theta = 30.16°$, $35.48°$, $43.13°$, $53.49°$, $56.91°$ and $62.71°$ were recognized for this case. For sample 1S (figure 1(b)) only four peaks were realized and the XRD pattern had a high background.
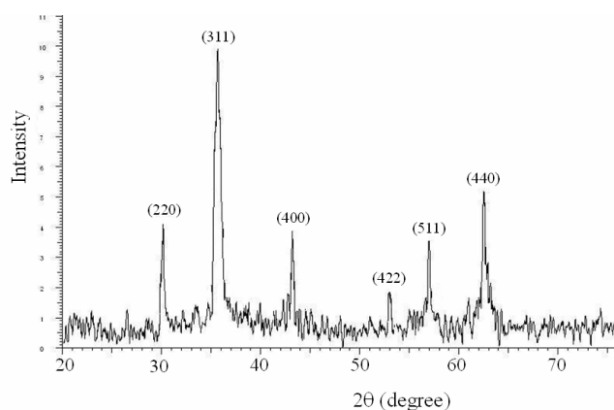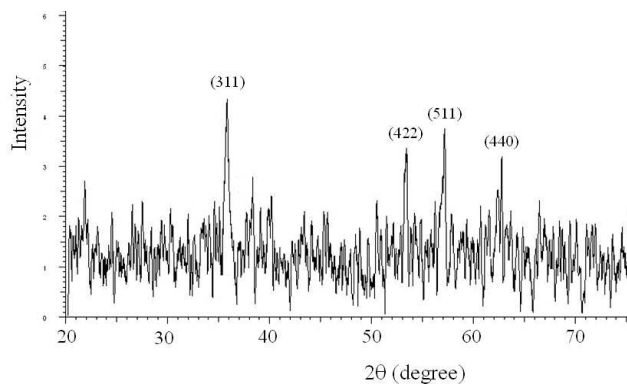
(b)

Fig. 1 XRD pattern of the Fe3O4 nanoparticles for sample (a) 1U and (b) 1S
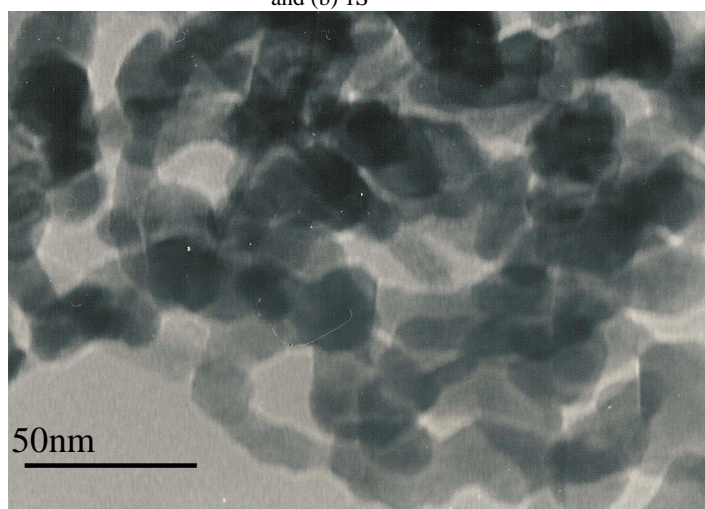

Fig. 2 TEM image for sample 1U, produced with Cystein under ultrasonic irradiation

TEM image of sample 1U which is shown in figure 2, represents a semi-uniform particle size distribution with the average size of 20 nm. Narrow size distribution of Fe$_3$O$_4$ nanoparticles is because of the homogeneity caused by presence of ultrasonic irradiation in synthesis process. Figure 3 shows VSM diagram for sample 1U. Superparamagnetic behaviour of sample 1U is due to the small particle size. Ferrofluid produced in this sample shows good stability which can be suitable for medical applications.

(a)

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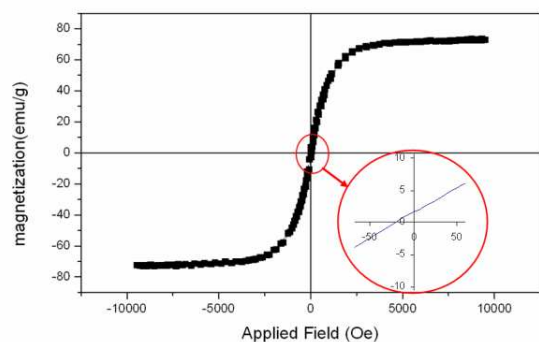International Journal of Chemical and Molecular Engineering
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Fig. 3 VSM diagram for sample 1U, produced with Cystein under ultrasonic irradiation.

