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IN PURE AND APPLIED SCIENCES

SYNTHESIS AND INVESTIGATION OF THE RHEOLOGICAL PROPERTIES OF Fe_3O_4 AND MnZn FERRİTE BASED FERROFLUIDS

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APPROVAL

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ABSTRACT

SYNTHESIS AND INVESTIGATION OF THE RHEOLOGICAL PROPERTIES OF Fe_3O_4 AND MnZn FERRİTE BASED FERROFLUIDS

Ferrofluids (FF) are stable colloidal dispersions of very fine superparamagnetic particles. The design and synthesis of ferrofluids has been under intensive investigation due to their broad application areas. Different kinds of FFs such as water-based or organic liquid based ferrofluids have been obtained and widely used in dynamic loudspeakers, computer hardware, dynamic sealing, and environmental engineering. The application of aqueous ferrofluids is attracting great attention in biological and medical diagnosis and therapy, in pharmacy, and in biosensors. The particle content, saturation magnetization, suspension viscosity and surfactants for stabilizing the ferrofluids are vital and dominate the process performances. Prevention of particle agglomeration is one of the critical issues to be overcome in producing stable ferrofluids. Thus, nanoparticle stabilizers such as organic surfactants or polymeric compounds have been used in order to modify nanoparticle surface and/or increase their dispersion stability.

In this research, nano-sized magnetite (Fe_3O_4) and MnZn ferrite nanoparticles that are produced by co-precipitation technique are coated with Levan polysaccharide. Levan is a fructose homopoly-saccharide that is produced by a variety of microorganisms in sucrose-based media and it is mainly associated with wide range of applications. Levan used in this study is obtained from the halo-philic *Halomonas smyrnensis* AAD6T bacteria isolated from Turkey. In this study, the magnetic properties, dispersibility and the rheological properties of levan coated Fe_3O_4 ve MnZn ferrite based aqueous ferrofluids are investigated. Visual observations revealed a very little settling of the particles and rheological measurements showed a shear thinning behavior which increased with increasing magnetic field. This indicates that levan coated magnetite and MnZn ferrite could be a potential application in biomedical areas.

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ÖZET

Fe_3O_4 VE MnZn FERRİT BAZLI FERROAKIŞKANLARIN SENTEZLENMESİ VE REOLOJİK ÖZELLİKLERİNİN İNCELENMESİ

Ferroakışkanlar çok küçük süperparamanyetik partiküllerin kararlı kolloidal dispersiyonlarıdır. Geniş kullanım alanlarından dolayı bu akışkanların tasarımı ve sentezlenmesi yoğun şekilde incelenmektedir. Su bazlı ya da organik yağ bazlı olarak sentezlenebilen değişik tip ferroakışkanların, dinamik hoparlör, bilgisayar donanımı, dinamik sızdırmazlık ve çevre mühendisliği gibi geniş uygulama alanı vardır. Su bazlı ferroakışkanlar biyolojik ve tıbbi teşhis ve tedavi, eczaclık ve biyosensör gibi uygulama alanlarında büyük dikkat çekmektedir. Partikül konsantrasyonu, doygunluk mıknatıslanması, dispersiyon viskozitesi ve yüzey aktif maddeler süreç için çok önemlidir ve akışkanın performansına hükmederler. Stabil ferroakışkanların sentezlenmesinde aglomerasyonun önlenmesi başarılması gereken en önemli konulardan biridir. Bu yüzden organik surfaktantlar ya da polimerik bileşikler nanopartikül yüzeyini modifiye etmek ve stabiliteyi arttırmak için kullanılmaktadır.

Bu çalışmada ortak çöktürme metodu ile üretilen manyetit (Fe_3O_4) ve MnZn ferrit nanopartiküller levan polisakkariti ile kaplanır. Levan, sukroz bazlı ortamlarda bulunan çeşitli mikroorganizmalar tarafından üretilen bir homopolisakkarittir ve çok geniş uygulama alanları vardır. Bu çalışmada kullanılan levan Türkiye'den izole edilmiş halofilik *Halomonas smyrnensis* AAD6T bakterisiden elde edilmiştir. Bu çalışmada levan kaplanmış Fe_3O_4 ve MnZn ferrit bazlı sucul ferroakışkanların, manyetik özellikleri dispersibiliteleri ve reolojik özellikleri incelenmiştir. Görsel incelemede ferroakışkanda çok az bir çökelme olduğu görülmüştür ve ayrıca reolojik incelemerde manyetik alanla artan bir kayma incelmesi gözlenmiştir. Bu çalışmalar sonucunda elde edilen levan kaplı manyetit ve MnZn ferrit ferroakışkanlar biyomedikal alanlarda potansiyel uygulamalar olabilirler.

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SYMBOLS

SiO_2	: Silica
TiO_2	: Titania
Al_2O_3	: Alumina
Fe_3O_4	: Magnetite
γ - Fe_2O_3	: Hematite
CdTe	: Cadmium Telluride
GaAs	: Gallium Arsenide
Ag	: Silver
Au	: Gold
MnO	: Manganese(II) oxide
CoO	: Cobalt(II) oxide
NiO	: Nickel(II) oxide
$CuCl_2$	: Copper(II) chloride
Ms	: Saturation Point
H	: Magnetic Field
Mr	: Magnetization Point
Hc	: Coercivity
°C	: Celsius

ABBREVATIONS

nm	: Nanometer
MNPs	: Magnetic nanoparticles
FFs	: Ferrofluids
NPs	: Nanoparticles
XRD	: X-Ray Diffraction
SEM	: Scanning Electron Microscope
FT-IR	: Fourier Transform Infrared Spectroscopy
VSM	: Vibrating Sample Magnetometer
EDS	: Energy Dispersive Spectrometer
MRI	: Magnetic Resonance Imaging

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1. INTRODUCTION

Magnetic fluids are specific subset of smart materials that can adaptively change their physical properties due to external magnetic field. Magnetic control of the properties and behavior of liquids are promising fields for advanced applications and a challenge for basic research. Two main types of magnetic fluids are known since the middle of the 20th century; magnetorheological (MR) fluids and ferrofluids. The former are suspensions of micrometer-sized particles of magnetizable materials dispersed in a liquid carrier. On the other hand, ferrofluids are colloidal suspensions of ultrafine (typically 5-10 nm) single domain magnetic nano-particles such as iron oxide (γ-Fe_2O_3, Fe_3O_4), MnZn ferrites Fe and Co in either polar or non-polar liquid carriers.

The study and applications of ferrofluid involve the multidisciplinary sciences of chemistry, fluid mechanics and magnetism. Because of the small particle size, ferrofluids involved nanoscience and nanotechnology from their inception. Research and development on the preparation, characterization and application of the ferrofluids have been very studied since mid-1960s.

The most important advantage of these fluids is their ability to achieve a wide range of viscosity in a fraction of millisecond. Although they can respond to the action of external magnetic fields, stable ferrofluid show a relatively modest magnetorheological effect, increase in yield strength, compared to magnetorheological fluids (MR) in which micron sized magnetic particles are dispersed in oil. In MRF, the application of magnetic field causes an enormous increase of the viscosity, so that, for strong enough fields, they may behave like a solid. On the other hand ferrofluid keeps its fluidity even if subjected to strong magnetic fields (~10 kG). Since the particle size of the magnetic phase is very small, under ordinary field strengths, thermal agitation gives rise to Brownian forces that can overcome the alignment of the dipoles.

Different kinds of ferrofluids such as water based or organic compound based ferrofluids have been obtained and widely used in dynamic loudspeakers, computer hardware, dynamic sealing, electronic packaging, aerospace, and bioengineering.

Also the treatment of waste water and separation of heavy metals are another area of usage for nanoscaled materials and ferrofluids. In order to detoxify heavy metals, various techniques like photocatalytical oxidation, chemical coagulants, electrochemical, bioremediation, ion-exchange resins, reverse osmosis, and adsorption is used. Among these tecnics nano-based adsorbents are the more convenient. Application of iron oxide based nanomaterial is more attractive for removal of heavy metals contamination from the water because of their important features like small size, high surface area, and magnetic property Magnetic property of iron oxide nanaparticles enables easy separation of adsorbents from the system and could be reused for further application. Reusability of iron oxide based nanomaterial leads to a decrease in the economic loss (Dave and Chopda, 2014).

Use of polysaccharide is a common method for the stabilization of the MNP. Among of these polysaccharides alginate, chitosan, dextran, levan, acacia gum, carrageenan and agarose are placed. Mentioned polysaccharides can be prepared in various ways, and each one provides different features to MNP. Reacting feature with various functional groups of MNP surface makes possible to coat with polysaccharides easily. Hydroxyl carboxylic acid groups or amino acid groups exist in different polysaccharides form strong bonds by interacting with the groups on the surface of MNP. Adsorption of stabilizing agents to surface of MNP is thought to happen with one or more of electrostatic interactions, the formation of surface complexes, hydrophobic interactions, entropic effects, hydrogen bonding, or covalent bond formation cation bridge mechanisms.

In this thesis we have produced levan coated Fe_3O_4 nanoparticles by coprecipitation method and used these particles for water based ferrofluid preparation. Effect of levan coating and concentration of coated magnetic particles in ferrofluid was observed. The coprecipitation method was used due to it is probably the most convenient and simplest way to product magnetic nanoparticles. It is also appropriate for industrial manufacturing. This production route is a cost effective method and allows to large scale production. In the other hand coating material levan was produced by the Bioengineering group under the supervision of Prof. Dr. Ebru Toksoy Öner in Marmara University. Levan is a non-toxic, biologically active, extracellular pollysaccharide that can be produced by plants and micro-organisms. It is a sugar polymer composed of fructose. Levan is a homopolysaccharide containing fructose and this makes the levan a unique carbohydrate polymer.

2. BACKGROUND

Nanotechnology is a science that deals nanosize structures and their applications. Nanotechnology is an interdisciplinary area that involves fundamental sciences; physics, chemistry, biology and applied sciences electronics and materials. Figure 2.1 gives the size ranges of different particles and substances. Nanotechnology is likely to have a profound impact on the economy and society in the early twenty-first century. Research in nanotechnology promises breakthroughs in such areas as materials and manufacturing, nanoelectronics, medicine and healthcare, energy, biotechnology, information technology, and national security.

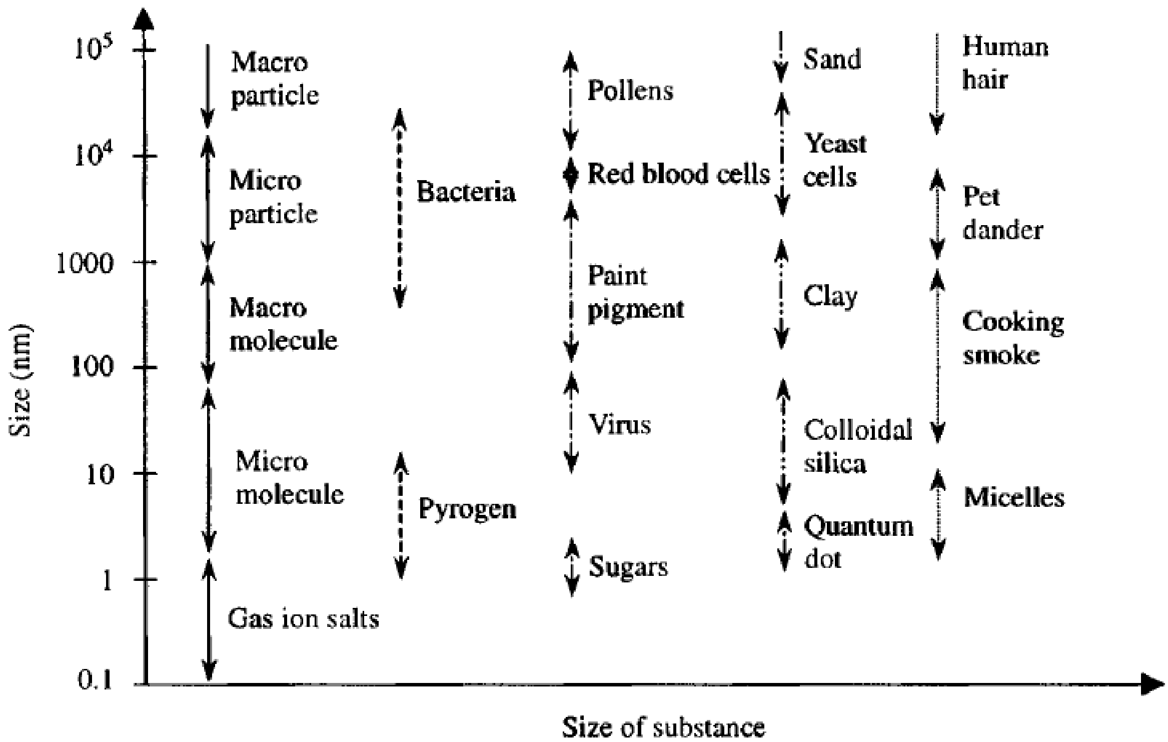


Figure 2.1 Size ranges of different particles and substances (Cao, 2004)

The change in the properties of materials at the nanoscale from those at a larger scale makes these materials attractive. When the dimension of a material is reduced from a larger size, the properties remain the same at the beginning, as the size gets smaller little changes occur, and when the size drops below 100 nm, dramatic changes in properties can occur (Bhushan, 2010)

Nanoparticles can have a variety of sizes and morphologies (amorphous, crystalline, spherical, needles, etc.). Some could be in the form of dry powders or liquid dispersions. The dispersion is obtained by combining nanoparticles with an aqueous or organic liquid to form a suspension or paste. In order to have a stable dispersion it may be necessary to use chemical additives (surfactants, dispersants). Industrial scale production of some types of nanoparticulate materials like carbon black, polymer dispersions or micronised drugs has been studied and established for a long time (Luther, 2004)

2.1. Classification of Nanomaterials

All materials like metals, semiconductors, glass, ceramic or polymers which can be inorganic or organic, crystalline or amorphous particles can be manufactured technically in nanoscale. Table 2.1 summarizes the classification of materials in terms of dimensions, phase compositions, and manufacturing processes.

Table 2.1 Classification of nanoparticles according to different parameters (Luther, 2004)

Classification	examples
Dimension	
• 3 dimensions < 100nm	particles, quantum dots, hollow spheres, etc.
• 2 dimensions < 100nm	tubes, fibers, wires, platelets, etc.
• 1 dimension < 100nm	films, coatings, multilayer, etc.
Phase composition	
• single-phase solids	crystalline, amorphous particles and layers, etc.
• multi-phase solids	matrix composites, coated particles, etc.
• multi-phase systems	colloids, aerogels, ferrofluids, etc.
Manufacturing process	
• gas phase reaction	flame synthesis, condensation, CVD, etc.
• liquid phase reaction	sol-gel, precipitation, hydrothermal processing, etc.
• mechanical procedures	ball milling, plastic deformation, etc.

