

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**PREPARATION AND CHARACTERIZATION
OF MAGNETITE NANOPARTICLES
BY VARIOUS METHODS**

by
Hatice ARDAR

July, 2020
İZMİR

**PREPARATION AND CHARACTERIZATION
OF MAGNETITE NANOPARTICLES
BY VARIOUS METHODS**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Master of
Science in Nanoscience and Nanoengineering Program**

**by
Hatice ARDAR**

**July, 2020
İZMİR**

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **“PREPARATION AND CHARACTERIZATION OF MAGNETITE NANOPARTICLES BY VARIOUS METHODS”** completed by **HATİCE ARDAR** under supervision of **PROF. DR. MEHMET KADİR YURDAKOÇ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

.....
Prof. Dr. Mehmet Kadir YURDAKOÇ

Supervisor

.....
Prof.Dr. Levent BALLICE

(Jury Member)

.....
Assoc.Prof.Dr.Kinyas POLAT

(Jury Member)

.....
Prof.Dr. Özgür ÖZÇELİK

Director

Graduate School of Natural and Applied Sciences

ACKNOWLEDGMENT

I wish to thank my supervisor, Prof. Dr. Mehmet Kadir YURDAKOÇ, for his encouragement, support, patient, guidance and advice at all stage of this thesis.

I thank Dr. Hüseyin AL (EKO BOYA, Akhisar-Manisa) for his contributions and help.

This work was supported as a Research Project. Therefore, I am also grateful to Research Foundation of Dokuz Eylül University (Project 2018.KB.FEN.037) for the financial support.

Finally, I would like to thank my family who has always been with me. And, I always present this work to my dear father, whom I always carry in my heart. I know you're proud of me, thank you for everything.

Hatice ARDAR

PREPARATION AND CHARACTERIZATION OF MAGNETITE NANOPARTICLES BY VARIOUS METHODS

ABSTRACT

Magnetite nanoparticles are used in various fields including iron-containing fluid, catalyst, pigments, magnetic recording media, medical diagnosis and treatment. Size of the particles and their morphology, electrical, optical and magnetic properties and limit their use. Synthesis methods determine the morphological homogeneity and size distribution of nanoparticles. Currently there are printing materials called toners that are imported for use in many printers of various brands and models. Iron-based inorganic minerals with different magnetic properties are used in these materials.

The aim of this study is to prepare and characterize magnetite nanoparticles for use in printers and photocopiers. In this context, co-precipitation, thermal synthesis, sol-gel synthesis, reverse micelle synthesis, hydro-/solvo-thermal, sonochemical, microwave, and biosynthesis have been proposed. Magnetite nanoparticles were synthesized by co-precipitation and solvothermal/ hydrothermal methods. Stability of the nanoparticles stability is achieved by coating with oleic acid (OA), stearic acid (SA), sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium bromide (CTAB), (3-aminopropyl)triethoxysilane (APTES), oleyl amine (OAm) and hexadecyltrimethoxysilane (HDTMS). Characterization of the prepared samples was performed by techniques such as XRD, FTIR, TGA, SEM, XPS and VSM.

Keywords: Magnetite, Nanoparticle, Coprecipitation method, Surface coating
Magnetic property

ÇEŞİTLİ YÖNTEMLERLE MAGNETİT NANOTANECİKLERİN HAZIRLANMASI VE KARAKTERİZASYONU

ÖZ

Magnetit nanotaneçikler, demir içeren akışkan malzeme, katalizör, pigmentler, manyetik kayıt ortamları, tıbbi teşhis ve tedavi olmak üzere çeşitli alanlarda kullanılmaktadır. Taneciklerin büyüklüğü ve morfolojileri, elektriksel, optik ve manyetik özelliklerini etkiler ve kullanım alanlarını sınırlar. Sentez yöntemleri, nanotaneçiklerin morfolojik homojenliğini ve boyut dağılımını belirlemektedir. Halen çeşitli marka ve modellerde çok sayıdaki yazıcıda kullanılmak üzere ithal edilen ve toner denilen baskı malzemeleri vardır. Bu malzemelerde değişik magnetik özellik gösteren demir tabanlı inorganik mineraller kullanılmaktadır.

Çalışmada, yazıcı ve fotokopi cihazlarında kullanılmak üzere magnetit nanotaneçik hazırlanması ve karakterizasyonu amaçlanmaktadır. Bu kapsamda, birlikte çöktürme, termal parçalanma, sol-jel sentez, ters misel sentezi, hidrotermal/solvotermal, sonokimyasal, mikrodalga, ve biyosentez gibi çeşitli sentez yöntemleri önerilmiştir. Magnetit nanotaneçikleri, birlikte çöktürme ve solvotermal/hidrotermal yöntemlerle sentezlenmiştir. Magnetit nanotaneçiklerin kararlılığı, oleik asit (OA), stearik asit (SA), sodyum dodesil sülfat (SDS), heksadesil trimetilamonyum bromür (CTAB), (3-aminopropil)trioksisilan (APTES), oleyil amin (OAm) heksadesiltrimetoksil silane (HDTMS) ile kaplanarak sağlanmıştır. Örneklerin karakterizasyonu, X-ışını kırınımı (XRD), Fourier Transform Infrared (FTIR), Thermogravimetric Analysis (TGA), Taramalı elektron mikroskopisi (SEM), X-ışını fotoelektron spektroskopisi (XPS) ve Titreşimli örnek magnetometrisi (VSM) gibi tekniklerle yapılmıştır.

Anahtar kelimeler: Magnetit, Nanotaneçik, Birlikte çöktürme yöntemi, Yüzey kaplama, Magnetik özellik

CONTENTS

	Page
M.Sc THESIS EXAMINATION RESULT FORM	ii
ACKNOWLEDGMENT	iii
ABSTRACT	iv
ÖZ	v
LIST OF FIGURES	ix
LIST OF TABLES.....	xiii
 CHAPTER ONE - INTRODUCTION	 1
 1.1 Nanoscience-Nanotechnology and Magnetite Nanoparticles.....	 1
1.2 Synthesis of Magnetic Nanoparticles.....	2
1.2.1 Synthesis by Co-precipitation Method.....	3
1.2.2 Hydrothermal Synthesis Method	4
1.3 Stabilization of Magnetic Particles	5
1.3.1 Oleic Acid.....	5
1.3.2 Stearic Acid	6
1.3.3 Sodium dodecyl sulfate (SDS).....	7
1.3.4 Hexadecyltrimethylammonium bromide (CTAB)	7
1.3.5 Oleylamine (OAm)	8
1.3.6 (3-Aminopropyl)triethoxysilane (APTES).....	8
1.3.7 Hexadecyltrimethoxysilane (HDTMS)	9
 CHAPTER TWO - STRUCTURAL AND PHYSICOCHEMICAL CHARACTERIZATION OF MAGNETITE NANOPARTICLES	 11
 CHAPTER THREE - APPLICATIONS AND USAGE OF MAGNETITE NANOPARTICLES.....	 13
 3.1 The Aim of the Study.....	 16

CHAPTER FOUR - MATERIALS AND METHODS 17

4.1 Materials	18
4.2 Preparation of Magnetite, Magnetite/Oleic acid, Magnetite/Stearic acid, Magnetite/SDS and Magnetite/CTAB Nanoparticles	19
4.2.1 Preparation of Magnetite Nanoparticles	19
4.2.2 Preparation of Magnetite/Oleic acid Nanoparticles	23
4.2.3 Preparation of Magnetite/Stearic acid Nanoparticles	24
4.2.4 Preparation of Magnetite/SDS Nanoparticles	25
4.2.5 Preparation of Magnetite/CTAB Nanoparticles	26
4.2.6 Preparation of Magnetite/OAm coated Nanoparticles	27
4.2.7 Preparation of Magnetite/APTES Nanoparticles	28
4.2.8 Preparation of Magnetite/(HDTMS) Nanoparticles	29
4.3 Characterization Methods	30
4.3.1 Crystallinity by X-Ray Diffraction (XRD)	30
4.3.2 Fourier Transform Infrared (FTIR) Spectra of the Samples	30
4.3.3 Thermogravimetric Analysis (TGA) of the Samples	30
4.3.4 Scanning Electron Microscopy (SEM)	30
4.3.5 X-ray Photoelectron Spectroscopy (XPS)	31
4.3.6 Vibrating-Sample Magnetometer (VSM)	31

CHAPTER FIVE - RESULTS AND DISCUSSION 32

5.1 Characterization Results of the Samples	32
5.1.1 XRD pattern of Fe ₃ O ₄ MNPs	32
5.1.2 Fourier Transform Infrared FT-IR Spectra of the Samples	42
5.1.3 Thermogravimetric (TG/DTG) Analysis of the Samples	55
5.1.4 Scanning Electron Microscopy (SEM) Analysis of the Samples	62
5.1.5 X-ray Photoelectron Spectroscopy (XPS) Analysis of the Samples	75
5.1.6 Vibrating-Sample Magnetometer (VSM) Analysis of Samples	101