Figures 4(a) and 4(b) show XRD patterns for sample 2L and 2H. It can be seen from these figures that the characteristic peaks of sample 2H are wider than sample 2L. This phenomena is due to the inverse effect of Dextran content on nanoparticles size which is in agreement with the previous experiments [23]. Also, sample 2H is more stable than sample 2L
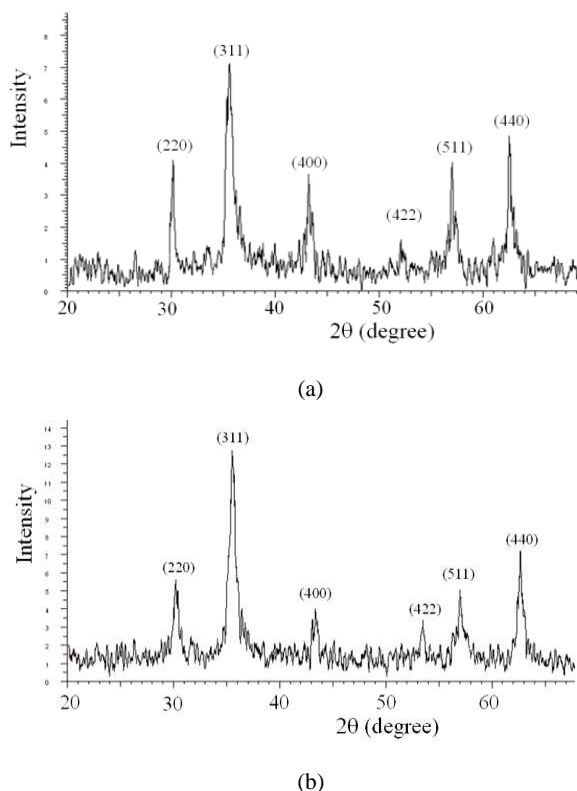

(a)

(b)

Fig. 4 XRD pattern of (a) sample 2L and (b) sample 2H

TEM images of Fe_3O_4 nanoparticles of sample 2L and 2H are shown in Figures 5(a) and 5(b). It can be seen that as the weight ratio of Dextran increases, distribution of the size of nanoparticles becomes narrower and the average size of nanoparticles decreases remarkably. (Average size of samples

2L and 2H are 19nm and 5nm, respectively.) Agglomeration also declined with raising content of Dextran.
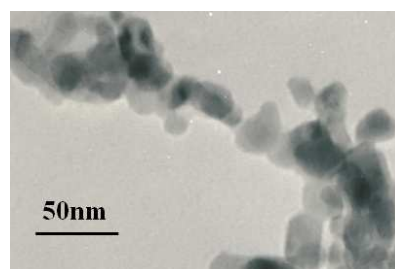
(a)
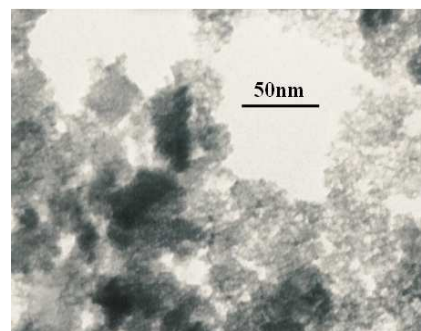
(b)

Fig. 5 TEM images (a) sample 2L (b) sample 2H

When weight ratio of Dextran in solution is large enough in comparison to Fe ions, much more magnetite nanoparticles are coated which prevents nanomagnetites from precipitation and agglomeration. Hence, the size of particles will decrease and stability of solution will increase. When the weight ratio of Dextran to Fe is above 5, solution shows great stability. For the higher ratio, magnetite nanoparticles attach to the Dextran macromolecules and make very big agglomerated areas. FT-IR test shows that attaching mechanism consists of van der Waals forces, hydrogen bounds and electrostatic interactions. Our Experiments showed that two repugnant effects take place when Dextran used as surfactant. Dextran macromolecules could act as the coating for nanoparticles and stop their aging process. On the other hand, entanglement of macromolecules and attachment of magnetite nanoparticles to them could make big clusters in solution. Intensity of ultrasonic irradiation, which increases the nucleation places, also affects the optimum Dextran/Fe ratio in solution.

Figure 6 shows VSM diagram for sample 2L and 2H. Absence of hysteresis loop is an evidence for superparamagnetic behavior. Sample L4H has less saturation magnetization and smaller nanoparticles due to the bigger Dextran content.
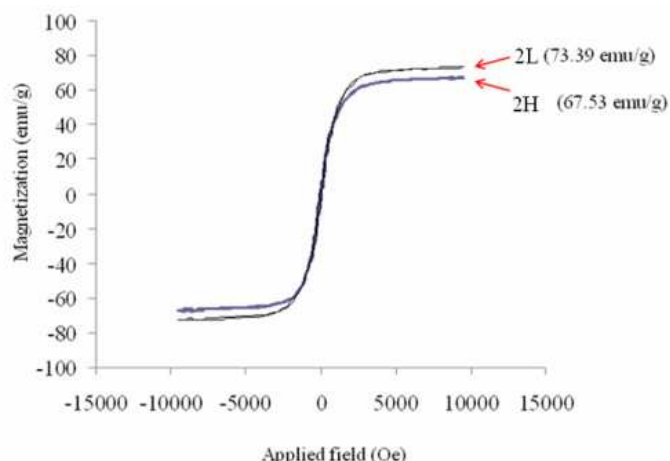
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Fig. 6 VSM diagram of sample 2L and 2H

IV. CONCLUSION

A biocompatible ferrofluid containing Fe_3O_4 nanoparticles was produced by co-precipitation method with Cystein under ultrasonic irritation and without it. The experiments done in this research showed the optimum particle size, narrow particle size distribution, and superparamagnetic properties in ultrasonic assisted produced sample. Due to the next step results, the effect of increase of surfactant Dextran to Fe ion weight ratio on solution stability, agglomeration, reduction in nanoparticle size, particle size distribution, and superparamagnetic properties was verified

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