2.1.1. Nanoparticles

Nanoparticles are consist of tens or hundreds of atoms or molecules. They can have different sizes and morphologies such as amorphous, crystalline, spherical, or needles like. Commercially important class of nanoparticulate materials are metal oxide nanoarticles, such as silica (SiO_2), titania (TiO_2), alumina (Al_2O_3) or iron oxide (Fe_3O4,

Fe_2O_3). Nanoparticulate substances like compound semiconductors (e.g. cadmium telluride, CdTe, or gallium arsenide GaAs) metals (especially precious metals such as silver Ag, gold Au) and alloys are finding increasing product application as well. Besides these powders nanoparticles are combined with aqueous or organic liquids to form colloidal suspensions that can be used to fabricate coatings, component or devices.

2.1.2. Nanowires and tubes

Nanowires, nanodots and nanotubes can be produced by different techniques such as lithography, electrochemical deposition, chemical vapor deposition etc (Pan et al., 2008)(Cao and Liu, 2007)(Hu et al., 1999) and made from different materials such as metals, semiconductors or carbon (Pribat et al., 2009) (Azlin-Hasim et al., 2015) (Feng et al., 2014). Carbon nanotubes can be accepted as one of the most important linear nanostructures and they have diverse modifications such as single- or multiwalled, filled or surface modified (Peci et al., 2015)(Monteiro et al., (2014)(Jaušovec et al., 2015). Logics, data storage or wiring, cold electron sources for flat panel displays and microwave amplifiers are the important application area of nanoelectronics of carbon nanotubes. They are used as fillers to provide special features to materials for nanocomposites as well (Cao, 2004) (Mittal, G., 2015).

2.1.3. Nanoporous materials

Materials which have nanosized pores have importance in industrial applications because of their special properties that include thermal insulation, controllable material separation and release and their applicability as templates or fillers for chemistry and catalysis. Aerogels are good example for nanoporous materials and they are fabricated by sol-gel method. The aerogels have wide range of applications such as catalysis (Xu, et al., 2015) thermal insulation, electrode materials (Fort et al., 2013), and controlled release drug carriers (Alnaief et al., 2012)

2.1.4. Nanolayers

Nanolayer modification is considered as one of the important subjects in the scope of nanotechnology. New functionalities and physical features can be obtained by surface and layer engineering in nanoscale (Tan et al., 2013). Some application fields of nanolayers and coatings are summarised in Table 2.2.

Table 2.2 Tunable properties by nanoscale surface design and their application potentials (Luther, 2004)

Surface Properties	Application examples
• Mechanical properties (e.g. tribology, hardness, scratch-resistance)	Wear protection of machinery and equipment, mechanical protection of soft materials (polymers, wood, textiles, etc.)
• Wetting properties (e.g. antiadhesive, hydrophobic, hydrophilic)	Antigraffiti, antifouling, Lotus-effect, self-cleaning surface for textiles and ceramics, etc.
• Thermal and chemical properties (e.g. heat resistance and insulation, corrosion resistance)	Corrosion protection for machinery and equipment, heat resistance for turbines and engines, thermal insulation equipment and building materials, etc.
• Biological properties (biocompatibility, anti-infective)	Biocompatible implants, abacterial medical tools and wound dressings, etc.
• Electronical and magnetic properties (e.g. magneto-resistance, dielectric)	Ultrathin dielectrics for field-effect transistors, magnetoresistive sensors and data memory, etc.
• Optical properties (e.g. anti-reflection, photo- and electrochromatic)	Photo- and electrochromic windows, antireflective screens and solar cells, etc.

2.2. Magnetic Nanoparticles (MNPs)

Nanoparticles possessing magnetic properties offer great advantages in which they can be attached to a functional molecule and can be manipulated by the control of a magnetic field produced by an electromagnet or permanent magnet. Widespread applications of magnetic nanoparticles (MNPs) in biotechnology, biomedical, material science, engineering, and environmental areas cause much attention to be paid to the synthesis of different kinds of MNPs. Each potential application of the magnetic nanoparticles requires having different properties. Magnetic nanoparticle carriers are composed of three functional parts: a magnetic core, a surface coating, and a functionalized outer coating. The superparamagnetic core is the part that allows magnetic manipulation of the particle in the presence of an external magnetic field. The composition of the magnetic core can vary or different applications. For example, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) have high oxidative stability which makes them acceptable nontoxic MNPs for medical applications (Luther, 2004) (Kamer, 2012). Magnetic cores could also be from the materials such as cobalt, nickel, and neodymium-iron-boron which may offer improved magnetic properties, however, susceptibility to oxidation and being toxic may hinder usage in the human body (Pribat et al., 2009) Magnetic nanoparticles may be synthesized by physical vapor deposition, mechanical attritioning and via chemical routes (Azlin-Hasim et al., 2015) (Feng et al., 2014).

2.3. Magnetic Properties

Basically, materials that give reaction to magnetic field are magnetic. Magnetic materials are classified mainly as five types and Figure 2.2 summerizes these classes:

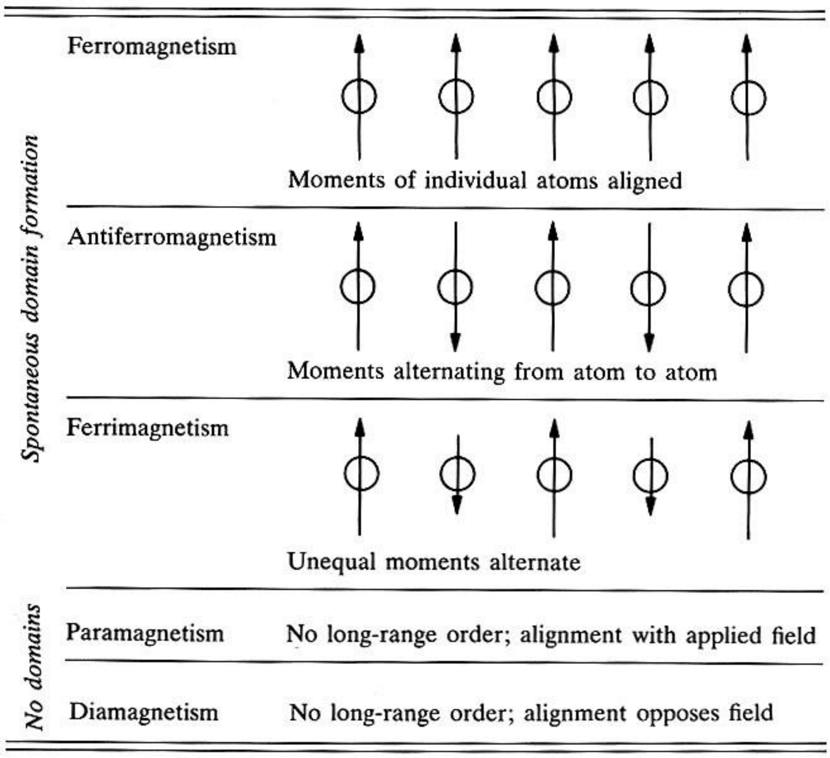


Figure 2.2 Magnetic material classes (Issa, 2013)

Ferromagnetic materials such as iron, nickel, and cobalt consist of domains that include many atoms that have magnetic moments. Ferromagnetic materials have a net magnetic moment because of an atom with unpaired electrons. In each domain the magnetic moments are align parallel and in certain direction and net magnetic moment of each domains points in different direction. The domains that have magnetic moments with different directions are randomly distributed and provide zero net magnetic moment to the material. If a magnetic field is applied to the material, all domains point same direction with field and produce a large net magnetic moment. Even if magnetic field is removed, the material has a magnetic moment.

Paramagnetic materials such as gadolinium, magnesium, lithium, and tantalum have magnetic moments because of their unpaired electrons but they don't have magnetic domains. When a magnetic field is applied to the material, magnetic moments of the atoms are ordered in same direction with applied magnetic field; however they have a weak net magnetic moment. When the magnetic field is removed, magnetic moment of material doesn't remain.

Diamagnetic materials such as copper, silver and gold have create an induced magnetic field in a direction opposite to an externally applied magnetic field, and are repelled by the applied magnetic field. And they don't sustain magnetic moment after external field is removed.

Antiferromagnetic materials such as MnO, CoO, NiO, and $CuCl_2$ are arrangement of two different atoms that have different lattice position. These two atoms have equal magnetic moment with opposite directions as indicated in Figure 2. 2. Hence net magnetic moment is zero.

Ferrimagnetic materials such as magnetite Fe_3O_4 and maghemite γ-Fe_2O_3, Ni ferrite, Cobalt Ferrite and MnZn ferrite are similar to antiferromagnetic materials. They have couples of atoms that occupy different latice sites. As it is seen in Figure 2.2 magnetic moments of these two atoms have opposite direction and they are paralel to each other. However, magnitudes of magnetic moments are different so the net magnetic moment is not zero. Behavior of antiferromagnetic and ferrimagnetic materials are similar with ferromagnetic materials under an external magnetic field, but they have lower magnetization than ferromagnetic materials (Issa, 2013) (Marinin, 2012)

Iron oxides of different compositions such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are most common and widely studied iron oxides. Ferrimagnetic iron oxides shows lower magnetic response than ferromagnetic materials but ferrimagnetic iron oxides are also more resistant to oxidation and so they sustain stable magnetic responses (Harris, 2002). Both magnetite and maghemite have cubic spinel structure. Magnetite and maghemite have similar physical properties and crystal structure (Table 2.3).

Table 2.3 Properties of maghamite and magnetite (Harris, 2002)

	Crystal system	Cell dimensions (nm)	Density (g/cm^3)	Color	Magnetic susceptibility (emu/g)	Curie Temperature (K)
magnetite	cubic	$a_0 = 0.839$	5.26	black	90 - 98	850
maghemite	cubic or tetragonal	$a_0 = 0.834$	4.87	reddish-brown	76 - 81	820 – 986

Magnetite includes Fe^{2+} and Fe^{3+} ions and its chemical formula is Fe_3O_4 or $FeO.Fe_2O_3$. The magnetite mineral has black or grayish black color. Saturation magnetization of bulk magnetite is 90-92 emu/g at 250 ^0C is 90-92 emu/g (Marinin, 2012). Magnetite has inverse spinel structure as it is seen in (Figure 2.3). It has tetrahedral and octahedral sublattices in which Fe^{3+} ions occupy tetrahdral spaces and Fe^{+2} and Fe^{+3} ions occupy octahedral spaces. Magnetite has sixteen iron atoms in octahedral vacancies and eight atoms in tedrahedral vacancies. There are thirty-two oxygen atoms which are cubically face centred. Fe^{2+} ions locate in half of octahedral sites and the other half is occupied with Fe^{3+} ions. All of the tetrahedral vacansies are occupied with Fe^{+3} whereby the iron (II) sits at half of the octahedral sites and the iron (III) is on the other half and all the tetrahedral positions. Spins of these sublattices are antiparalel therefore Fe^{2+} ions that occupy octahedral sublattice determine net magnetization (Thomas, 2010).

Mn-Zn ferrites are other ferromagnetic materials that are technologically important. Because of their high magnetic permeability and low core losses. These ferrite nanoparticles have been widely used in electronic applications such as transformers choke coils, noise filters, and recording heads. Performance of these materials depends on many factors (pH value, temperature, composition etc.).

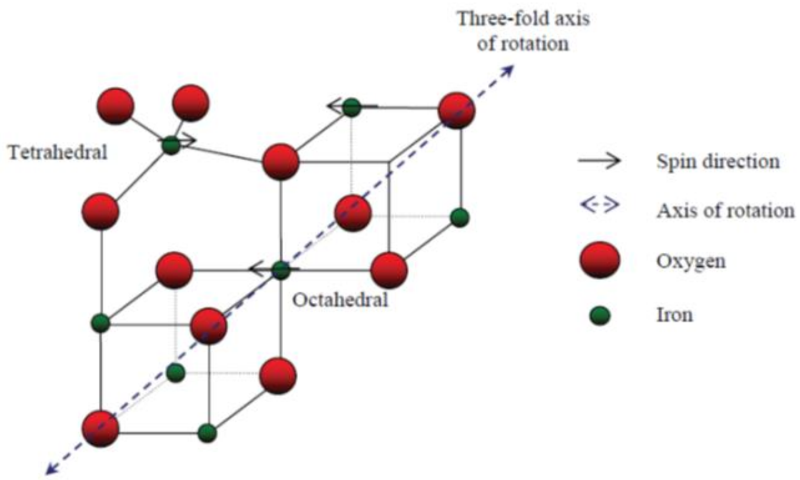


Figure 2.3 Inverse spinel structure of magnetite (Lakay, 2009)

2.3.1. Superparamagnetism

Effect of an external magnetic field on the materials is presented by magnetization hysteresis loop as shown in Figure 2.4. Material type, shape, structure, size, the orientation of the magnetizing field and the interactions between the nanoparticles are also effective on the magnetization and hysteresis loop (Zengin, 2010). When ferromagnetic materials exposes an external magnetic field, a hysteresis loop is obtained as in Figure 2.4.