CHAPTER SIX - CONCLUSIONS AND PERSPECTIVES	112
REFERENCES	116

LIST OF FIGURES

	Page
Figure 1.1 Molecular Formula of Oleic acid	5
Figure 1.2 Magnetic nanoparticle formation and surface coating	6
Figure 1.3 Molecular Formula of Stearic acid (SA)	7
Figure 1.4 Molecular Formula of Sodium dodecyl sulfate (SDS)	7
Figure 1.5 Molecular Formula of Hexadecyltrimethylammonium bromide (CTAB) ..	8
Figure 1.6 Molecular Formula of Oleylamine (OAm)	8
Figure 1.7 Molecular Formula of (3-Aminopropyl)triethoxysilane (APTES)	9
Figure 1.8 Molecular Formula of Hexadecyltrimethoxysilane (HDTMS)	9
Figure 1.9 Study overview	17
Figure 4.1 Experimental design of the preparation studies	21
Figure 4.2 Experimental design of the preparation studies	21
Figure 4.3 Experimental design of the preparation studies	22
Figure 4.4 Experimental design of the preparation studies	22
Figure 4.5 Reaction scheme of Fe ₃ O ₄ Nanoparticles with OA	23
Figure 4.6 Reaction scheme of Fe ₃ O ₄ Nanoparticles with SA	24
Figure 4.7 Reaction scheme of Fe ₃ O ₄ Nanoparticles with SDS	25
Figure 4.8 Reaction scheme of Fe ₃ O ₄ Nanoparticles with CTAB	26
Figure 4.9 Reaction scheme of Fe ₃ O ₄ Nanoparticles with OAm	27
Figure 4.10 Reaction scheme of Fe ₃ O ₄ Nanoparticles with APTES	28
Figure 4.11 Reaction scheme of Fe ₃ O ₄ Nanoparticles with HDTMS	29
Figure 5.1 XRD peaks of synthesized magnetite nanoparticles	32
Figure 5.2 XRD patterns coated with Fe ₃ O ₄ and Oleic acid	33
Figure 5.3 XRD pattern of Fe ₃ O ₄ nanoparticles.....	33
Figure 5.4 XRD pattern of HA1	36
Figure 5.5 XRD pattern of HA2	37
Figure 5.6 XRD pattern of HA3	37
Figure 5.7 XRD pattern of HA4	38
Figure 5.8 XRD pattern of HA5	38
Figure 5.9 XRD pattern of HA6	39
Figure 5.10 XRD pattern of HA7	39

Figure 5.11 XRD pattern of HA8	40
Figure 5.12 XRD pattern of HA11	40
Figure 5.13 XRD pattern of HA12	41
Figure 5.14 XRD pattern of HA13.....	41
Figure 5.15 FTIR spectra of HA3 (Fe ₃ O ₄ standard)	42
Figure 5.16 FTIR spectra of HA1, HA2 and HA3	43
Figure 5.17 FTIR spectra of HA4 and SDS	43
Figure 5.18 FTIR spectra of HA5 and CTAB	45
Figure 5.19 FTIR spectra of HA6 and OA	46
Figure 5.20 FTIR spectra of HA7 and SA	47
Figure 5.21 FTIR spectra of HA8	48
Figure 5.22 FTIR spectra of HA11	48
Figure 5.23 FTIR spectra of OAm	49
Figure 5.24 FTIR spectra of HA12	51
Figure 5.25 FTIR spectra of APTES	51
Figure 5.26 Schematic presentation of Interaction of APTES with surface hydroxide groups	52
Figure 5.27 FTIR spectra of HA13 HDTMS	53
Figure 5.28 FTIR spectra of HDTMS	53
Figure 5.29 Interaction of HDTMS with surface hydroxide groups of Fe ₃ O ₄	54
Figure 5.30 TG/DTG thermograms of HA4	55
Figure 5.31 TG/DTG thermograms of HA5	56
Figure 5.32 TG/DTG thermograms of HA6	57
Figure 5.33 TG/DTG thermograms of HA7	58
Figure 5.34 TG/DTG thermograms of HA8	59
Figure 5.35 Carl Zeiss 300VP SEM Carl Zeiss 300VP SEM and QUORUM Q150 RES device	62
Figure 5.36 SEM Images of HA1 with 50 00 K× magnifications	63
Figure 5.37 SEM Images of HA2 with 50 00 K× magnifications	63
Figure 5.38 SEM Images of HA3 with 50 00 K× magnifications	64
Figure 5.39 SEM Images of HA4 with 50 00 K× magnifications	65
Figure 5.40 SEM Images of HA5 with 50 00 K× magnifications	66

Figure 5.41 SEM Images of HA6 with 50 00 K $\times$ magnifications	66
Figure 5.42 SEM Images of HA7 with 50 00 K $\times$ magnifications	67
Figure 5.43 SEM Images of HA8 with 100 $\times$ magnifications	67
Figure 5.44 SEM Images of HA8 with 1 00 K $\times$ magnifications	68
Figure 5.45 SEM Images of HA8 with 1 00 K $\times$ magnifications	68
Figure 5.46 SEM Images of HA8 with 5 00 K $\times$ magnifications	69
Figure 5.47 SEM Images of HA8 with 50 00 K $\times$ magnifications	69
Figure 5.48 SEM EDX Images of HA8 with 50 00 K $\times$ magnifications	70
Figure 5.49 SEM EDX Spectrum of HA8(area 1)	70
Figure 5.50 SEM EDX Spectrum of HA8(area 2)	71
Figure 5.51 SEM EDX Spectrum of HA8(area 3)	72
Figure 5.52 SEM Images of HA11 with 50 00 K $\times$ magnifications	73
Figure 5.53 SEM Images of HA11 with 50 00 K $\times$ magnifications	73
Figure 5.54 SEM Images of HA12 with 50 00 K $\times$ magnifications	74
Figure 5.55 SEM Images of HA12 with 50 00 K $\times$ magnifications	74
Figure 5.56 SEM Images of HA13 with 50 00 K $\times$ magnification	75
Figure 5.57 The XPS spectrum of Fe2p from the surface of the Fe ₃ O ₄ standard sample	76
Figure 5.58 XPS analysis of HA3	77
Figure 5.59 XPS analysis of Fe2p for HA3	78
Figure 5.60 XPS Spectra of the samples HA1, HA2 and HA3 for Fe ₃ O ₄ (Fe2p)	79
Figure 5.61 XPS Spectra of the samples HA3, HA4, HA5, HA6 and HA7 for Fe ₃ O ₄ (Fe2p)	79
Figure 5.62 XPS Spectrum of HA1.....	81
Figure 5.63 XPS Analysis results of HA1 for Fe2p	82
Figure 5.64 XPS Spectrum of HA2	83
Figure 5.65 XPS Analysis results of HA2 for Fe2p	84
Figure 5.66 XPS Spectrum of HA4	85
Figure 5.67 XPS Analysis results of HA4 for Fe2p	86
Figure 5.68 XPS Spectrum of HA5	87
Figure 5.69 XPS Analysis results of HA5 for Fe2p	88

Figure 5.70 XPS Spectrum of HA6	89
Figure 5.71 XPS Analysis results of HA6 for Fe2p	90
Figure 5.72 XPS Spectrum of HA7	91
Figure 5.73 XPS Analysis results of HA2 for Fe2p	92
Figure 5.74 XPS Spectrum of HA8	93
Figure 5.75 XPS Analysis results of HA11 for Fe2p	94
Figure 5.76 XPS Analysis results of HA12 for Fe2p	95
Figure 5.77 XPS Spectrum of HA12	96
Figure 5.78 XPS Analysis results of HA13 for Fe2p	97
Figure 5.79 XPS Spectrum of HA13	98
Figure 5.80 The relationship between magnetization M and the applied field H	101
Figure 5.81 Magnetization curve of the sample HA1 at 298 K	103
Figure 5.82 Magnetization curve of the sample HA2 at 298 K	103
Figure 5.83 Magnetization curve of the sample HA3 at 298 K	104
Figure 5.84 Magnetization curve of the sample HA8 at 298 K	104
Figure 5.85 Magnetization curves of the samples (HA1-3 and HA8) at 298 K	104
Figure 5.86 Magnetization curve of the sample HA4 at 298 K	105
Figure 5.87 Magnetization curve of the sample HA5 at 298 K	106
Figure 5.88 Magnetization curve of the sample HA6 at 298 K	106
Figure 5.89 Magnetization curve of the sample HA7 at 298 K	107
Figure 5.90 Magnetization curves of the samples (HA3-HA7) at 298 K	108
Figure 5.91 Magnetization curve of HA11 at 298 K	109
Figure 5.92 Magnetization curve of HA12 at 298 K	110
Figure 5.93 Magnetization curve of HA13 at 298 K	110