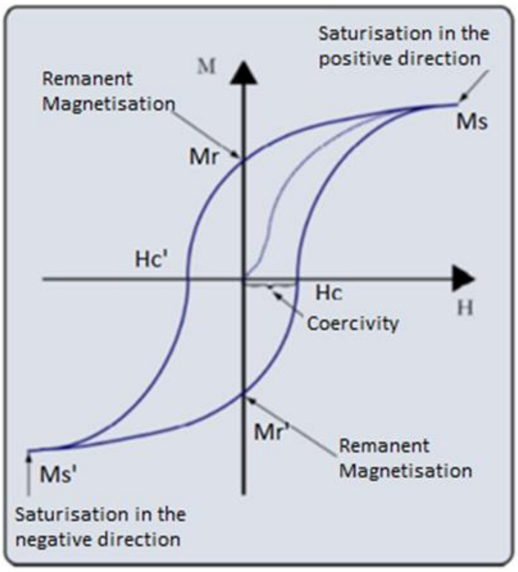


Figure 2.4 A typical hysteresis curve of ferromagnetic materials (Thomas, 2010)

When a ferromagnetic material is encountered with an external field, the material follows the curve of initial magnetization starting from zero magnetic fields on hysteresis curve and reaches the magnetic saturation point (Ms) as the magnetic field (H) increases. Magnetic moment of the domains which ordered randomly at the beginning, have perfect orientation at the saturation magnetization, Ms. All domains align in the same direction. If the applied magnetic field is removed, magnetization of the material decreases to the remanent magnetisation point (Mr). This magnetization level is permanent in the material. Another magnetic field with opposite direction is necessery to bring magnetisation of the material to zero magnetization. This force is called coercivity (Hc'). At this point the orientation of magnetic domains is random again. If magnetic field with opposite direction is continued to apply, hysteresis reaches magnetic saturation point on opposite area (Ms'). After opposite magnetic field is removed, a residual coersive force remains. Opposite coercive force signed as Ms' point. Another magnetic field has to be applied to reach Hc point (opposite of coercive force Hc'). Thus magnetization hysteresis loop is complated (Sülek, 2011)

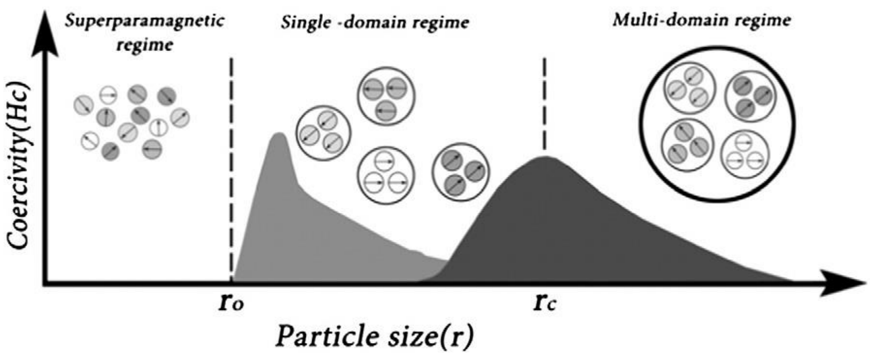


Figure 2.5 Relation between coercivity force with partical size (Karimi et al., 2013)

In 1930, Frenkel and Dorfman talked about superparamagnetic features of nano sized particles for the first time. According to this approach as the particle dimension decreases, the number of magnetic domain of particle decreases and under a critical particle size the material becomes superparamagnetic. Domain structure turns into single domain from multidomain. Coercive force of single domain particles is usually bigger than multidomain particles (Figure 2.5). Due to superparamagnetism, materials don't have a hysteresis, remanent magnetisation (Mr) and coercivity (Hc). Also superparamagnetic materials have stronger magnetization and due to the absence of further magnetisiation after external magnetic field is removed, agglomeration is not observed and this specialty provides to prefer superparamagnetic materials in biomedical application (Karimi et al., 2013)

2.4. Sythesis of Nanoparticles

There are many different production techniques for nanoparticles synthesis and classification of these routes are shown in Figure 2.6. Two approaches have been known in the preparation of small particles. One of these is top-down method where an external force is applied to a solid that leads to its break-up into smaller particles. The second is the build-up (bottom-up) method that produces nanoparticles starting from atoms of gas or liquids based on atomic transformations or molecular condensations (Horikoshi and Serpone, 2013)

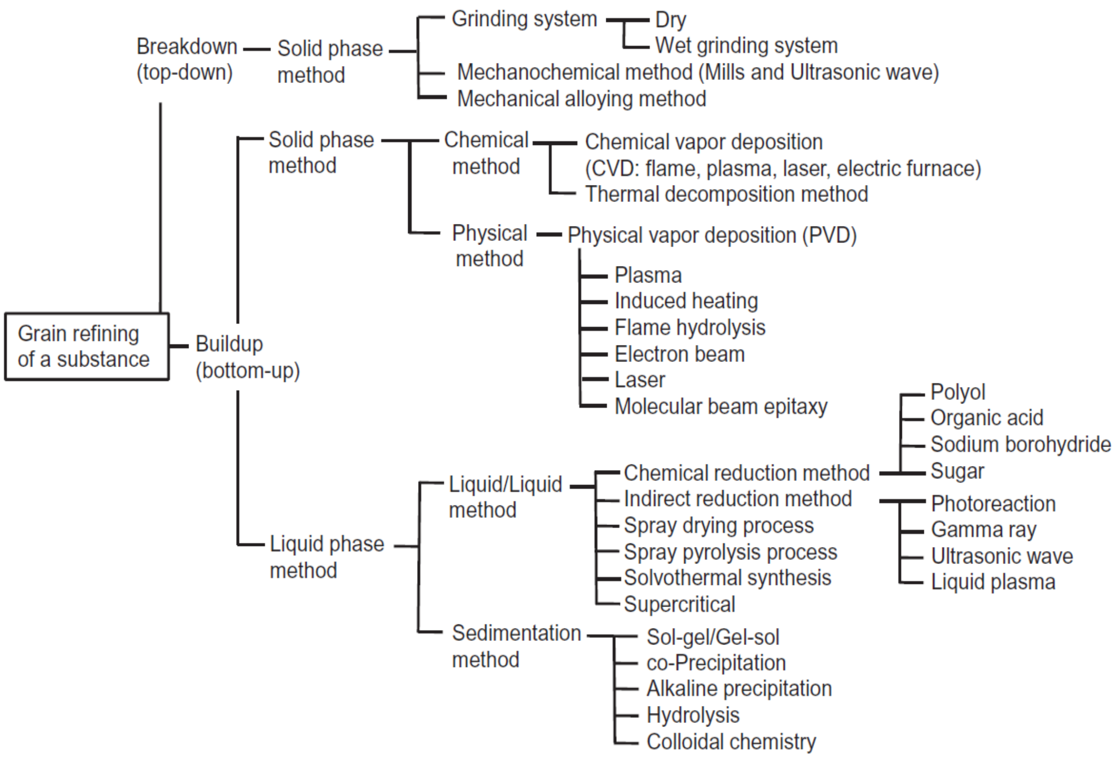


Figure 2.6 Typical synthesis methods for nanoparticles. (Horikoshi and Serpone, 2013)

The co-precipitation method is probably the most convenient, simplest and cost effective method to produce magnetic nanoparticles. According to this method; magnetite is obtained from aqueous Fe^{2+}/Fe^{3+} salt solutions by the addition of a base

(NaOH, NH_4OH or $N(CH_3)_4OH$) under inert atmosphere at room temperature or at elevated temperature. Complete precipitation of Fe_3O_4 occurs at a pH between 8 and 14 with a stoichiometric ratio of 2:1 (Fe^{3+}/Fe^{2+}) in a non-oxidizing environment

The chemical reaction of Fe_3O_4 formation; eq 1.

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \longrightarrow Fe_3O_4 + 4H_2O \quad (1)$$

However, magnetite (Fe_3O_4) is not very stable and is sensitive to oxidation. Magnetite is transformed into maghemite (γ-Fe_2O_3) in the presence of oxygen (Laurent et al., 2008) (Geppert, 2012)

$$Fe_3O_4 + 2H^{+} \longrightarrow \gamma Fe_2O_3 + Fe^{2+} + H_2O \quad (2)$$

There are two steps in the coprecipitation process. Small nuclei form in the medium when the concentration of the species reaches critical supersaturation, and then the slow growth of the crystal occurs by diffusion of the solutes to the surface of the crystal. The nucleation should not occur during the crystal growth step to produce monodisperse nanoparticles. The nucleation and growth should occur separately. Nucleation that occurs at same the time in supersaturated solution provides to narrow size distribution and also particle size control should be accomplished in short nucleation period to achieve small particle distribution. Total particle number doesn't change in growth period, it is determined at the end of nucleation (Laurent, 2008) (Fu, 2012). Precipitated magnetic particles are seperated from solution by a magnetic field at the end of the process. Nanoparticle size, morphology, magnetic properties can be controlled by changing pH of solution, ionic strength, temperature, reaction time, type of salts (Marinin, 2012)

2.5. Coating of Magnetic Nanoparticles

Coating of magnetic nanoparticles is an important approach in the development of magnetic nanoparticles. Due to their high reactivity, nanoparticles have a high tendency to build agglomerates, which causes to lose their particular properties. For this reason, it is often necessary to stabilise the nanoparticles. Functionality of nanoparticles in a particular application usually depends on the stability of dispersions in water or organic fluids with controlled rheology. According to this requirement, coatings are applied to nanoparticles. On the other hand coating nanoparticles is a simple way to change the surface properties of particles (Luther, 2004).

Generally, if iron oxides are the core, its structure can roughly be three types: core-shell, matrix, and $shell_a$-core-$shell_b$ (Figure 2.7). Core-shell nanostructure are achieved by coating iron oxide nanoparticles with organic material. In these structures, any kind of iron oxide particles can be the cores, such as magnetite or maghemite. The shells may consist of all kind of materials that are organic.

Matrix structure has two typical structures; mosaic and shell-core. The shell-core structure consists of organic nanoparticle core and iron oxide particle shell. Iron oxide nanoparticles connect with the organic core by the interaction of chemical bonds (Wu et al, 2008)

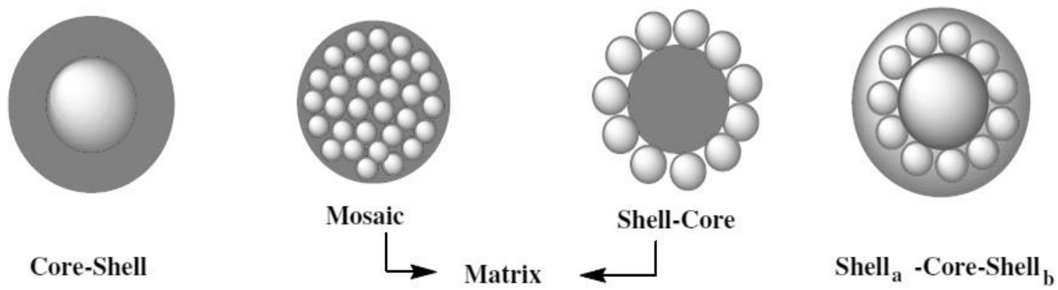


Figure 2.7 Organic materials coated iron oxide nanoparticels structures (Wu et al, 2008)

The mosaic structure comprising the shell layer is made of organic molecules coated to a lot of uniformly iron oxide magnetic nanoparticles. Among the different matrixes that can be used to embed the NPs, polymers are of particular interest because of their wide range of properties.

Furthermore, if a shell-core structure coated with a shell layer made of organic molecules that will form the $shell_a$-core-$shell_b$ structure. The $shell_a$ may be the polymer or biomolecules, also the $shell_b$ can be the same or different functional materials.

There are different kind of approaches to coat magnetic nanoparticles, including during synthesis and postsynthesis coating, which is known as core-shell MNPs. The during synthesis methods have several advantages in comparison with post-synthesis surface modification. These advantages contain reduced agglomeration due to immediate coating of the particles and fewer processing procedures. However, the presence of polymers during nanocrystal nucleation and growth can have a significant impact on the crystal structure and morphology of the MNPs obtained through these processes. For example, Lee et al found that agglomeration, particle size and crystallinity decrease with increasing of poly (vinyl alcohol) (PVA) concentration during the synthesis of iron oxide particles due to immediate coating of the particles (Karimi, 2013, Sun et al., 2008, Lee et al, 1996).

Dipole-dipole attraction cause to aggregation of magnetic nanoparticles. Stability of the magnetic colloid depends on the thermal contribution and on the balance between attractive (van der Waals and dipole–dipole) and repulsive (steric and electrostatic) interactions. Besides the Brownian motion, electrostatic and steric repulsions are the main mechanisms supporting the ferrofluid colloidal stability. Electrostatic interaction is the dominant mechanisms in ionic ferrofluids whereas steric repulsion is the dominant mechanism supporting the colloidal stability in organic based ferrofluids (Genc and Derin, 2014).

Magnetic nanoparticles have hydrophobic surfaces and a large surface to volume ratio. Because of hydrophobic interactions of the the particles with each others, they have poor dispersion in water and organic solvents. This situation between particles causes agglomeration and large clusters. So particle size increases and superparamagnetic properties are lost. For effective stabilization of magnetic nanoparticles, often a coating is desirable.

All metal based magnetic nanoparticles, pure metals and nanoalloys due to their high surface-to-volume ratio, have to be protected from oxidation and corrosion. Iron oxides are less sensitive to oxidation but because of the existence of Fe^{2+} in Fe_3O_4 MNPs, these nanoparticles may be oxidized and converted to α-Fe_2O_3. For example, Hong et al. showed that Fe_3O_4/SiO_2 core/shell MNPs show excellent oxidation resistance, and better in comparison with bare Fe_3O_4 MNPs (Karimi, 2013) (Hong et al., 2009).

Magnetic nanoparticles can be coated different kind of materials such as; organic materials (e.g., polymers such as dextran and polyethylene glycol (PEG)) or inorganic metallic materials (e.g., gold) or metal oxides, active carbon, silica and alumina (Karimi, 2013).

Polymers have more attention among other coating materials and they take increasing interest. Polymeric coatings on magnetic nano particles offer a high potential in several areas of applications. Precipitation of inorganic particles in a cross-linked polymer matrix or network of gel often prevents agglomeration of particles and provide to obtain monodisperse particles Polymeric coatings provide a steric barrier to prevent nanoparticle agglomeration. In addition, these coatings provide to tailor the surface properties of MNPs such as surface charge and chemical functionality (Sun et al., 2008) (Gupta and Gupta, 2005).

Polymeric coating materials can be classified as synthetic and natural. Poly (ethylene-co-vinyl acetate), poly (vinyl pyrrolidone) (PVP), poly (lactic-co-glycolic acid) (PLGA), poly (ethylene glycol) (PEG), and poly (vinyl alcohol) (PVA), are typical examples of synthetic polymeric systems. Natural polymer systems include gelatin, dextran, chitosan, pullulan, starch, etc (Table 2.4) (Karimi, 2013) (Gupta and Gupta, 2005).

Table 2.4 Some of the polymeric coating materials can be classified as on the table (Wu et al., 2008)

Polymers	Advantages	
Natural Polymers	Dextran	Enables optimum polar interactions with iron oxide surfaces, improves the blood circulation time, stability, and biocompatibility
	Starch	Improves the biocompatibility, good for MRI, and drug target delivery
	Gelatin	Used as a gelling agent, hydrophilic emulsifier, biocompatible
	Chitosan	Non-toxic, alkaline, hydrophilic, widely used as non-viral gene delivery system, biocompatible, and hydrophilic
Synthetic Polymers	Poly(ethyleneglycol) (PEG)	Enhance the hydrophilicity and water-solublility, improves the biocompatibility, blood circulation times
	Poly(vinyl alcohol) (PVA)	Prevents agglomeration, giving rise to monodispersibility
	Poly(lactide acid) (PLA)	Improves the biocompatibility, biodegradability, and low toxicity in human body
	Alginate	Improves the stability and biocompatibility
	Polymethylmethacrylate (PMMA)	Generally used as thermosensitive drug delivery and cell separation
	Polyacrylic acid (PAA)	Improves stability and biocompatibility as well as bioconjugation

Properties of polymeric coating material, -as nature of the chemical structure of the polymer (e.g. hydrophilicity/hydrophobicity, biodegradation characteristics, etc.), the length or molecular weight of the polymer, the manner in which the polymer is anchored or attached (e.g. electrostatic or covalent bonding), the conformation of the polymer, and the degree of particle surface coverage- affect performance of magnetic nanoparticle system (Sun et al., 2008).

2.6. Ferrofluids and Rheological Properties

The first studies about ferrofluids have began at mid-1960s. Investigations about ferrofluids involve the multidisciplinary sciences of chemistry, fluid mechanics and magnetism. Besides these science fields, because of the small particle size, nansocience and nanotechnology are also basis of these studies. The most important advantage of these fluids is their ability to achieve a wide range of viscosity in a fraction of millisecond.

There are two main types of magnetic fluids that are known since the middle of the 20th century; magnetorheological (MR) fluids and ferrofluids. The first one is magnetizable micrometer-sized particles dispersed in a liquid carrier. On the other hand, ideal ferrofluids are colloidal suspensions of ultrafine (5–10 nm) single domain magnetic nano-particles. Between ~15 and ~40 nm, the magnetic fluid is still considered as ferrofluids. Above this limit, the fluid is considerd into the area of the MR fluids

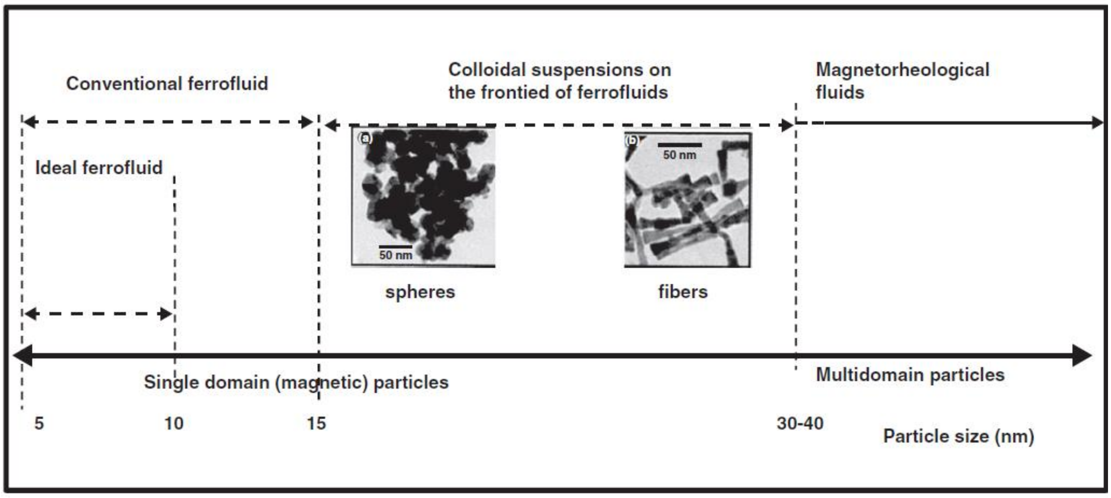


Figure 2.8 Magnetic fluid classification (Genc and Derin, 2014)

Lopez-Lopez and coworkers developed 2 new kinds of ferrofluids. The differences of these fluids with a conventional fluid are particle size and particle morphology. One of them is produced with larger particle size (diameter = 24 nm) and the other one poduced with fibers. (Figure 2.8) gives their classification due to the particle features. These fluids have a larger yield stress and viscosities upon application. However, the stability of these new ferrofluids is worse than the conventional ferrofluids (Genc and Derin, 2014) (Lopez-Lopez et al., 2012).

Magnetic field-responsive materials are an important group of smart materials. They can adaptively change their physical properties due to external magnetic field. Magnetic liquids or ferrofluids (FFs) are colloidal system of ferro or ferrimagnetic single domain nanoparticles (NPs) that are dispersed either in aqueous or organic liquids. The particles that are used in these fluids usually made from magnetite (Fe_3O_4). Also a surfactant is coated for stabilization of particles. Long chained molecules are used as surfactant. The typical thickness of the surfactant layer is about 2-3 nm (Figure 2.9). Thermal energy can prevent sedimentation due to a gravitational field or agglomeration because of dipole interaction. Unfortunately, coagulation that is van der Waals attraction causes, can not be prevented without coating (Khosroshahi and Ghazanfari, 2012) (Odenbach, 2003).

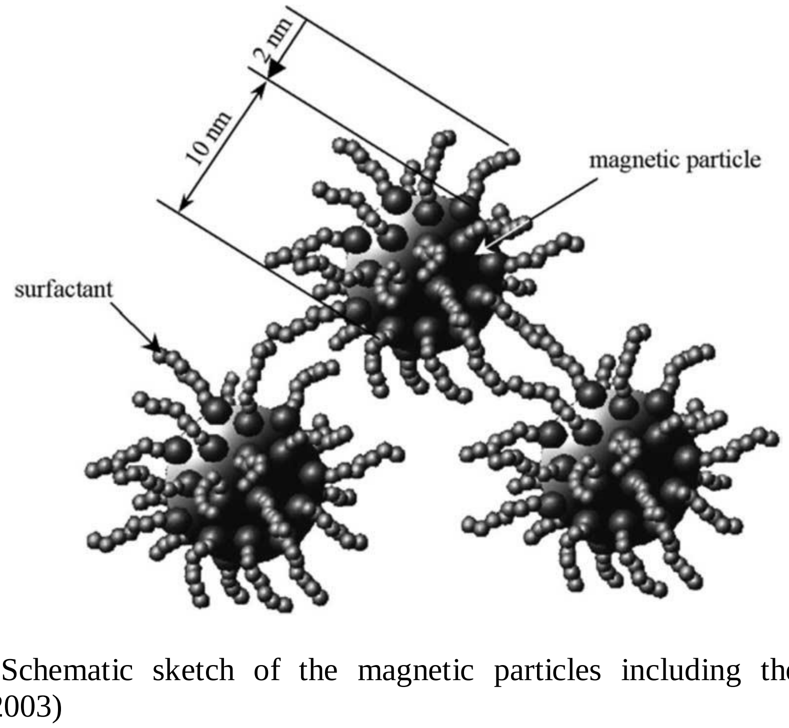


Figure 2.9 Schematic sketch of the magnetic particles including their surfactant (Odenbach, 2003)

Coated surfactant layer provides to sterical stabilization to prevent agglomeration. The type and quality of surfactant will determine the efficiency of particle surface covering and, thus, the balance between attractive and repulsive interactions of particles are adjusted. The attractive interactions may cause to several types of aggregates. The shape of these aggregates are usually linear chains quasi-parallel to the magnetic field or drop-like. The agglomeration is not desired in most applications, so a microstructural characterization is needed for their physical properties. If the agglomeration process is negligible, the physical properties are determined by the orientation of permanent magnetic moments of individual nanoparticles in the presence of an external field (Vekas et al., 2000).

Some investigations (Fujita et al., 1999) (Patel et al., 2003) (Wagh and Avashia, 1996) that are measured under magnetic field, revealed that the viscosity of the magnetic fluid is greater than that of the original carrier liquid in the absence or the presence of an external magnetic field. Strength and direction of the magnetic field are very affective on the viscosity of the magnetic fluid. The viscosity increases with the strength of the magnetic field applied in either the parallel or the perpendicular direction to the main flow and finally reaches a constant as the magnetization of the fluid saturates. But the existing experimental data indicated that the viscosity increase due to the parallel and perpendicular magnetic field to the flow direction is deniable (Li et al., 2005).

Rheology is a major subject of investigating the flow and deformation of materials in an applied magnetic field. Most studies have been focused on measurement of field-induced effects in FFs under shear flow (Pop and Odenbach, 2006) (Borin and Odenbach, 2009), and shear stress versus shear rate (Hassanpour at al., 2007) (Welch et al., 2006). Magnetic particle dispersions are multi-component systems that include magnetic particles and polymers. The polymers are not only present in the solvent but is also adsorbed onto the particle surface. Because of these different components, the rheology of a magnetic particle dispersion is very complicated (Khosroshahi and Ghazanfari, 2012).

Viscosity is very important factor for reology of ferrofluids. Many factors such as solid content, particle size distribution, pH value, temperature and surfactants affect the viscosity (Genc and Derin, 2014).

A ferrofluid sustains of flowibility in a magnetic field, even when it is fully magnetized but the rheology is affected by the magnetic field. Viscosity of the ferrofluids increases with the increase in the magnetic field and the solid concentration (Moeen et al., 2012) (Gu et al., 2008). The increase in the viscosity under magnetic field can be due to the formation of particle chains in the direction of the magnetic field. The interaction between nanoparticles becomes stronger and the particle chains become longer with increase of the magnetic field. If the length of the chains increases, the resistance of the fluid to flow increases and because of this situation the viscosity increases (Genc and Derin, 2014).

2.6.1. Applications of ferrofluids

2.6.1.1. Ferrofluids in cooling applications

The thermal transport properties of ferrofluids are used in loudspeakers. A layer of ferrofluid is placed by the permanent magnet in the loudspeaker. Ferrofluid is replaced with airgap that is between magnet and voice coil. The thermal conductivity of ferrofluid is about five times greater than that of air. Ferrofluids provide to enhance cooling of the coil. Thus, unwanted damping effects, that may be occured due to a solid in the gap, are prevented (May, 2005) (Lee and Kim, 2014).

2.6.1.2. Ferrofluids in magnetic drugs targeting

Drugs are bounded to ferrofluids and injected in cancer tumor. Drug bounded ferrofluid is kept by a magnetic field from outside of body and drugs are applied to target area. The amount of drug necessary is much less than what would be necessary if it were dispersed in the whole body amount. When the magnetic field is turned off the drug will disperse in the body, but, since the total amount is very small, there will be practically no side effects (Scherer and Neto, 2005)

2.6.1.3. Ferrofluids in waste sorting

A ferrofluid that is placed in a magnetic field gradient has local concentration. When a ferrofluid bath placed between inclined magnet poleshoes which develops an artificial density gradient, materials of different densities float at different depths. Peter

Ram et al. are used this method for sorting of polypropylene (PP) and polyethylene (PE) from polymers mixed waste streams. (May, 2005, Rem et al., 2012)

2.6.1.4. Ferrofluids as frictionless seals

A ring of ferrofluid held in place by a magnet around a non-magnetic shaft acts simultaneously as a virtually frictionless bearing and as a seal against dust, moisture etc. Ferrofluid is used commonly in computer hard drives, as a vacuum seal (May, 2005)

2.6.1.5. Ferrofluids in clinical hyperthermia

In treatment of hyperthermia, ferrofluids are injected directly into the tumor. A permanet magnet is applied from outside of the body and ferrofluid is stayed in the tumour. A high-frequency AC magnetic field is then applied, causing the colloidal particles to oscillate rapidly due to the Brownian relaxation process. The oscillation heats the tumour by friction, destroying it from within. Magnetic nanoparticles have an extraordinarily high focused heating effect on target tumor tissues in contrast to surrounding tissues due to the surface and small size effects of the nanoparticles. MFH easily enables the selective heating of different target tissues with different morphologies at various depths in order to avoid excessive damage to normal tissues and treatment-related side effects (Yue et al., 2014)

3. THE STUDY

In this part of the research, the synthesis of the magnetic Fe_3O_4 and MnZn ferrite nanoparticles and the coating process of these particles with levan polysaccharide will be discussed as well as the characterization tehcniques such as, X-ray Diffraction (XRD), Scanning Electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), Zeta Potential and Vibrating Sample Magnetometer (VSM). After the synthesis of the nanoparticles, synthesis of ferrite based aqueous ferrofluids and their characterizations will be described.

3.1. Synthesis of Levan Coated Magnetite (Fe_3O_4) Nanoparticles

Co-precipitation method is used as the synthesis route of the MNP in this study. Nano sized Fe_3O_4 particles are produced from aqueous salt solutions: 9,94 gr $FeCl_2.4H_2O$ (Sigma- Aldrich, ≥ 99.0 %) and 27 gr $FeCl_3.6H_2O$ (Merck, 99,0 – 102,0 %) were dissolved in 300 ml distilled water. Molar ratio of Fe^{+2}: Fe^{+3} was 1:2 according to the reaction given in equation 1. This mixture was stirred vigorously at 500 rpm under nitrogen atmosphere as a non-oxidizing protective gas for fifteen minutes. If the reaction had occured under oxidizing atmosphere, then the molar ratio of Fe^{+2}: Fe^{+3} would have been taken as 2:3 (Maity, 2007)

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O \qquad \text{(Eq. 1)}$$

Meanwhile in another beaker 0.75 g of levan polymer was added in 75 ml distilled water (1 wt %) and mixture was stirred vigorously to achieve a complete dissolution of levan and to obtain a homogeneous solution. Levan was produced by the Bioengineering group under the supervision of Prof. Dr. Ebru Toksoy Öner in Marmara University. It is a homopolymer of fructose units (polyfructose, fructan) and mainly linked by β-(2,6)-glycosidic bonds, with some β -(2,1)-linked branch chains and it is given in Figure 3.1.

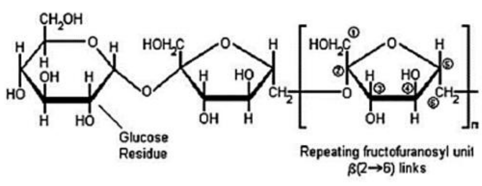


Figure 3.1 Structure of levan (Arvidson et al., 2005)

It is extracellularly produced from sucrose-based substrates by a variety of microorganisms. The bacterium that produces levan is known as Halomonas smyrnensis AAD6 (T) which is isolated from Çamaltı Saltern Area in İzmir. It is a Gram-negative, aerobic, exopolysaccharide-producing, and moderately halophilic bacterium.