LIST OF TABLES

	Page
Table 5.1 Average crystallite size and related parameters of the Fe ₃ O ₄ Samples	35
Table 5.2 FTIR spectral data of SDS and SDS-coated magnetite	44
Table 5.3 FTIR band assignments of OAm.....	50
Table 5.4 The summary of TG/DTG data of HA4, HA5, HA6, HA7 and HA8	60
Table 5.5 EDX Data of HA8 from selected area 1	71
Table 5.6 EDX Data of HA8 from selected area 1	71
Table 5.7 EDX Data of HA8 from selected area 1	72
Table 5.8 XPS Analysis Data Survey Scan for HA3.....	77
Table 5.9 XPS Analysis Data of HA3 for Fe2p	78
Table 5.10 XPS Analysis Data Survey Scan for HA1	81
Table 5.11 XPS Analysis Data of HA1 for Fe2p	82
Table 5.12 XPS Analysis Data Survey Scan for HA2	83
Table 5.13 XPS Analysis Data of HA2 for Fe2p	84
Table 5.14 XPS Analysis Data Survey Scan HA4	85
Table 5.15 XPS Analysis Data of HA4 for Fe2p	86
Table 5.16 XPS Analysis Data Survey Scan HA5	87
Table 5.17 XPS Analysis Data of HA5 for Fe2p	88
Table 5.18 XPS Analysis Data Survey Scan HA6	89
Table 5.19 XPS Analysis Data of HA6 for Fe2p	90
Table 5.20 XPS Analysis Data Survey Scan HA7	91
Table 5.21 XPS Analysis Data of HA7 for Fe2p	92
Table 5.22 XPS Analysis Data Survey Scan HA8	93
Table 5.23 XPS Analysis Data Survey Scan for HA11	94
Table 5.24 XPS Analysis Data of HA12 for Fe2p.....	95
Table 5.25 XPS Analysis Data Survey Scan for HA12	96
Table 5.26 XPS Analysis Data of HA13 for Fe2p.....	97
Table 5.27 XPS Analysis Data Survey Scan for HA13	98
Table 5.28 XPS Data Analysis of The Samples for Fe2p	100
Table 5.29 Magnetization parameters of the Fe ₃ O ₄ samples at 298 K.....	105

Table 5.30 Magnetization parameters of the samples at 298 K	107
Table 5.31 Magnetization parameters of the Fe_3O_4 samples at 298 K.....	111

CHAPTER ONE

INTRODUCTION

1.1 Nanoscience-Nanotechnology and Magnetite Nanoparticles

Nanotechnology offers wide opportunities for many professionals in the field of science and medicine. Thus, interest in nano-scale materials in modern science is increasing day by day. Magnetic nanoparticles and their applications attract many researchers and industrialists. Their size in general is in the scale of 1-100 nm.

Among magnetic nano materials, Fe_3O_4 , is magnetite, is an important material, it has both wide structure and wide application area. Magnetite nanoparticles have important physical properties as magnetization, biocompatibility, high durability and low toxicity. Due to these properties, it has been used in various variety of applications.

Magnetite (Fe_3O_4) nanoparticles are impressive technological interests for their superior properties and used various fields such as iron-containing fluids, catalysts, black pigments, magnetic recording media, medical diagnosis and treatment. The size and morphology of the particles are important that affect their electrical, optical and magnetic properties. For this reason, a certain size, shape, surface and magnetic properties of particles are sought in terms of application areas. Synthesis of nanoparticles, morphological homogeneity and size distribution can determine. For good synthesis, the particles must be monodispersing, superparamagnetic and stable at room temperature. In recent years, preparation conditions have become one of the most important topics in nanoscience and nanoengineering (Petcharoen & Sirivat, 2012).

Magnetite has a wide range of applications in medicine as contrast agents in MRI, in cell separation, in drug delivery, anti-bacterial materials, in protein separation, and in a biomedical application as hyperthermia.

On the other hand, in the field of industry, it can be used as a magnetic catalyst in the production of new energy storage materials and novel ink powder as toner. Toner is a polymer composite contains pigments, magnetic materials and organic based resin compounds containing some other additives used for electro-photography printing and photocopying. Magnetite (Fe_3O_4) nanoparticles are required as a toner carrier material (Fahlepy & Tiwow, 2018).

The desirable magnetite is its magnetic properties resulting from its crystal structure. It is a magnetic material having a cubic reverse spinel structure over 120K.

Magnetic nanoparticles and Fe_3O_4 have been of interest due to structural differences, for example, cubes, rods, rings, fibers, films, spheres, tubes etc (Gong, et al., 2007; Jagadeesan, Mansoori, Mandal, Sundaresan, & Eswaramoorthy, 2008).

1.2 Synthesis of Magnetic Nanoparticles

Newly, important works have been made of the improvement of magnetic nanoparticles, the insight of their behaviour and the advancement of their feasibility in various areas.

In nanotechnology, nanoscale particle production in the appropriate size and shape is still the most important research area.

In the nanoscale particle synthesis, the desired size and shape is still the most important problem that can be solved (Lu, Salabas, & Schüth, 2007; Koch, Papademetris, Rothman, & de Graaf, 2006).

Various methods have been reported in the synthesis of magnetite nanoparticles, such as chemical reduction (Chaki, Malek, Chaudhary, Tailor, & Deshpande, 2015), sol-gel (Xu et al., 2007), electrochemical (Cabrera, Gutierrez, Menendez, Morales, & Herrasti, 2008), flow injection (Salazar-Alvarez, Muhammed, & Zagorodni, 2006), solvothermal (Lu, Jiao, Chen, & Li, 2009), hydrothermal (Taniguchi, Nakagawa,

Watanabe, Matsushita, & Yoshimura, 2009), microwave-assisted (Hong, Pan, & Li, 2006), polyol method (Vega-Chacón, Picasso, Avilés-Félix, & Jafellicci Jr, 2016) and co-precipitation (Kandpal, Sah, Loshali, Joshi, & Prasad, 2014).

The most common synthesis method is the common precipitation method because the process is simple, easy and inexpensive (Alp & Aydogan, 2016).

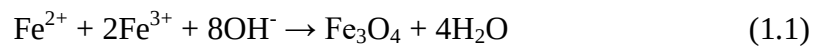
1.2.1 Synthesis by Co-Precipitation Method

Among the synthesis methods of magnetic nanoparticles, co-precipitation is the most effective, easy and low cost. It is possible to obtain large amounts of fast polydisperse particles.

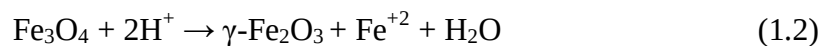
In co-precipitation, a stoichiometric mixture of iron (II) and iron (III) precursors in aqueous medium is used as the source of iron, followed by the addition of an alkaline solution to precipitate the superparamagnetic iron nanoparticles.

In order to ensure controlled chemical precipitation of Fe^{2+} and Fe^{3+} ions mixed in stoichiometric ratios of 2:1, precipitating solutions are used in the appropriate pH range.

Commonly used solutions; NaHCO_3 , Na_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$. In a basic medium (ammonia or sodium hydroxide solution), the iron ions are precipitated under a strong stirrer. For the precipitation of Fe_3O_4 nanoparticles, alkaline medium is necessary (Laurent et al., 2008). The reaction for Fe_3O_4 nanoparticles is as follows:



The synthesized product according to equation (1.1) is not very stable. It can be converted to maghemite by oxidizing in acidic and oxygenated environment as in equation (1.2).



In this method, the size, shape and composition of the particles related with kinetic factors and test conditions. $\text{Fe}^{2+} / \text{Fe}^{3+}$ ratio varies depending on the salt (chloride, sulfate, nitrate) used, pH, temperature, base type, ionic strength. The size of the magnetic nanoparticles is achieved by changing conditions. The synthesis can be carried out at room temperature or at elevated temperatures. It is possible to obtain nanoparticles between 3-20 nm.

In this method, surfactant selection is the most important step to keep the particles stable. The high surface energy of the magnetic nanoparticles easily leads to agglomeration. Therefore, stability is important (Shen et al., 2014).

Surfactant usage in the synthesis affects the size of the nanoparticles and maintains the interaction between the particles. It has been observed that the compounds used reduce the particle size and therefore depend on the substrate used (Klekotka, Satuła, Spassov, & Kalska-Szostko, 2018).

1.2.2 Hydrothermal Synthesis Method

This technique, unlike other techniques, is often used to obtain single crystal particles. In the hydrothermal method, ultra-fine magnetite powder, FeCl_3 and iron powders are used in alkaline medium for the preparation of highly nanoscale Fe_3O_4 particles (Wang, Sun, Sun, & Chen, 2003).

During the hydrothermal process, the synthesis of Fe_3O_4 nanoparticles depends on some variables. Sensitive to reaction time, concentration of reagents and temperature factors (Majidi, Zeinali Sehrig, Farkhani, Soleymani Goloujeh, & Akbarzadeh, 2016; Ozel, Kockar, & Karaagac, 2015).

Among the synthesis methods, hydrothermal method is preferred for its simple application, conditions and large amount of production (Chen, Du, Li, Yang, & Lv, 2017).

It is known that magnetic properties are affected by crystal structure. At the same time, the crystal structure of the particles depends on the synthesis conditions (Wang, Sun, Sun, & Chen, 2003). Magnetite particles resulting from hydrothermal synthesis in an alkaline medium may be a better crystalline than those obtained in other methods (Guan et al., 2013).

1.3 Stabilization of Magnetic Particles

The nanoparticles are very unstable, so aggregation may occur in the solution in which they are present, resulting in a reduced surface area / volume ratio.

Surface modification strategies have been developed to prevent aggregation in solution. The use of surfactants is a solution that prevents the formation of aggregation. Stabilizing agents interact with the surfaces of the particles to cover the particle surface while the nanoparticles are suspended and prevent aggregation by electrostatic repulsion of the same charged particles. Fe_3O_4 nanoparticles tend to aggregate, so surface treatment is a necessity for the distribution of nanoparticles.

1.3.1 Oleic Acid (OA)

Oleic acid is common fatty acid composed of a long chain hydrocarbon and carboxylic group as shown in Figure 1.1. The mechanism of the interaction is between hydrophilic surface of the iron oxide and carboxylic group and gains hydrophobic properties.

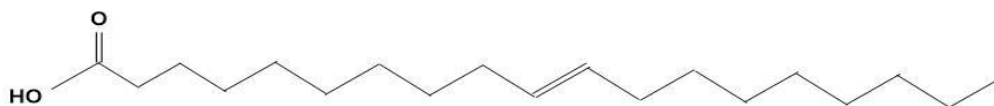


Figure 1.1 Molecular Formula of Oleic acid

The oleic acid with a long hydrocarbon chain binds strongly to the surface of the oxide nanocrystals as the well-known surfactant. Thus, the magnetic properties of the particles change at low temperatures.

Widely used as hydrophobic ligand. Stability results from the attachment of carboxylic groups to the particle surface and a long hydrophobic layer is formed in Figure 1.2 (Liu et al., 2006).

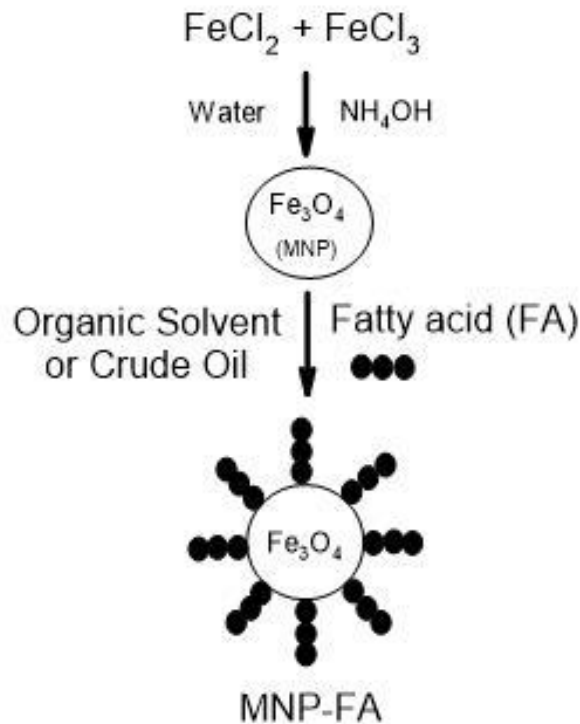


Figure 1.2 Magnetic nanoparticle formation and surface coating

1.3.2 Stearic Acid (SA)

Long chain fatty acids such as stearic acid are preferred in the synthesis of magnetic nanoparticles. The carboxylic acid group bound to the metal surface forms a protective layer. In the usage of stearic acid, the nanoparticles have an inverted spinel cubic structure (Dutra et al., 2017).

Production of the same quality as in oleic acid is not possible, since stearic acid is not used as a ligand in the preparation of iron oxide nanoparticles (Willis, Turro, & O'Brien, 2005).



Figure 1.3 Molecular Formula of Stearic acid

1.3.3 Sodium dodecyl sulfate (SDS)

SDS is anionic surfactant for transition to stabilization in nanoparticle synthesis. It is very soluble in all solvents but not soluble in toluene (Pollard, Shi, & Göklen, 2006).

The morphological changes of nanospheres, nanoneedles and nanocubes were observed depending on the amount of SDS of magnetite nanoparticles synthesized by co-precipitation (Shen et al., 2014).



Figure 1.4 Molecular Formula of Sodium dodecyl sulfate (SDS)

1.3.4 Hexadecyltrimethylammonium bromide (CTAB)

CTAB is a commonly used surfactant for transition to stabilization in nanoparticle synthesis. It is water soluble and cationic. The cationic surfactant CTAB is ionic in nature and has little solubility in less polar solvents (Pollard, Shi, & Göklen, 2006).

CTAB is important in controlling sphere growth. Many Fe₃O₄ morphologies are obtained at different concentrations. The reason for the formation of different structures is due to the interaction between the layers of adsorbed CTAB molecules (Wang, Cheng, Wen, & Zhao, 2012).

The non-polar CTAB chain can be used to alter the hydrophobic phase on the surface of the MNPs. As a result, the hydrophobic layer is formed around the particles and it stabilizes particles in aqueous medium (Guivar, Sanches, Magon, & Fernandes, 2015).

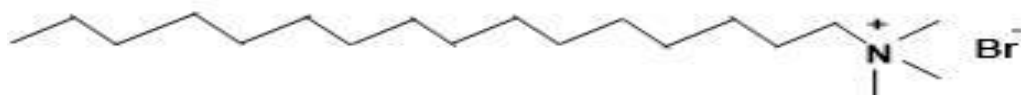


Figure 1.5 Molecular Formula of Hexadecyltrimethylammonium bromide (CTAB)

1.3.5 Oleylamine (OAm)

OAm is a long-chain primary alkyl-amine that can function as an electron donor at high temperatures. Oleylamine is liquid at room temperature, inexpensive and commonly used in the preparation of magnetic particles (Mourdikoudis & Liz-Marzán, 2013).

The molecular formula of OAm is given in Figure 1.6. As you can see, there is a double bond in the middle part of the molecule. Since it has a high boiling point (350°C), it requires high heating conditions when used.



Figure 1.6 Molecular Formula of Oleylamine (OAm)

1.3.6 (3-Aminopropyl)triethoxysilane (APTES)

APTES, an organosilane, is used as a coating material due to its biocompatibility, less toxicity and amino groups for the binding various biologic molecules (Gupta & Gupta, 2005; Asenath Smith & Chen, 2008).

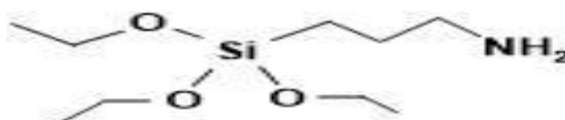


Figure 1.7 Molecular Formula of (3-Aminopropyl)triethoxysilane (APTES)

As can be seen from Figure 1.7, APTES has an amino group and facilitates further functionalization and can be covalently bonded with a carboxyl group. This active amino group in its structure can bind with biomolecules and metals. Therefore, coated nanoparticles are non-toxic and biocompatible (Cao, He, Deng, & Gao, 2009).

APTES, an amino-silane coupling agent, is capable of forming a single layer of amino-silane, surface modification, and the design and synthesis of magnetic carriers and their association with anti-cancer drugs (Sundar, Mariappan, & Piraman, 2014).

1.3.7 Hexadecyltrimethoxysilane (HDTMS)

Hexadecyltrimethoxysilane ensures that nanoparticles have a hydrophobic surface in non-polar oil environments. It stabilizes nanoparticles and is also biocompatible (Storozhuk & Iukhymenko, 2019).

Chemical interaction occurs between organo silane compounds and hydroxyl groups on the surface (Yoshida, Castro, Jou, & Cohen, 2001; Chiarakorn, Areerob, & Grisdanurak, 2007).

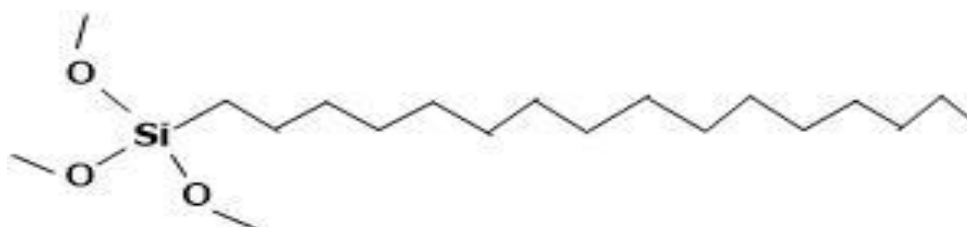


Figure 1.8 Molecular Formula of Hexadecyltrimethoxysilane (HDTMS)

The reaction of HDTMS with Fe_3O_4 surface is first a hydrolysis reaction and then the condensation of the hydrolysis products on magnetite surface. The resulting products depend on the conditions of synthesis (Xu, Wang, Shen, Ding, & Cai, 2015).

One of the promising aspects of the modification of magnetite nanoparticles with HDTMS is that it allows magnetic material to be diagnosed, delivered and retained in the tumor and subsequently sessions of magnetic hyperthermia. In this application, Fe_3O_4 NPs, modified with HDTMS, prevent accumulation with their super paramagnetism and ensure their rapid disintegration after removal of the magnetic field (Dutz et al., 2007).

CHAPTER TWO

STRUCTURAL AND PHYSICOCHEMICAL CHARACTERIZATION OF MAGNETITE NANOPARTICLES

The magnetic properties and biological behavior of nanoparticles related with size, shape, microstructures and current chemical conditions of the particles. Various physicochemical techniques are used to determine these properties.

Crystalline and amorphous parts of the synthesized Fe_3O_4 nanoparticles, total particle size, and number-weighted average values can be estimated by the Transmission Electron Microscopy (TEM) technique (Shen et al., 2014).

XRD analysis can be carried out to identify crystal structure of the particles. Iron oxide ratio measurement can also be provided by comparing the crystal structure. It is also possible to compare the experimental patterns with the pattern of the reference peaks of Fe_3O_4 MNPs (Wei, 2020).

The crystal size of the particles can be determined from the XRD data by using the Scherrer Formula (Phan & Nguyen, 2017).

SEM and related technique EDX analysis can be investigated to estimate the surface morphology, size of the particles and chemical composition on the surface in some respect.

The thermal stabilities and also magnetic properties of the magnetite nanoparticle must be determined before usage of these in the applications in biosciences and medicine.

X-Ray Photoelectron Spectroscopy (XPS) is applied for composition analysis on the surfaces of conductive and non-conductive materials. In this method, X-rays are used as a radiation source.