After mixing the salt solutions for 15 minutes, levan solution was added into the salt solution. After these two solutions were stirred together for 30 minutes under nitrogen atmosphere, ammonium hydroxide solution NH_4OH (Sigma – Aldrich, 28.0 – 30.0 %), was added until pH value was 9. A black precipitate occurred immediately. The mixture was then heated up to 60 ^{o}C and kept for 30 minutes with vigorous stirring and under protective gas atmosphere to complete the reaction. Because of levan polymer may be affected at temperatures above 60 ^{o}C, this incubation temperature was not increased above 60 ^{0}C. The experimental setup can be seen at Figure 3.2

Figure 3.2 The experimental setup

Following these steps, mixture was left to cool down to room temperature and washed several times with distilled water. Then, the dark magnetite nano-particles were separated from the solution using a strong NdFeB magnet. The MNP slurry was dried under vacuum, at 60 ^{o}C for 12 hours. The synthesis steps are summarized in Figure 3.3.

Consequently, 11 grams of Fe_3O_4 were obtained. Product was a little chunky and black colored.

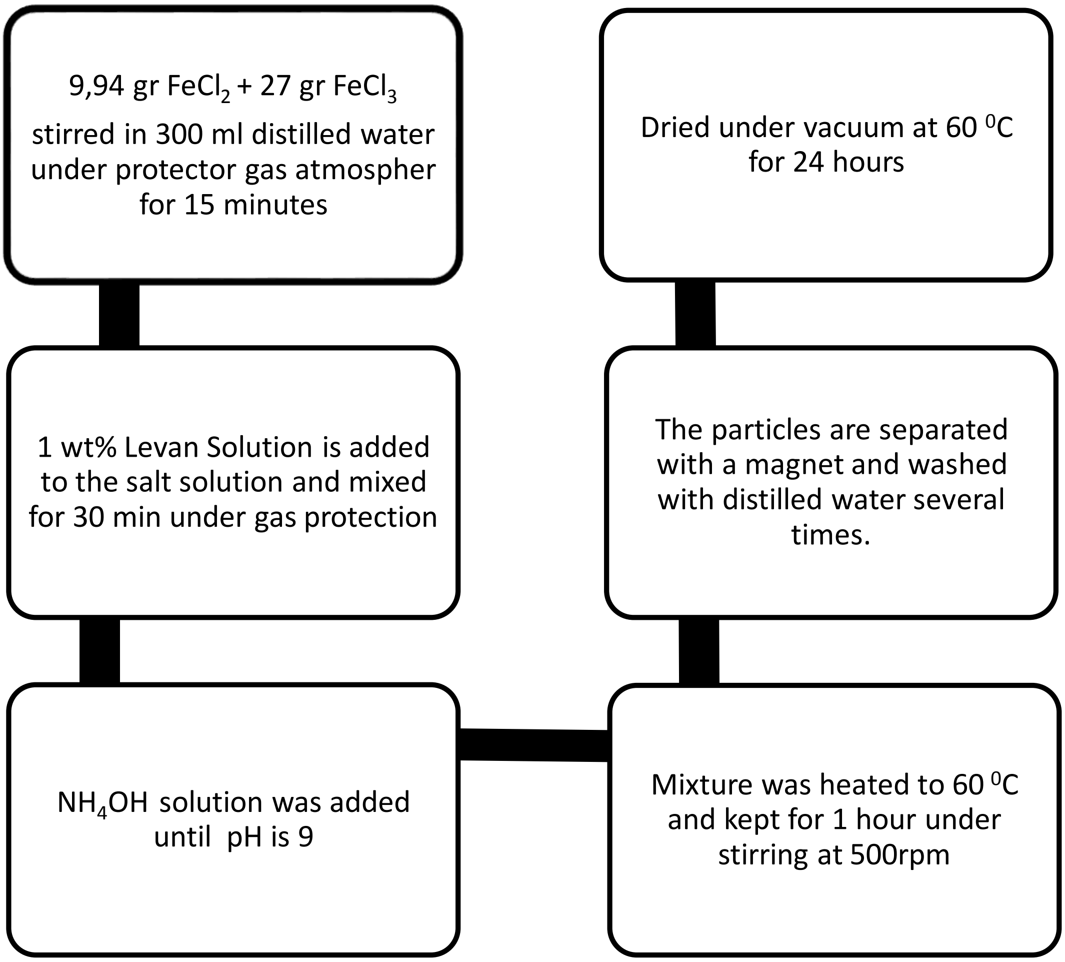


Figure 3.3 Flowchart of experimental study

3.2 Synthesis of Levan Coated MnZn Ferrite Nanoparticles

Co-precipitation method was used as the synthesis route for levan coated MnZn ferrite nanoparticles as well. Nano sized MnZn ferrite particles are produced from aqueous salt solutions: 0.6187 gr $MnCl_2.4H_2O$, 0.798 gr $ZnSO_4.7H_2O$ and 0.8446 gr $FeCl_3.6H_2O$ were dissolved in 20 ml distilled water and mixed for 30 minutes. In another beaker, 0.48 gr levan was dissolved in 50 ml distilled water and mixed for 15 minutes. Then the levan solution was added into the salt solution and mixed for another 15 minutes at 500 rpm. At the end of 15 minutes NH_4OH solution was added until pH was 12. Then the mixture was heated to 60 ^{0}C and mixed for one hour. After cooling down to room temperature, the precipitate was separated with a magnet and washed with distilled water 3-4 times. The particles were dried at 60 ^{0}C for 12 hours. The flow chart of the synthesis procedure is given in Figure 3.4.

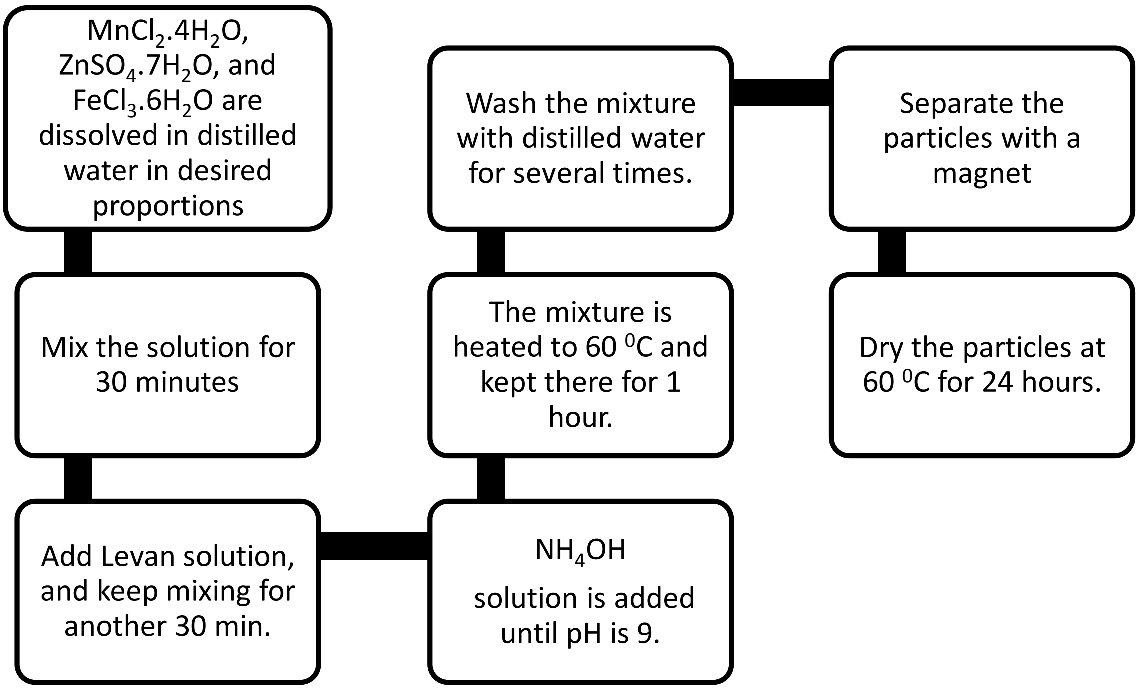


Figure 3.4 MnZn ferrite nanoparticles synthesis process

3.3. X-Ray Diffraction (XRD) Analysis

The structural phase identification of the magnetite nanoparticles and the crystallite size calculations were performed using Rigaku diffractometer (Figure 3.5). The XRD peaks were collected in the 2θ range 20^o -80^o, using CuKα (λ =0,154nm) radiation. Average particle size was calculated using Scherer equation

$$d = \frac{k\lambda}{B\cos\theta} \qquad \text{(Eq. 2)}$$

Where λ is the X-ray wavelength (0.15406 nm), B is the full width at half maximum (FWHM), 2θ is the corresponding Bragg angle, and k is the shape parameter, which is 0.89 for magnetite. The line widths of the most intensive peak were used (311) to calculate average particle size.

Figure 3.5 X-Ray diffractometer

3.4. Scanning Electron Microscope (SEM) Analysis

The morphology and qualitative size distribution of magnetite particles were examined using JEOL JSM-5910LY scanning electron microscope under 20kV (Figure 3.6). After the synthesis was completed, one drop of aqueous dispersion of magnetite was taken by a pipette and dropped on an aluminum stub and it was let for drying. Before the examination by SEM, the sample was coated with Au-Pd to get a better image and to prevent the charging of the particles. Also an energy dispersive spectrometer (EDS) was used with microscope for elemental analysis.

Figure 3.6 Scanning electron microscope, SEM

3.5. Zeta Potential Analysis

Zeta-potential measurements were performed to observe the change in the isoelectric point with coating and also to measure colloidal stability of the prepared ferrofluids. Malvern Instruments Zetasizer 2000 was used for this analysis (Figure 3.7). Magnetite particles of 0.1 grams were dispersed in 500 ml distilled water. The pH values of the dispersion were adjusted by the addition of acid, HCl and base. The measurements were performed by injecting the dispersion into the instrument with the help of a syringe and the zeta potential values were recorded at every different pH value. Before another sample with different pH values was injected into device, the cell was cleaned by injecting distilled water and then air several times.

Figure 3.7 Malvern Instruments Zetasizer 2000

3.6. Vibrating Sample Magnetometer

Vibrating Sample Magnetometer (VSM) systems are used to measure the magnetic properties of materials as a function of magnetic field, temperature, and time. If a material is placed within a uniform magnetic field H, a magnetic moment m will be induced in the sample. In a VSM, a sample is placed within sensing coils, and is made to undergo sinusoidal motion i.e., mechanically vibrated. The resulting magnetic flux changes induce a voltage in the sensing coils that is proportional to the magnetic moment of the sample. The magnetic field may be generated by an electromagnet, or a superconducting magnet. In order to determine the magnetic properties of the synthesized levan coated magnetic particles, the samples were sent to Middle East Technical University Central Laboratories. The hysteresis loop obtained by the VSM measurements gave us the magnetization of these particles.

3.7. Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. The FT-IR spectrum of levan coated Fe_3O_4 and MnZn ferrite nanoparticles were performed in METU Central Lab. The FT-IR scans were performed between 400 and 4000 cm^{-1} spectrum. The interpretation of the FT-IR spectra involves the correlation of absorption bands in the spectrum of the unknown compound with known absorption frequencies for types of bonds.

3.8. Ferrofluid Preparation

After the synthesis of the magnetite nanoparticles coated with levan polymer, ferrofluids with different concentration were prepared. Aqueous ferrofluids were prepared as 5 and 15% by weight of magnetite and MnZn ferrite nanoparticles. In order to have a stable dispersion ball milling procedure was applied. Ball milling could break up agglomerates that occurred during the drying of the MNPs. Dispersions and yttria stabilized zirconia grinding media with 0,5 mm diameter were placed into small vials shown in Figure 3.8 a and b, respectively. The powder occupied 1/3 of the vial, the grinding media occupied 1/3 of the vial as well. The rest of tubes were filled with distilled water.

(a)

(b)

Figure 3.8 a) Yttria stabilized zirconia grinding balls, **b)** Vial

The ferrofluid was mixed for 5 minutes under a high energy vibration by a ball mill (Figure 3.9). Due to the heating of the dispersion, the duration of the grinding was kept at 5 minutes.

Figure 3.9 Bead beater that is used for ball milling

3.9. Rheological characterization

Viscosity of synthesized fluids was determined by Bohlin Gemini 2 Rotonetic Drive 2 rheometer (Figure 3.10). Shear thinning and thixotropic properties of MR fluids were determined under the range of 0.1-100 1/s shear rate and also different constant shear rates (0.1, 1, 50, 100, 150 1/s). Shear thinning is a steady-state property, the speed and stresses will be applied until ferroluid raches the steady state. Reological properties of ferro-fluids will be determined at the room temperature.

(a) **(b)**

Figure 3.10 a) Bohlin Gemini 2 Rotonetic Drive 2 rheometer **b)** Anton Paar MRD

On-state rheological measuremets were performed using rotational magnetorheometer (Anton Paar MRD) in Sakarya University. Yield stress and viscosity characterization were performed by the rheometer.

4. RESULTS AND DISCUSSION

4.1.SEM Analysis Results

Particle size distribution morphology and degree of agglomeration was revealed by SEM analysis. Microstructure of particles can be seen at the Figure 4.1. Images were obtained under 20 kV and enlargement was 50000X. According to this micrograph; although agglomerations were occurred, particle shape is nearly spherical and size of particles are in the range of nano-dimension. It is believed that formation of agglomeration was occurred during drying process but these clusters were broken easily by mechanic forces.