Magnetometric analysis is used to study the magnetic properties of materials in the form of solid, crystalline, liquid, powder and film. The results are obtained in terms of area saturation, temperature and time, and are displayed as s-type curves (H-M). The method has been described as VSM analysis.

CHAPTER THREE

APPLICATIONS AND USAGE OF MAGNETITE NANOPARTICLES

Magnetic properties of ferromagnetic materials have been investigated for many years. In recent years, basic information about the magnetic behavior of iron-containing nanoparticles and especially small grains is very important in terms of the numerous formations of these particles in technological applications (Shah, Khan, Riaz, & Naseem, 2015).

Today, nanoparticles with magnetic properties are widely used in controlled hyperthermia. In this application, magnetic forces are very important in the transport of biological objects to the cells at the molecular level and are extremely useful for cell signaling and control of cell fate. The special abilities of these magnetic substances, especially nanoparticles, have been used in drug delivery to the address, contrast agents in imaging, disease therapy, and remote control of single cell functions (Hong et al., 2011; Yoon et al., 2011).

In terms of applications, there are two basic strategies for functionalizing magnetic particles. The first is the modification with biomaterials such as antibodies and oligonucleotides in the medical field, and the second is the integration of other nano components such as the quantum dots of inorganic materials for new, technological industrial applications (Gao, Gu, & Xu, 2009). In medicine, the usage of magnetic fluids is increasing in the treatment of hyperthermia. The challenge is that the nanoparticles have a uniform distribution and thus provide a well-controlled temperature increase in tumor tissue. These challenges can be overcome by specific antibody conjugated magnetic nanoparticles synthesis and their ability to target tumors (Dutz & Hergt, 2014).

Magnetic fluids are used in determining fossil fuels, especially oil reservoirs. This creates a great opportunity for the synthesis of dense stable hydrophilic and hydrophobic magnetite nanoparticles that can be used in the oil exploration industry. Researches, synthesis methods, oil tank applications; concentrated on optimum

superparamagnetic iron oxide nanoparticle concentration and iron determination in these dense environments. Especially, in the determination of iron in crude oil, NMR T_2 relaxation time measurement method has been developed. Fe_3O_4 nanoparticles are used as contrast materials (Ali et al., 2018).

Magnetic storage, catalysis, electrocatalysis, targeted drug delivery and the use of magnetic particles and composites in biomedical field are increasing. In particular, magnetic nanoparticles are investigated for drug agents, such as contrast agents for MRI and hyperthermia, which allow diagnosis and treatment (Kudr et al., 2017).

Basic approaches in the use of magnetite nanoparticles have helped in diagnosis and therapy of diseases. These, magnetic separation of biological materials, magnetic nanocarriers, radio frequency controlled magnetic nanoparticles contributed to the improvement of diagnosis, drug delivery, imaging and cancer treatment, respectively (Kudr et al. 2017).

Magnetic nanoparticles have various applications in the field of therapy, such as magnetic field, hyperthermia using MRI, drug and DNA distribution. Meanwhile, local increase (hyperthermia) in tumor tissue temperature is considered an effective additional cancer treatment (Issa, Obaidat, Albiss, & Haik, 2013).

As the biomedical applications of iron oxide nanoparticles are known, macrophage polymerization of the immune system for imaging, drug and gene transmission, hyperthermia and cancer treatment is extensively investigated. In recent years, brain blood barrier limitation has been used in studies on brain tumors. For the treatment, the current status, chemical composition, advantages and disadvantages of the brain-blood supply throughout the brain are discussed. Effective therapy of brain tumors and reduction of side effects are examined, magnetic targeting, drug loading and drug release are made possible. The systems are larger in size and make it difficult to achieve blood-brain barrier penetration (Israel, Galstyan, Holler, & Ljubimova, 2020).

Water pollution is a problem in itself, and Antimony(Sb) accumulation in polluted waters constitutes an environmental risk. The appropriate adsorbent selection and mechanism for its removal has been investigated. In studies, Fe_3O_4 magnetic nanoparticles were used to remove contamination. Fe_3O_4 magnetic nanoparticles are coated with cationic surfactants to remove pollution (Guo et al., 2020).

Magnetic hyperthermia was promising in glioblastoma tumor model by being tested in animals. Aminosilane coated superparamagnetic Fe_3O_4 nanoparticles are used (Rego et al., 2019).

Today, many semiconductor metal oxides, conductive polymers, polymer composites and magnetic structured materials are used as gas sensors in different fields (Dai, Liang, & Lee, 2019).

$\alpha\text{-Fe}_2\text{O}_3$ (hematite) has high sensitivity, selectivity and stability in gas detection. It can be used as a sensor in determining alcohol in air and breath (Mirzaei et al., 2016).

In summary, magnetic materials are widely used in medicine release systems in medicine, smart carriers, cell separation, protein purification, catalyst, data storage in computers, energy as magnetic fluid, electronic sensor, biological test kits, and molecule marking in biomedicine. It is also working on spintronic and medical device development. (Al-Ghamdi et al., 2013).

3.1 The Aim of the Study

Magnetite has a wide range of uses. Usage areas vary basically depending on the preparation method of magnetite, conditions, particle size and morphology of end product formed.

Magnetite is also present in nature as a mineral and can be synthesized by co-precipitation, solvothermal / hydrothermal, sono-chemical, sol-gel etc. methods in solution medium. Various crystalline magnetites are formed depending on the synthesis method, starting materials and conditions. In this case, it also changes the physicochemical properties of the magnetite prepared depending on the particle size.

Currently, there are printing materials called toner that are imported for use in a large number of printers in various brands and models. In these materials, iron-based inorganic minerals with different magnetic properties are used.

In the study, it is aimed to prepare and characterize magnetite nanoparticles to be used as printers, copiers, black dye and pigment.

In this context, the method of co-precipitation of iron (II) and (III) chloride salts will be used predominantly for ease of application. The formation of spherical and homogeneously distributed magnetite in 100-200 nm size are aimed. Prepared particles are inorganic origin; The final product is a composite because the toner main ingredient is organic, that is, of polymer origin. In order to provide composite formation, stability and homogeneity of prepared magnetite nanoparticles, the surfaces of nanoparticles must be coated with surfactants. In this context, surfactants with different properties such as OA, SA, SDS, CTAB, APTES, OAm and HDTMS, namely anionic, cationic and neutral, will be tested. First of all, the aim is to prepare homogeneous, spherical magnetite with the desired particle size and to determine physicochemical properties by various methods.

GRAPHICAL ABSTRACT



Figure 1.9 Study overview (Personal archive, 2019; Google, 2020)

CHAPTER FOUR

MATERIALS AND METHODS

4.1 Materials

Fe₃O₄, Iron oxide, Magnetic (Fischer Scientific UK Ltd, 1/1100/53) obtained as a commercial product, used as standard and labelled as HA3. FeCl₃ 6H₂O Iron(III) chloride hexahydrate (SIGMA-ALDRICH 236489; ACS reagent, 97%) and FeCl₂ 4H₂O Iron(II) chloride tetrahydrate (SIGMA-ALDRICH 220299, 98%) were used in the synthesis as precursors of Fe₃O₄.

Oleic acid, CH₃(CH₂)₇CH=CH(CH₂)₇COOH (Carlo-Erba 305704, Pure); Stearic acid, CH₃(CH₂)₁₆COOH (SIGMA-ALDRICH 175366; reagent grade, 95%); Oleylamine, CH₃(CH₂)₇CH=CH(CH₂)₇CH₂NH₂ (Acros 129540010; technical grade, C18 content, 80-90%); Sodium dodecyl sulfate, SDS, CH₃(CH₂)₁₁OSO₃Na (SIGMA-ALDRICH 62862, ≥90%); (3-aminopropyl)triethoxysilane, H₂N(CH₂)₃Si(OC₂H₅)₃, APTES (Fluka 09324, purum ≥98%, GC); cetyltrimethyl ammonium bromide, CTAB, C₁₉H₄₂BrN (SIGMA-ALDRICH H5882, ≥98%); Hexadecyl trimethoxy silane, HDTMS, (ALDRICH 52360, technical ≥85%, GC) were used during the synthesis as surfactants and coating agents.

Acetone, CH₃COCH₃ (SIGMA-ALDRICH 650501) and Ethanol, C₂H₅OH (Merck MILLIPORE 1.00974) were used for washing purposes to remove the excessive coating agent from the products at the end of the synthesis as solvents before the drying.

HCl (Riedel-de Haën, 07102, 37%) and NaOH (Fluka 71691, purum ≥98% small beads) have been used to adjust the pH values of the solutions. NH₃ (Merck 1005432) was for precipitation of iron precursors.

In the experiments, deionized water which produced in our laboratories were used.

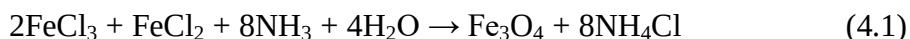
4.2 Preparation of Magnetite, Magnetite/Oleic acid, Magnetite/Stearic acid, Magnetite/SDS and Magnetite/CTAB Nanoparticles

4.2.1 Preparation of Magnetite Nanoparticles

In this method, 1.5 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 3.0 g FeCl_3 , were dissolved in 100 ml of deionized water. Fe(III) to Fe(II) ratio was selected as 1:2. The experiment was carried out under N_2 gas flow with stirring at 60°C . 10 mL, 25 wt% NH_4OH and (1.0%, v/v) oleic or stearic acids were used in HA6 and HA7 products. Then, the color of the solution suddenly turned black with the addition of a base. The black product was separated with outer magnet and the clear part was decanted. Black solid was washed with water and alcohol and dried at 80°C for 24 h. The end products were marked as HA1, HA2 and HA6 and HA7. Experiments for the product HA2 were carried out in an open atmosphere at 60°C .