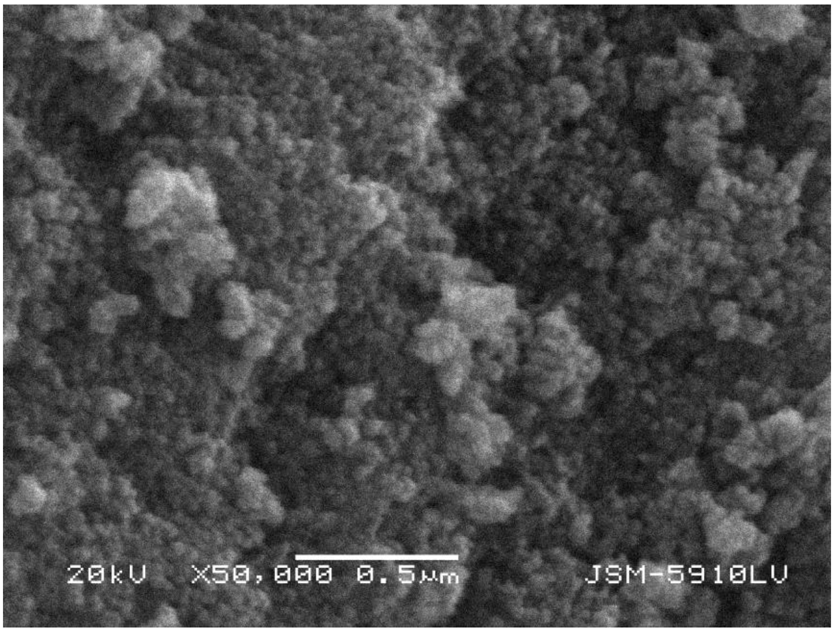
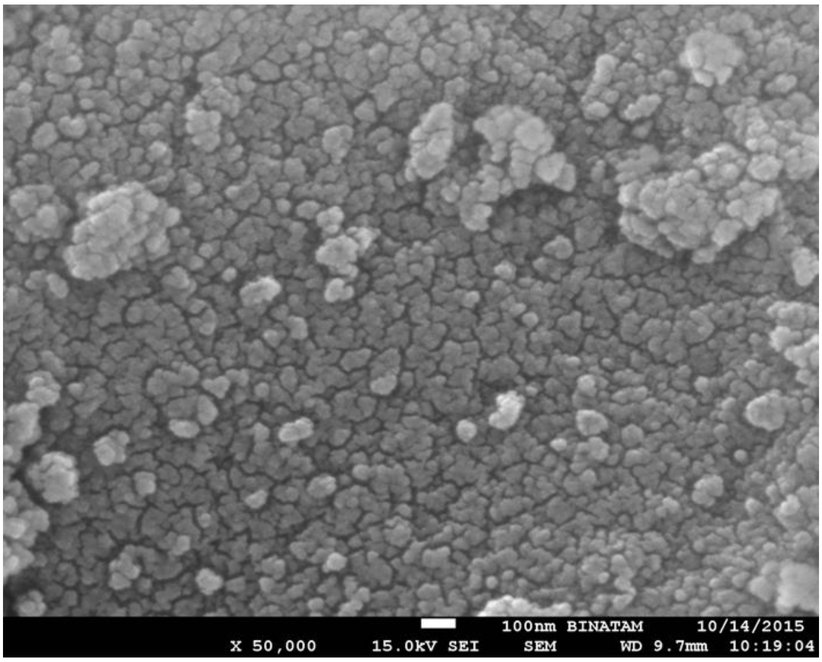
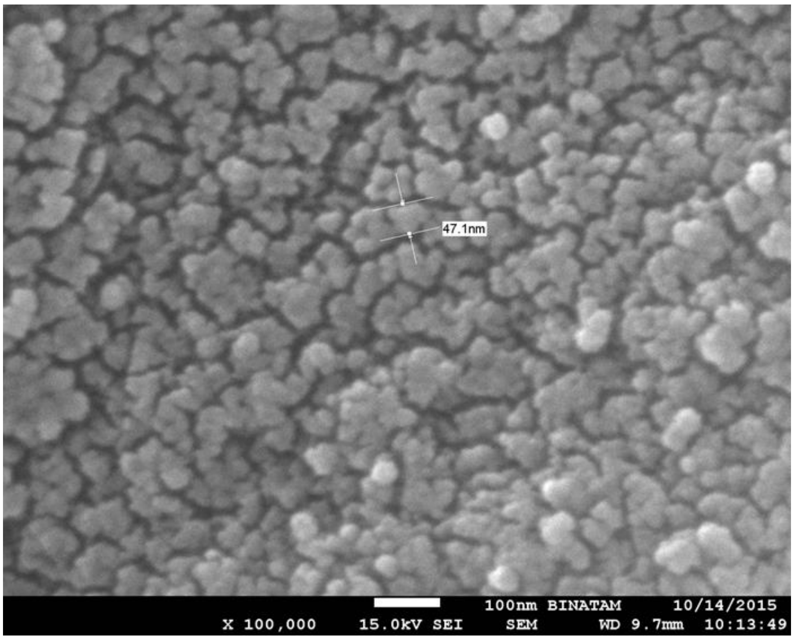


Figure 4.1. Microstructure of Fe_3O_4 nanoparticles



(a)



(b)

Figure 4.2 SEM analysis for MnZn ferrite. **a)** X50000 magnification **b)**X100000 magnification

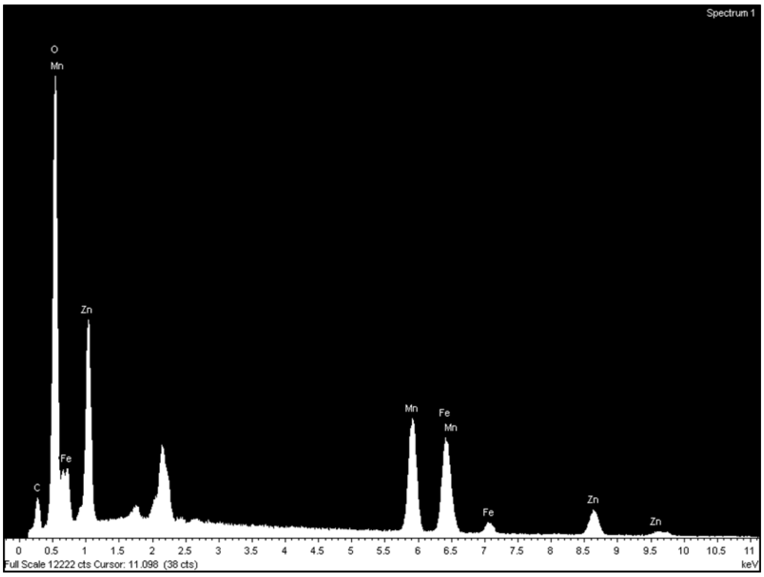


Figure 4.3 EDS analysis for MnZn ferrite

Table 4.1 Elemental analysis of MnZn ferrite

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	5.21	0.1303	13.32	0.44	23.32
O K	68.50	0.4761	47.92	0.33	62.95
Mn K	26.89	0.8037	11.14	0.12	4.26
Fe K	26.63	0.8226	10.78	0.12	4.06
Zn L	12.11	0.2398	16.82	0.19	5.41
Totals			100.00		

4.2 X-Ray Diffraction (XRD) Analysis Results

XRD pattern of the levan coated magnetite particles can be seen at the figure 4.4. This pattern demonstrates that, sample particles have spinel cubic lattice type and peaks correspond well to magnetite. (ICSD card no.01-083-0112) Also, particle size of the sample was calculated according to Scherrer equation using (311) peak as 17 nm .

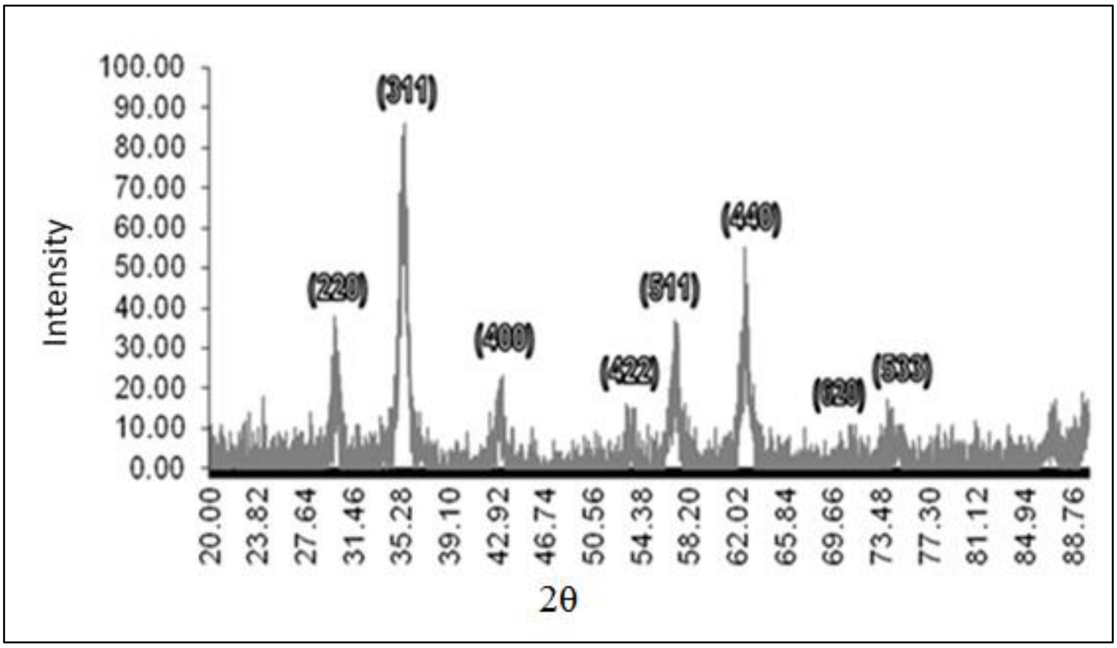


Figure 4.4 XRD analysis for Fe_3O_4 nanoparticles

XRD analysis for levan coated MnZn ferrite particles is given in Figure 4.5. This pattern also demonstrates that the MnZn ferrite sample has spinel cubic lattice type. Particle size of the sample was calculated according to Scherrer equation using (311) peak as approximately 52 nm.

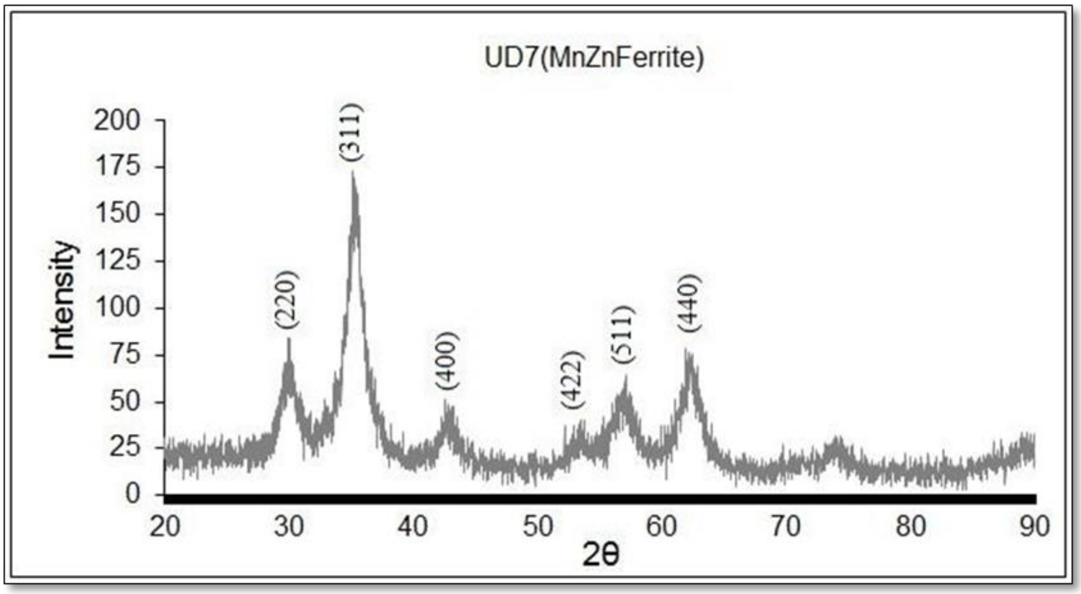


Figure 4.5 XRD analysis for MnZn ferrite nanoparticles

4.3 Fourier Transform Infrared Spectroscopy Results (FT-IR)

FT-IR analysis of levan, levan coated Fe_3O_4 and MnZn ferrite were given in Figure 4.6, 4.7, and 4.8. Figure 4.6 shows the characteristics spectrum for levan obtained and isolated from İzmir Çamaltı Saltern region. This spectrum is given absorption spectrum.

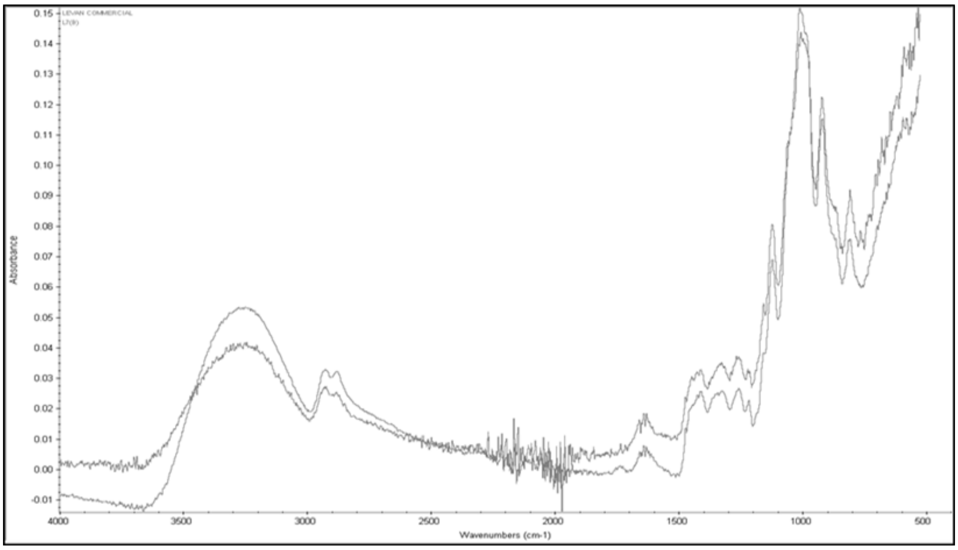


Figure 4.6 FT-IR analysis of levan

FT-IR spectrum of levan coated Fe_3O_4 is given in Figure 4.7. The absorption at 551 cm^{-1} and the broad peak at about 3400 cm^{-1} are assigned to the Fe−O and −OH groups, respectively. In Figure 4.7 characteristic levan peaks can also be seen which indicates the adsorption of levan on Fe_3O_4. Infrared spectroscopy showed that O–H groups are present in the levan polysaccharide, levan coated magnetite near wavenumber of 3500 cm^{-1} with similar intensities. These O–H groups correspond to that present in organic compounds (levan) and to the OH groups adsorb on the magnetic particle surface. The levan coated magnetite particles presented absorption band at 2934 and 2880 cm^{-1} due to stretching vibration of C–H bond band in 1081 cm^{-1} and due to stretching vibration of C–O–C bond. These bonds are also present in the levan polysaccharide with bands in approximately 2900 and 2880 cm^{-1} (stretching vibration of C–H bond),band in 1060cm^{-1} (stretching vibration of C–O–C) which in a way indicates of the presence of polysaccharide in the magnetic particles.