Another co-precipitation method according to the Berger et al. 1999:

The synthesis was carried out according to the following reaction.



According to the Equation 4.1, preparation of stock solutions of Fe^{2+} and Fe^{3+} precursors as follows;

2.0 M FeCl_2 stock Fe^{2+} solution was prepared by dissolving 39.76 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 100 mL of 2 M HCl. 1.0 M FeCl_3 stock Fe^{3+} solution was prepared by dissolving 67.58 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 250 mL of 2 M HCl. 0.7 M aqueous NH_3 solution was prepared from 48 mL of concentrated aqueous NH_3 diluted to 1 L with H_2O .

Procedure

1.0 mL FeCl_2 and 4.0 mL FeCl_3 solutions were added in a flask and vigorously stirred. To this solution, 50 mL of 0.7 M aqueous NH_3 solution was added dropwise by using a burette. It has been observed that addition rate of should be slow. A black precipitate formed immediately. Stir the solution carefully during the dropwise addition of ammonia solution. Then, stop stirring and allow the precipitate to settle in 5–10 min. by using an external magnet. After the collapse is complete, clear liquid in the upper part is filtered. The solid black precipitate is washed with deionized water and alcohol to neutrality for the removal of chloride ions. Finally, it is dried at 60°C . The products were marked as HA2 as for HA3.



Figure 4.1 Experimental design of the preparation studies (Personal archive, 2019)



Figure 4.2 Experimental design of the preparation studies (Personal archive, 2019)



Figure 4.3 Experimental design of the preparation studies (Personal archive, 2019)



Figure 4.4 Experimental design of the preparation studies (Personal archive, 2019)

4.2.2 Preparation of Magnetite/Oleic acid Nanoparticles

In this method, Fe_3O_4 were prepared by the thermal method by using iron oleate as iron source. However, sodium oleate was first prepared by adding 0.71 g of NaOH to 5.56 mL of oleic acid dissolved in 50 mL 70% ethanol. The mixture was stirred overnight at room temperature. The product was formed as a white soap as a result of removing the solvent under vacuum.

Iron oleate was prepared in our laboratories. 10.8 g of iron (III) chloride hexahydrate was dissolved in 36.5 g of sodium oleate in 140 mL n-hexane, 60 mL deionized water and 80 mL ethanol. Then the mixture heated to 70 °C for 4 h. As a result, two phases occurred. The organic layer was separated and washed with 30 mL of water three times for removal of NaCl. The blackish organic layer was separated and vacuum dried to remove hexane. The last black product was stored for future use. The experiment was conducted using the literature (Bear et al., 2015).

In another study, iron oleate complexes were used as the starting material in the synthesis of magnetite. The product was very sensitive to the temperature, extraction and drying conditions (Parkin et al. 2015).

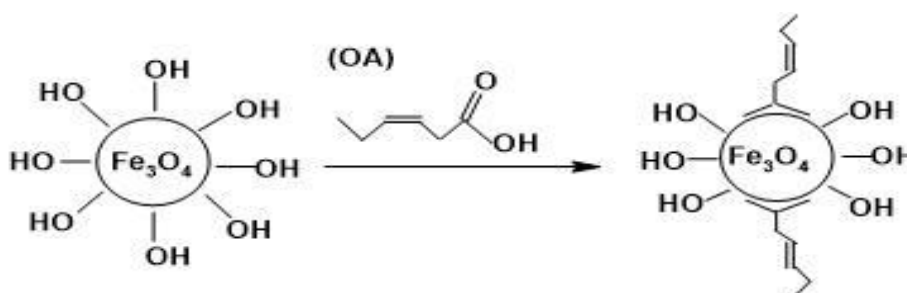


Figure 4.5 Reaction scheme of Fe_3O_4 Nanoparticles with OA

4.2.3 Preparation of Magnetite/Stearic acid Nanoparticles

HA7 sample were obtained by the co-precipitation. In the synthesis, stearic acid was used as a saturated long chain organic stabilizer.

About 2 g of stearic acid was dissolved in 8 g kerosene. Then, the solution was mixed with 100 mL of hot water containing 3 mL of concentrated aqueous ammonia to form a water kerosene emulsion. Then magnetite suspension was added to this emulsion. Due to adsorption of stearic acid to the surface of the magnetite particles, particles became hydrophobic and transferred to the organic kerosene phase. Two phases had been formed. The bulk organic liquid phase was separated and washed with hot water until neutrality and heated to 120 °C. The product was washed with petroleum ether, centrifuged, and dried (Lysenko, Astaf'eva, Yakusheva, & Balasoiu, 2019). The reaction scheme was given in Figure 4.6.

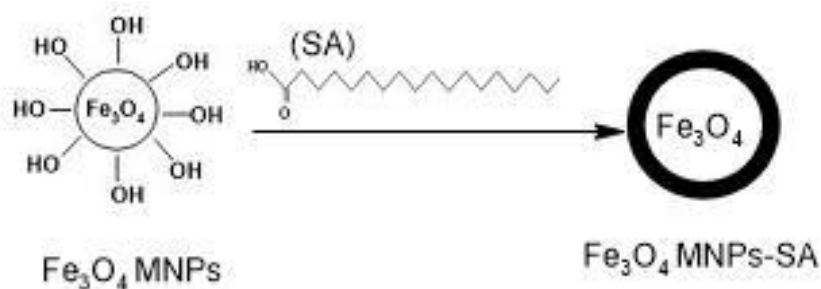


Figure 4.6 Reaction scheme of Fe_3O_4 Nanoparticles with SA

4.2.4 Preparation of Magnetite/SDS Nanoparticles

In the synthesis of this product, the work done by Shen and his friends was used (Shen et al., 2014). The method was briefly applied as follows. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ salts were used as precursors. They dissolved separately in distilled water for 5 minutes using a magnetic stirrer. 1.0 g SDS was added to this solution under stirring. The pH of the solution was adjusted to 12 with solid NaOH. The solution was stirred at room temperature for 20 minutes. Black solid colloidal product formed. The product separated and washed with distilled water and ethanol until neutrality. Finally, black precipitates were air-dried at room temperature. The products was marked as HA4. The reaction scheme was given in Figure 4.7.

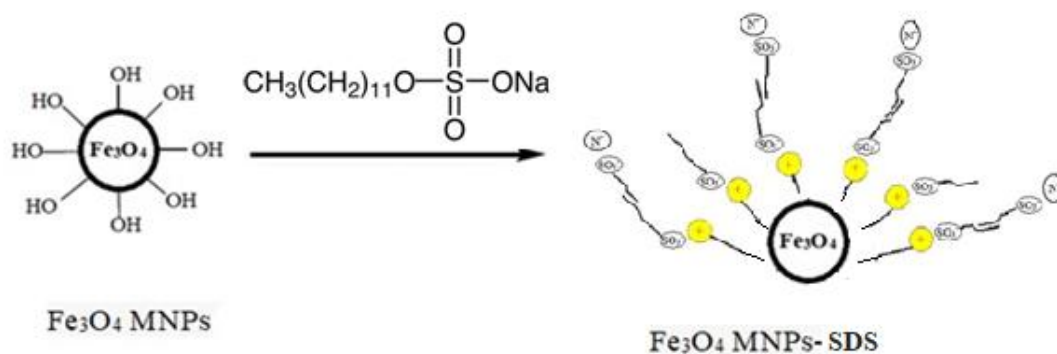


Figure 4.7 Reaction scheme of Fe_3O_4 Nanoparticles with SDS

4.2.5 Preparation of Magnetite/CTAB Nanoparticles

Magnetite (Fe_3O_4) and Cetyltrimethylammonium bromide (CTAB) coated particles were prepared by the co-precipitation method according to the reported procedure (Saksornchai, Kavinchai, Thongtem, & Thongtem, 2018). It is stated that this product had a high surface area with magnetic properties.

In the synthesis, 1 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 30 mL of distilled water. The solution stirred vigorously at 60°C for 30 minutes. The pH was adjusted to 13 using the NH_3 solution. Then, CTAB was added to the mixed solutions and heated continuously for 30 minutes to form precipitates. Black colloidal precipitates were filtered off. Product washed with distilled water and ethanol. Finally, it dried at 50°C for 12 hours. The product was marked as HA5. The reaction scheme was presented in Figure 4.8.