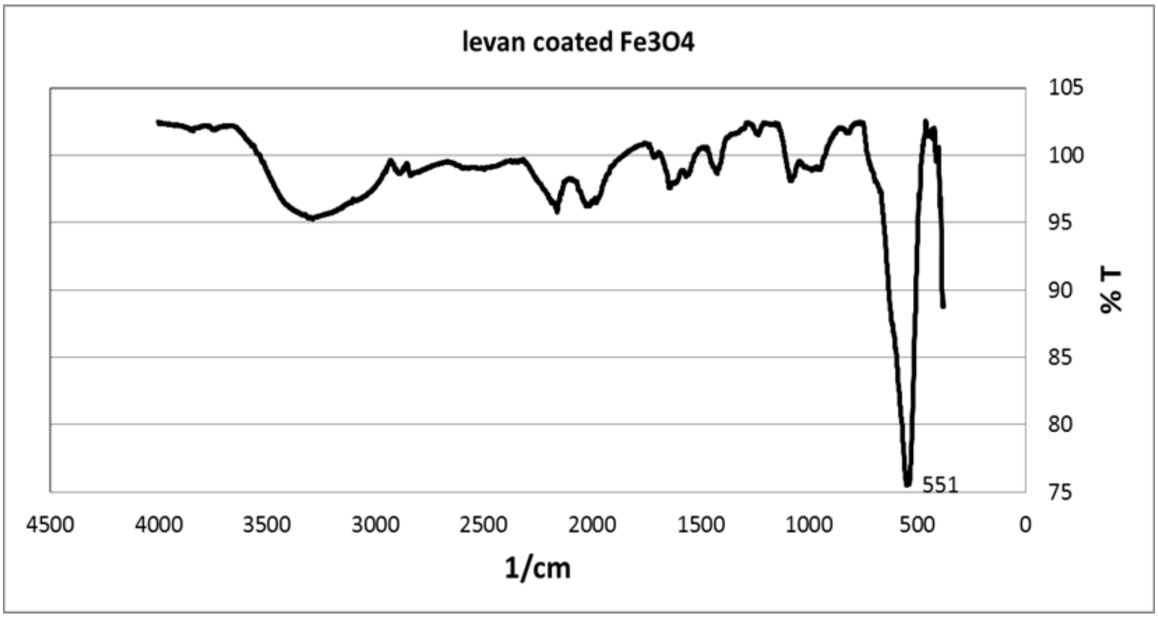


Figure 4.7 FT-IR analysis of Levan coated Fe_3O_4

Levan coated MnZn ferrite spectrum was given in Figure 4.8 and it was recorded in the range 400 to 4000 cm^{-1}. The spectrum shows two main absorption bands below 1000 cm^{-1} which was a common feature of ferrites. The high frequency band lies at 586 cm^{-1} while the low frequency band lies at 443 cm^{-1}. These bands are assigned to the vibrations of the metal ion-oxygen complexes in tetrahedral and octahedral sites, respectively. In Figure 4.8 characteristic levan peaks can also be seen which indicates the adsorption of levan on MnZn ferrite. Figure 4.9 gives the comparison of these magnetic ferrite particles.

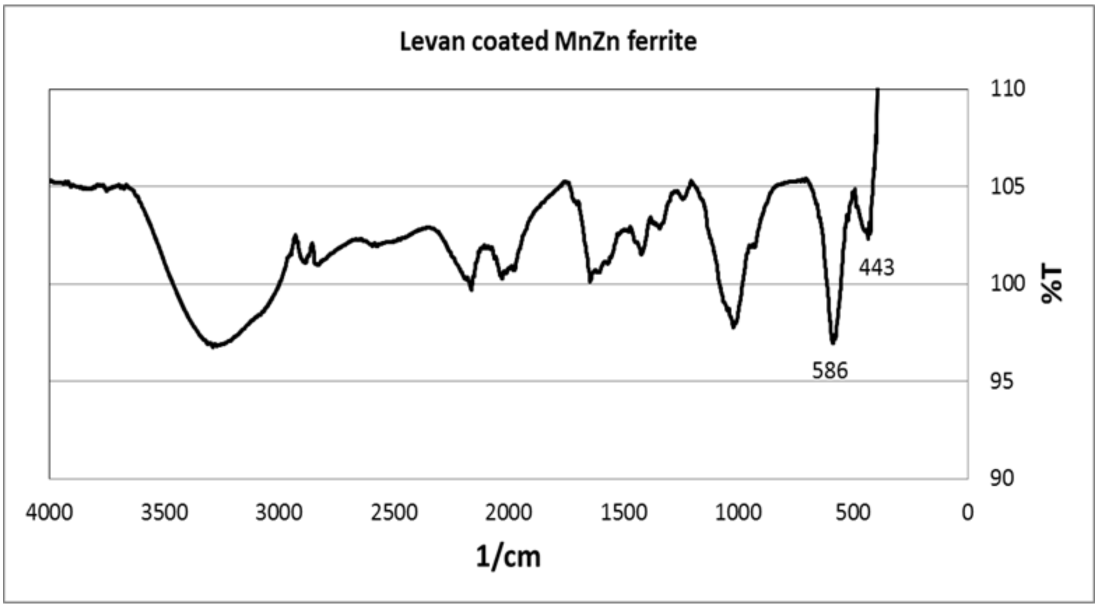


Figure 4.8 FT-IR analysis of levan coated MnZn ferrite

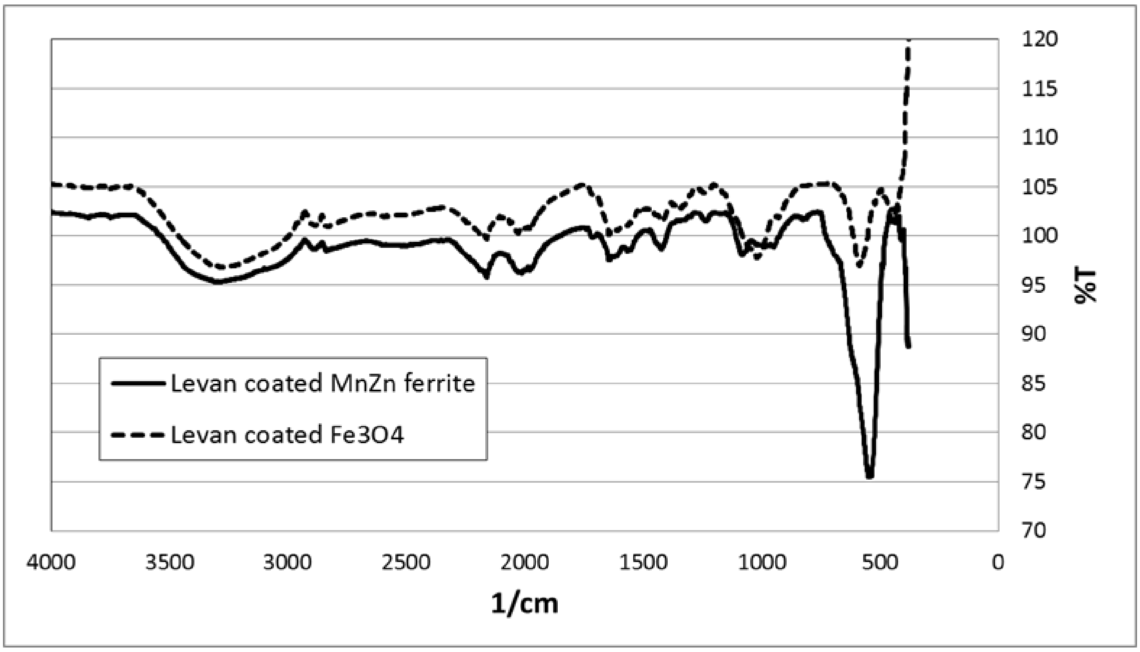


Figure 4.9 Comparison of FT-IR analysis of levan coated magnetite and MnZn ferrite

4.4 Magnetic Measurements

The magnetic properties of the ferrites depend on the size of the nanoparticles. The hysteresis curve obtained by Vibrating sample magnetometer revealed that the particles produced are superparamagnetic with no or very little coercivity. These properties of the magnetic particles provide reversibility in magnetization, i.e. the particles get magnetized under magnetic field and demagnetized completely when the magnetic field is removed. This will be a very important property in ferrofluids. The increase in viscosity with the applied magnetic field goes back to its initial values of viscosity as soon as the magnetic field was removed. The saturation magnetization depends on the particle size and in Figure 4.10, it is seen that the saturation magnetization is approximately 60 emu/gr.

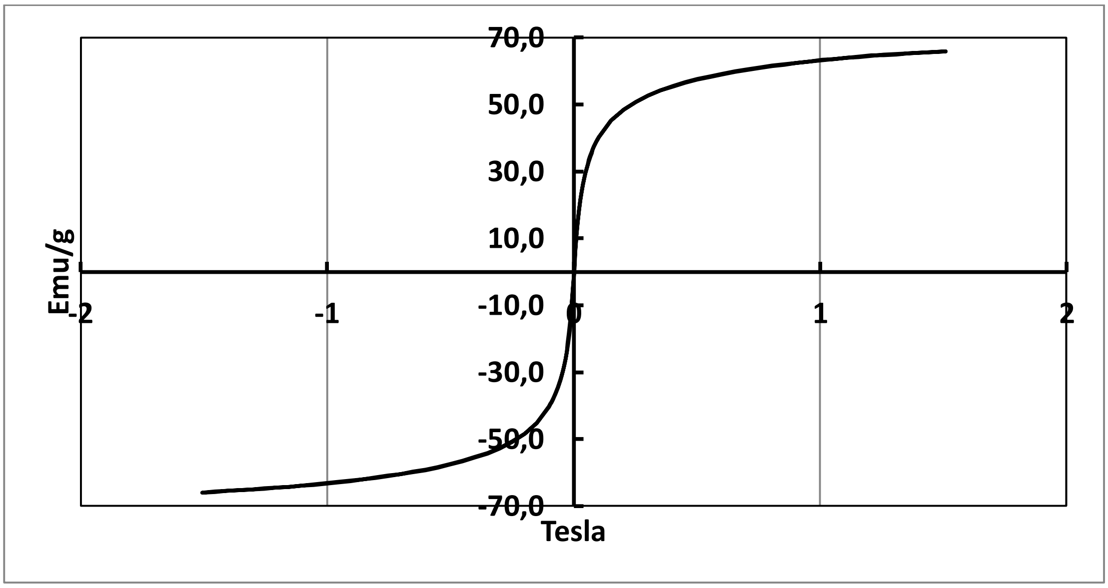


Figure 4.10 VSM analysis of Fe_3O_4 MNPs

4.5 Rheological Analysis

The rheological properties of 5 and 15 wt% magnetite and 5 wt% MnZn ferrite based aqueous ferrofluids were characterized by 2 different rheometers as described in Part III. Off-state rheological measurements were performed by Bohlin Gemini rheometer at Marmara University and on-state rheological properties were measured by Anton Paar rheometer. The viscosity increased as the magnetic field increased and shear thinning behavior was observed at all values of magnetic fields. The off-state (B=0T) viscosity of 5 wt% Fe_3O_4 ferrofluids showed a decrease from 0.12 Pa.s at 1 s^{-1} to 0.003 Pa.s at 50 s^{-1}. At the highest availbale magnetic field (B=0.048 T), the decrease was from 1.035 Pa.s at 1 s^{-1} to 0.024 Pa.s at 50 s^{-1}. Figure 4.11 shows the viscosities under different magnetic fields and Table 4.2 gives the viscosity values under 0, 0.014, 0.031, and 0.048 Tesla magnetic fields and at the lowest and highest shear rates (1 and 50 s^{-1}).

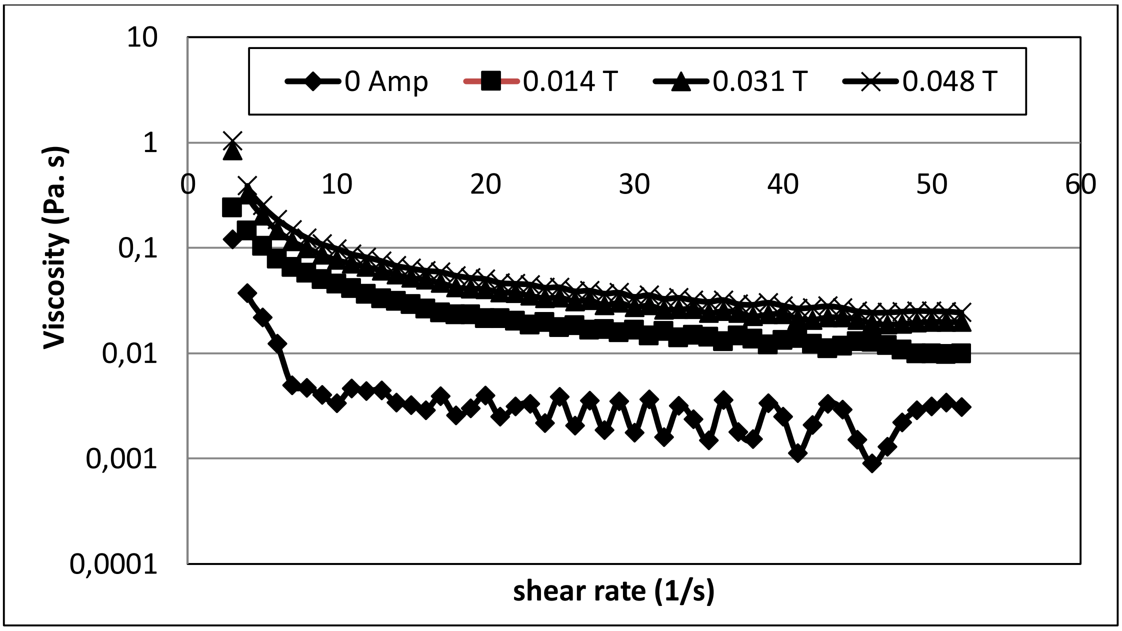


Figure 4.11 Viscosity vs shear rate of 5 weight% magnetite based ferrofluids.