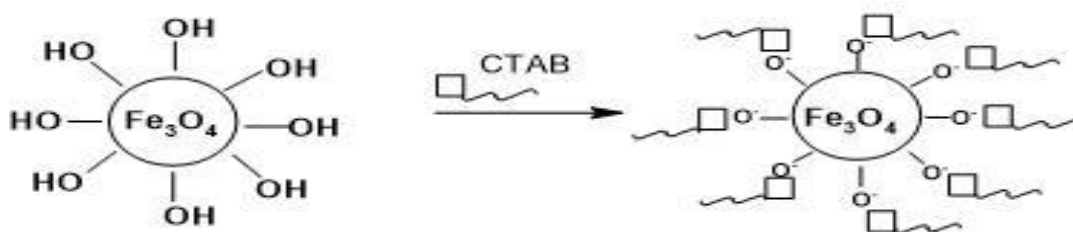


Figure 4.8 Reaction scheme of Fe_3O_4 Nanoparticles with CTAB

4.2.6 Preparation of Magnetite/OAm coated Nanoparticles

Fe_3O_4 MNPs were modified by oleylamine through a dispersion method (Li & Chang, 2004). Briefly, 2.315 g Fe_3O_4 MNPs was dispersed in 300 mL ethanol under magnetic stirring. Then 0.535 g oleylamine was added to this solution. The resulting solution was heated to 75 °C for 1 h. The product was separated by using an external magnet, washed with ethanol and dried at 60 °C in a vacuum oven and marked as HA11. The reaction scheme was indicated in Figure 4.9.

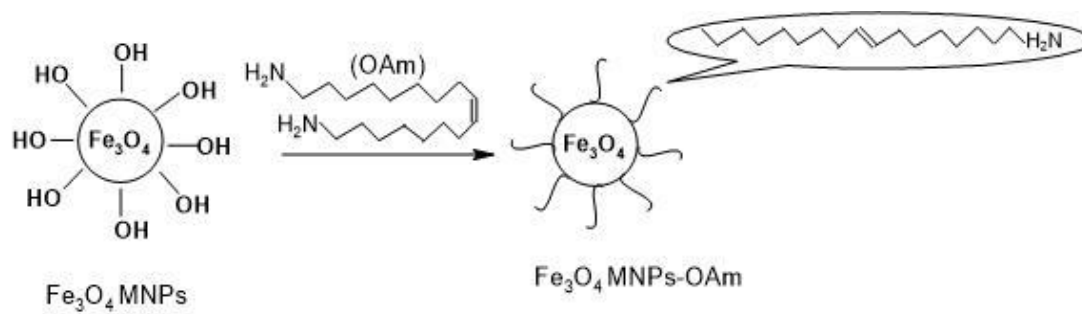


Figure 4.9 Reaction scheme of Fe_3O_4 Nanoparticles with OAm

4.2.7 Preparation of Magnetite/APTES Nanoparticles

In this method, amino groups of (3-aminopropyl)triethoxysilane (APTES) covers the surface of the magnetite nanoparticles over hydroxyl groups as a result of a silanization reaction. (Herrera, Barrera, & Rinaldi, 2008; Van de Waterbeemd, Sen, Biagini, & Bruce, 2010).

APTES coated MNPs were synthesized using the methods (Can, Ozmen, & Ersoz, 2009; Cao, He, Deng, & Gao, 2009; Saif, Wang, Chuan, & Shuang, 2015). Briefly, 4.23 g Fe_3O_4 NPs were dispersed in 150 mL ethanol/water (v/v, 1:1) for 30 min by sonication. Then, 16.16 g of APTES was added at 40 °C for 2 h. APTES to Fe_3O_4 mol ratio was found as 4:1 (Shen et al. 2004). The APTES coated Fe_3O_4 NPs were separated with a magnet, and washed with ethanol and deionized water. Product was dried under vacuum at 70 °C and marked as HA12. The reaction scheme was shown in Figure 4.10.

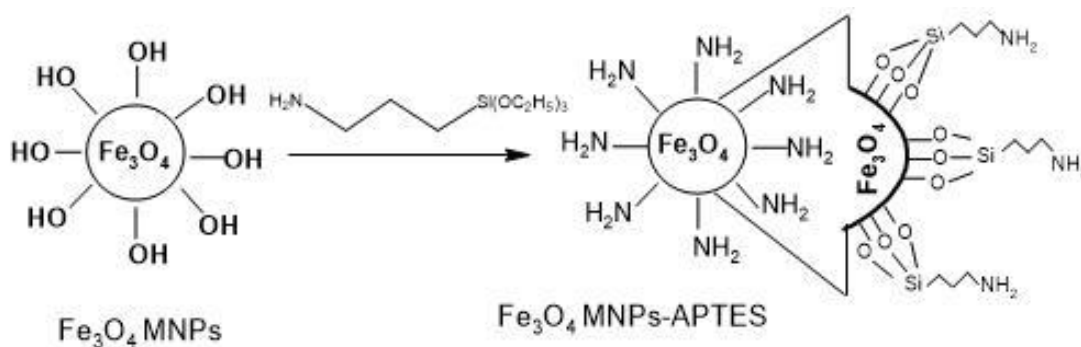


Figure 4.10 Reaction scheme of Fe_3O_4 Nanoparticles with APTES

4.2.8 Preparation of Magnetite/HDTMS Nanoparticles

HDTMS coated MNPs were synthesized using the methods (Zhang, Niu, Pan, Shi, & Cai, 2010; Storozhuk & Iukhymenko 2018 and 2019). Briefly, 1.2 g dry Fe_3O_4 was dispersed by using 60 mL dry toluene. The mixture was stirred a little more for 10 min for the formation of a homogeneous solution. After that, it was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed, then heated up to 120 °C for 6 h. The reactor is opened after cooling to room temperature and black product is removed. The product was washed with anhydrous alcohol and acetone, dried at 60°C for 12 hours, and marked as HA13. The possible reaction scheme was presented in Figure 4.11.

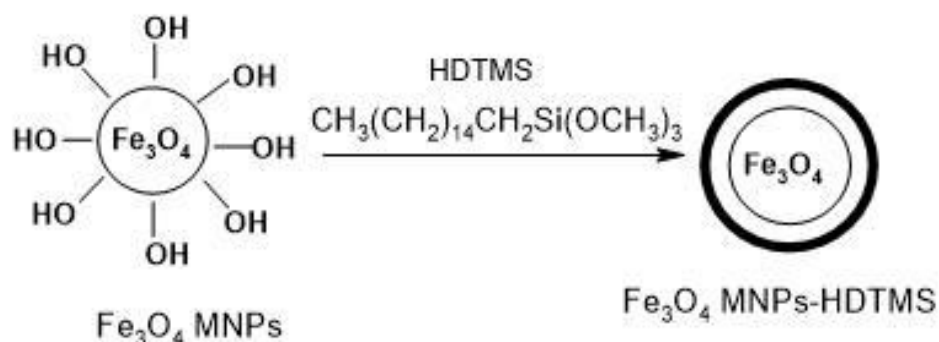


Figure 4.11 Reaction scheme of Fe_3O_4 Nanoparticles with HDTMS

4.3 Characterization Methods

4.3.1 Crystallinity by X-Ray Diffraction (XRD)

XRD patterns of the nanoparticles were recorded on a Rigaku Ultima Model X-Ray diffractometer using Cu K α (1.54 Å) radiation. The scanning scope, 2θ was 20°-80° with a scanning rate of 4°min.⁻¹. These studied in XRD Laboratory of Metallurgy and Materials Engineering Department of Engineering Faculty of Dokuz Eylül University.

4.3.2 Fourier Transform Infrared (FTIR) Spectra of the Samples

The nanoparticles were characterized by FTIR spectroscopy. FTIR spectra of powdered samples were investigated in Perkin Elmer BX II model spectrometer as KBr disks, collecting 25 scans in the wavenumber range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

4.3.3 Thermogravimetric Analysis (TGA) of the Samples

The thermal stabilities of the prepared samples were analyzed by thermogravimetric analysis. TG/DTG profiles of the samples were performed from 30°C to 480°C at heating rate of 10°C /min with a Perkin Elmer Diamond TG/DTA instrument.

4.3.4 Scanning Electron Microscopy (SEM)

The morphology of the samples was monitored by SEM were taken at various magnifications at 5 kV on Carl Zeiss 300VP SEM at Research Center of Katip Çelebi University. The samples were coated with Au by using QUORUM Q150 RES device.

4.3.5 X-ray Photoelectron Spectroscopy (XPS)

XPS spectra were done with Thermo Scientific K-Alpha spectrometer in Dokuz Eylul University, Center for Fabrication and Application of Electronic Materials. The instrument uses a monochromated Al-K α X-ray source. General survey scans were carried out in the binding energy range of 0–1200 eV. C1s binding energy at 284.60 eV was used as reference.

4.3.6 Vibrating-Sample Magnetometer (VSM)

Magnetic parameters of the samples were investigated by using Dexion Magnet VSM 550 (Dexion Magnet Tech. Co. Ltd.) model VSM – Vibrating Sample Magnetometer in Dokuz Eylul University, Center for Fabrication and Application of Electronic Materials. The magnetometer operated under the features of Magnetic Field: 0 – 3.5 T; Magnetic Moment: 10-2 emu – 300 emu; Temperature Range: -196 – 900°C; Sample: Powder, Min. 300 mg; Solid: Max. 4 x 4 x 6 mm or Liquid: Min. 5 mL. The experiments were carried out at 298K.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Characterization Results of the Samples

XRD patterns of HA3, OA coated Fe_3O_4 and Fe_3O_4 (El-Gahandoor, 2012) were given in Figures 5.1, 5.2 and 5.3 respectively.