Table 4.2 Viscosity values under different magnetic fields for 5 wt% magnetite based ferrofluids

	Viscosity (Pa.s) 5 wt%			
Shear Rate	B= 0 T (off-state)	B=0.014 T	B=0.031 T	B=0.048 T
1.0 s^{-1}	0.12	0.24	0.84	1.035
50 s^{-1}	0.003	0.0099	0.01981	0.02424

The viscosities for 15 wt% magnetite based ferrofluid were given in Figure 4.12 in which the same characteristic was also observed in this sample. The viscosities increased with increasing magnetic field. Table 4.3 gives the viscosity values under magnetic fields of 0, 0.014, 0.031, 0.048, and 0.068 Tesla and at the lowest and highest shear rates (1 and 50 s^{-1}). The off-state (B=0T) viscosity of 15 wt% Fe_3O_4 ferrofluids showed a decrease from 0.03 Pa.s at 1 s^{-1} to 0.064 Pa.s at 50 s^{-1}. At the highest available magnetic field (B=0.068 T), the decrease was from 13.04 Pa.s at 1 s^{-1} to 0.19 Pa.s at 50 s^{-1}.

A discrepancy was observed in the off-state viscosities of 5 wt% Fe_3O_4 and 15 wt% Fe_3O_4 based ferrofluids in which the off-state viscosity of 5 wt% Fe_3O_4 based ferrofluid was higher than that of 15 wt% ferrofluid at the lowest shear rate. This could be due to the fact that with higher concentrations at the low shear rates, the viscosity could only be measured close to the walls. For this measurement, the fluid could have been sheared longer time.

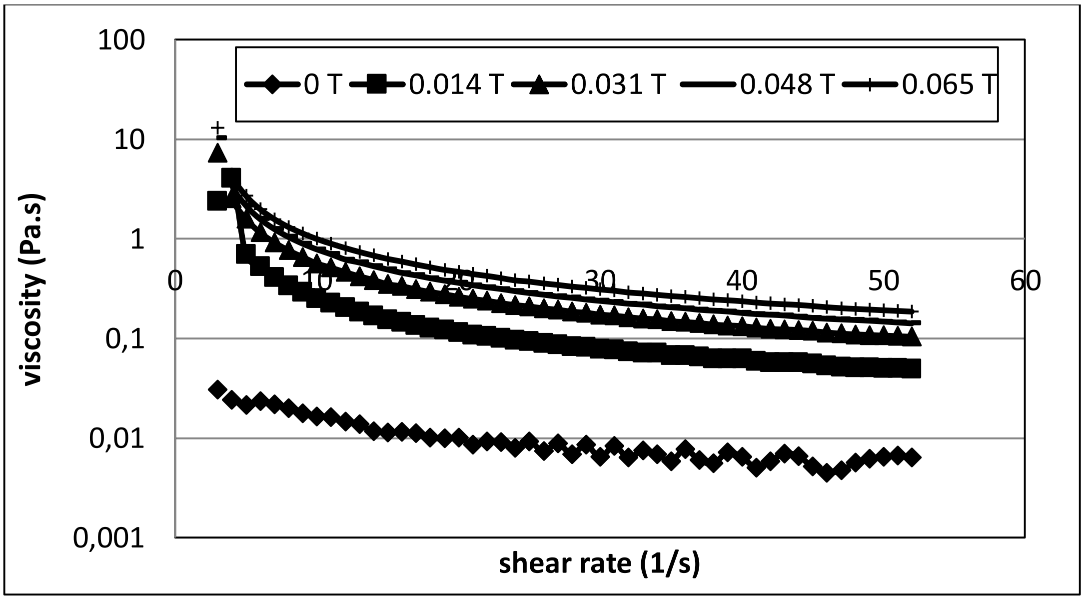


Figure 4.12 Viscosity vs shear rate of 15 weight% magnetite based ferrofluids

Table 4.3 Viscosity values under different magnetic fields for 15 wt% magnetite based ferrofluids

	Viscosity (Pa.s) 15 wtl%				
Shear Rate	B= 0 T	B=0.014 T	B=0.031 T	B=0.048 T	B=0.065 T
1 s^{-1}	0.03	5	7.27	10.31	13.04
50 s^{-1}	0.0064	0.049	0.104	0.14	0.19

The viscosity of the ferrofluids increased with increasing magnetic field. Figure 4.13 shows the increase of the viscosity with respect to concentration and magnetic field at shear rate of 50 s^{-1}. The origin of the viscosity enhancement is a single particle effect caused by the magnetic restoring torque experience by each suspending particle, **m** x **H**, where m is the magnetic dipole moment of the particle and H is the magnetic field. This torque favors the alignment of the permanent dipoles along the direction of the applied field and thus opposes the rotation of particles in a shear flow, giving rise to an increase in the viscosity.

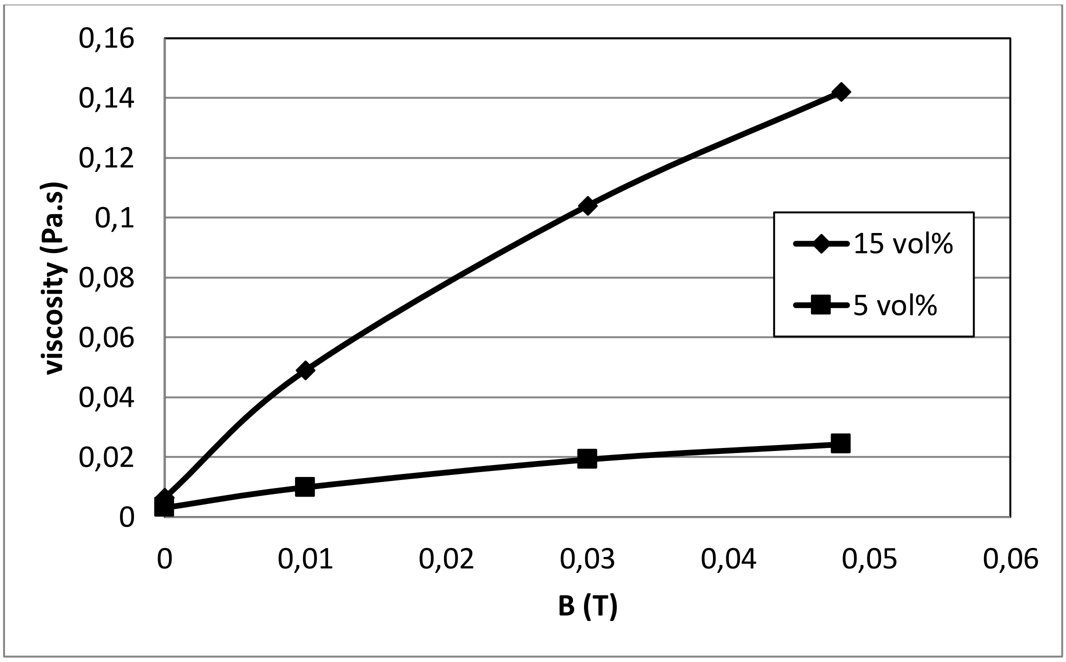


Figure 4.13. The effect of magnetic field on the viscosity of the ferrofluids

4.6 Stability of Ferrofluids

Stability is the one of the most important properties of the ferrofluids. A good dispersion is characterized by the ability of the particles to stay suspended in the carrier fluid. Colloidal suspensions are stabilized in one of two ways. Surface charge, naturally occurring or added, enhances electrostatic stability and adsorption of non-polar surfactants or polymers enhances stability by steric stabilization. In order to prevent Fe_3O_4 and MnZn ferrite nanoparticles from agglomeration, levan polysaccharite was coated around the particles which caused steric hinderance.

Figure 4.14 shows the dispersion of the 2 different weight percent Fe_3O_4 based aqueous ferrofluids. These fluids were observed over almost 6 months. Since there is no clear separation of the liquid and the MNPs, the sedimentation vs time plot was could not be drawn. The visual observation revealed a very small sedimentation at the tip of the cup, but the appearance did not change throughout 6 months. The settled particles could be the ones that were not broken during ball milling. In Figure 4.14 a there is a smaller cup with a dilute ferrofluid. That one was prepared by taking a small drop from the larger cups and dropped it into water. No settling was observed in that sample. The Figure 4.14 b shows the same cup with magnet underneath and the liquid became clearer indicating the separation of the MNPs under magnetic field.

(a) (b)

Figure 4.14 The Fe_3O_4 based ferrofluids **a)** without magnetic field **b)** with magnetic field.

There are electrostatic or charge repulsion/attraction between particles and these affect stability. Zeta potential is a measure of these attraction and repulsion that are paramenters that affect the stability of the colloidal suspensions. For stability +/- 30mV considered as a suitable threshold value. The zeta potential experiments for coated and uncoated Fe_3O_4 based ferrofluids revealed a more stable suspensions at almost pH=7 value. In Figure 4.15 it was seen that as the pH value increases for the levan coated Fe_3O_4 nanoparticles, zeta potential approached toward -40 eV which indicated a more stable suspension.

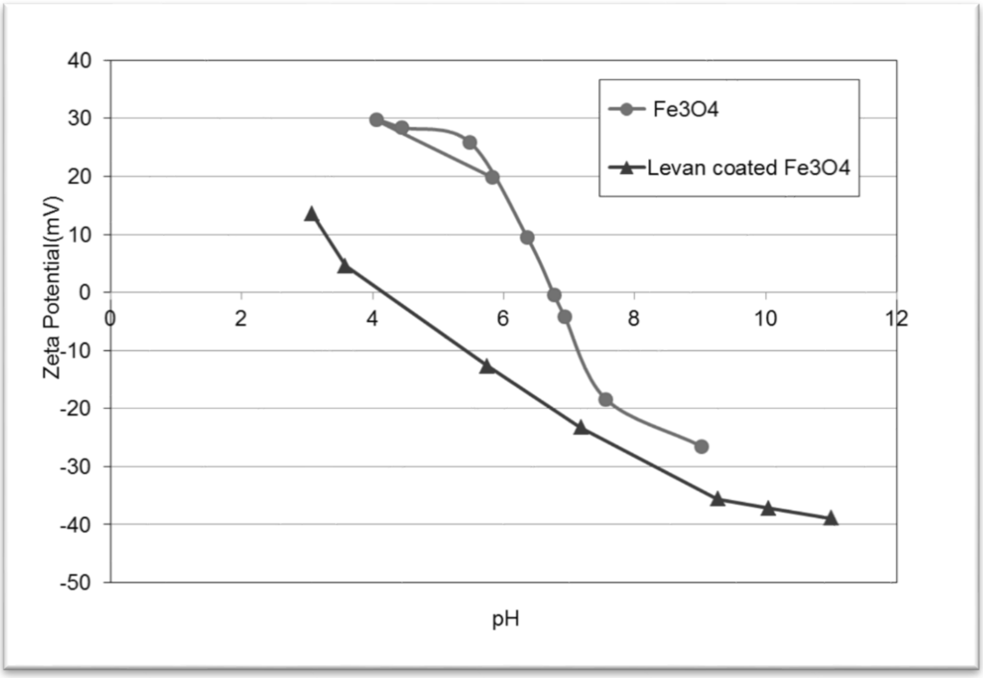


Figure 4.15 Zeta Potential of coated and uncoated Fe_3O_4 nanoparticles.

5. CONCLUSION

Ferrofluids are colloidal dispersions of very fine magnetic particles in a polar or a non-polar liquid. Under magnetic field, they have a modest magnetorheological effect. Stability is an important property of the ferrofluids. In order to prevent the particles from settling down, the particles are coated providing steric hinderance. In this work, we analyzed the synthesis of levan coated magnetite (Fe_3O_4) and MnZn ferrite nanoparticles. Synthesis of aqueous ferrofluids and their characterization are also reported in this thesis.

The mangetic nanoparticles were synthesized by co-precipitation method. Levan was coated as the particles were precipitated. Another method was to coat the particles after the synthesis of the MNPs. The reason to follow the first method was to have smaller size particles. The synthesized levan coated particles were characterized by uzing XRD, SEM, VSM, and FT-IR methods. The XRD spectrum revealed the formation of magnetite and MnZn ferrite particles and the particulate size was calculated using Scherrer equation. The magnetite and MnZn ferrite particles were 17 nm and 52 nm, respectively. The clearer SEM image for MnZn ferrite nanoparticles gave the particle size as 47 nm that was not too different from the calculated size. SEM images showed spherical and nanosized particle formation as well as some agglomeration of the particles.

The FT-IR analysis revealed the coating of MNS with levan polysaccharite. The levan coated magnetite particles presented absorption band at 2934 and 2880 cm^{-1} due to stretching vibration of C–H bond band in 1081 cm^{-1} and due to stretching vibration of C–O–C bond. These bonds are also present in the levan polysaccharide with bands in approximately 2900 and 2880 cm^{-1} (stretching vibration of C–H bond), band in 1060 cm^{-1} (stretching vibration of C–O–C) which in a way indicates of the presence of polysaccharide in the magnetic particles. Levan coated MnZn ferrite spectrum shows two main absorption bands below 1000 cm^{-1} which is a common feature of ferrites. The high frequency band lies at 586 cm^{-1} while the low frequency band lies at 443 cm^{-1}. These bands are assigned to the vibrations of the metal ion-oxygen complexes in tetrahedral and octahedral sites, respectively. Characteristic levan peaks can also be seen which indicates the adsorption of levan on MnZn ferrite.

The magnetic measurements of the magnetite and MnZn ferrite nanoparticles revealed superparamagnetic behavior with almost zero coercivity. The saturation magnetization of levan coated magnetite nanoparticles is 60 emu/gr.

Ferrofluids were synthesized based on 5 and 15 wt% magnetite and MnZn ferrite nanoparticle. The production of these fluids was done by ball milling for 10 min. These fluids showed good stability with very little sedimentation.

The rheological measurements revealed shear thinning behavior of these ferrofluids. The off-state (B=0T) viscosity of 5 wt% Fe_3O_4 ferrofluids showed a decrease from 0.12 Pa.s at 1 s^{-1} to 0.003 Pa.s at 50 s^{-1}. At the highest available magnetic field (B=0.048 T), the decrease was from 1.035 Pa.s at 1 s^{-1} to 0.024 Pa.s at 50 s^{-1}. The viscosities for 15 wt% magnetite based ferrofluid increased with increasing magnetic field. The off-state (B=0T) viscosity of 15 wt% Fe_3O_4 ferrofluids showed a decrease from 0.03 Pa.s at 1 s^{-1} to 0.064 Pa.s at 50 s^{-1}. At the highest availbale magnetic field (B=0.068 T), the decrease was from 13.04 Pa.s at 1 s^{-1} to 0.19 Pa.s at 50 s^{-1}.

In this study, the synthesis of MNPs, coating of these particles and synthesis of the ferrofluids were succesfully performed and it was seen that these ferrofluids could be potential applications for biomedical applications. As the future work, the coating process and the effect of coating on the stability of the particles could be investigated.

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