5.1.1 XRD pattern of Fe_3O_4 MNPs

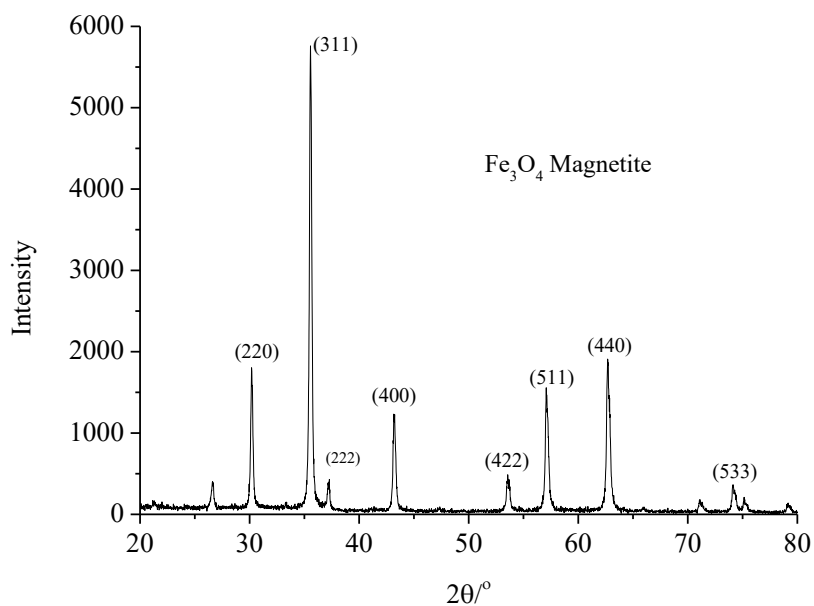


Figure 5.1 XRD pattern of HA3 as standard magnetite nanoparticles

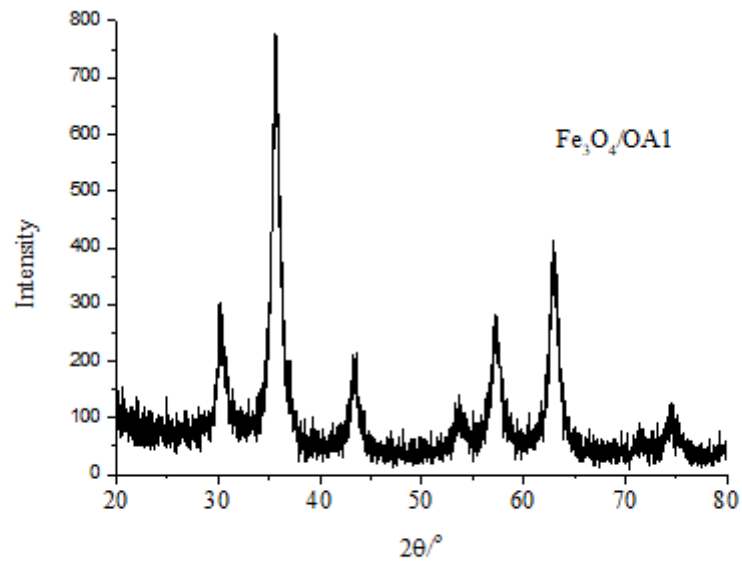


Figure 5.2 XRD patterns oleic acid coated Fe_3O_4

Seven peaks ($2\theta / ^\circ$: 30.20° , 35.56° , 43.16° , 53.56° , 57.82° , 62.38° , 74.14°) were observed in the MNP XRD patterns coated with Fe_3O_4 and Oleic acid. Miller indices of the reflection planes are: (220), (311), (400), (422), (511), (440), (533). The structure shows the surface-centered cubic Fe_3O_4 crystal and fits the standard Fe_3O_4 inverted cubic spinel structure (JCPDS card: 89-691).

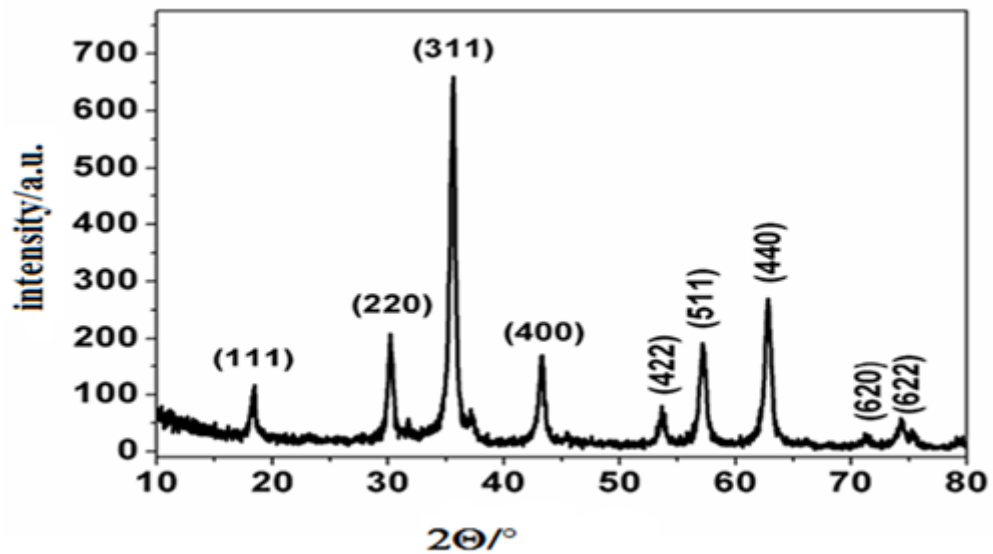


Figure 5.3 XRD pattern of Fe_3O_4 nanoparticles (El Ghandoor, Zidan, Khalil, & Ismail, 2012)

XRD data was used to characterize the crystallinity and average size of nanoparticles. The lattice constant was calculated as 8.310 Å, which was 8.39 for magnetite and a cubic phase structure (Abd, Latif, & Wasna'a, 2016).

However, the crystallite size, strain value and dislocation values of the particles were calculated as 57-111 nm, 5.85 and 3.39×10^{14} lines/m² respectively (Ghandoor et al 2012).

As shown in Figure 5.3, six peaks of Fe₃O₄ observed at 2θ/° of 30.1, 35.5, 43.2, 53.5, 57.0 and 62.8, which had Miller indices of (220), (311), (400), (422), (511) and (440), respectively. These peaks revealed Fe₃O₄ particles with a spinel structure (JCPDS file, PDF No. 65-3107).

By using XRD data, the crystallite size, D as nm was calculated by the Debye-Scherrer Formula (Scherrer, 1918; Langford & Wilson, 1978) as $D = K\lambda/\beta\cos\theta$. Where K is the Scherrer constant, λ is the X-ray wavelength, β is the peak width at half-maximum (FWHM) in radians, θ is the Bragg diffraction angle or peak position in radians.

The dislocation density is a measure of the number of dislocations in a unit volume of a crystalline material arising from crystal imperfections (Bindu & Thomas, 2014).

Table 5.1 shows the crystallite sizes, dislocation densities and microstrain values of the samples.

Table 5.1 Average crystallite size and related parameters of the Fe₃O₄ Samples

Sample	(311) 2 θ ^o (Radians)	β (FWHM) (Radians)	Crystallite Size, D (nm)	Average Crystallite Size D (nm)	Dislocation density, $\delta \times 10^{-3}$ (nm ⁻²) Average	Microstrain, $\epsilon \times 10^{-3}$ Average
HA1	35.75	1.56	5.33	8.73	40.49	3.66
HA2	35.59	1.42	5.89	6.77	41.39	3.03
HA3	35.57	0.28	29.38	26.88	1.73	0.69
HA4	35.64	1.28	6.51	13.73	8.02	1.65
HA5	35.67	1.40	5.95	10.10	30.31	2.39
HA6	35.68	1.18	7.05	7.91	20.86	2.34
HA7	35.65	1.24	6.72	18.91	21.63	2.41
HA8	36.05	0.23	36.28	32.29	1.02	0.59
HA11	35.64	0.27	30.44	28.25	1.38	0.67
HA12	36.02	0.27	30.53	28.56	1.38	0.68
HA13	35.49	0.28	29.43	28.40	1.33	0.65

From Table 5.1, it can be said that the Fe₃O₄ nanoparticles are nanoparticles with as average crystallite size of about less than 32 nm. It can be said that the XRD patterns of the Fe₃O₄ samples revealed good crystallinity and phase purity. The diffraction peaks reflect pure Fe₃O₄ with a spinel structure (JCPDS file, PDF No. 65-3107). No other peaks were observed either from the precursors.

The sharpness, strong intensity and narrow width of Fe₃O₄ diffraction peaks in XRD pattern indicated that Fe₃O₄ samples were well crystallized. XRD pattern of HA3 MNPs demonstrate peaks at 2 θ of 26.6°, 30.20°, 35.57°, 43.22°, 53.60°, 57.13°, 62.74° corresponding to the (hkl), (220), (311), (400), (422), (511), (440), for face-centered cubic Fe₃O₄ and expressed as JCPDS card: 89-691.

After calculation of the crystallite sizes, it can be possible to calculate the parameters of the strain value (ε) and dislocation values (δ) of the nanoparticles particles. In this work, the parameters were also calculated by using the equations in the following;

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad \delta = \frac{1}{D^2} \quad (5.1)$$

Our values were given in Table 5.1. There is a good correlation among the samples HA3 (Standard), HA8(Commercial product), HA11 and HA12. In terms of dislocation values (δ) of these samples are about $1 \times 10^{-3} \text{ nm}^{-2}$. As can be seen, for the other samples calculated as $20\text{-}40 \times 10^{-3} \text{ nm}^{-2}$. Same results were also found for the strain values as 0.6×10^{-3} and $2\text{-}3 \times 10^{-3}$, respectively.

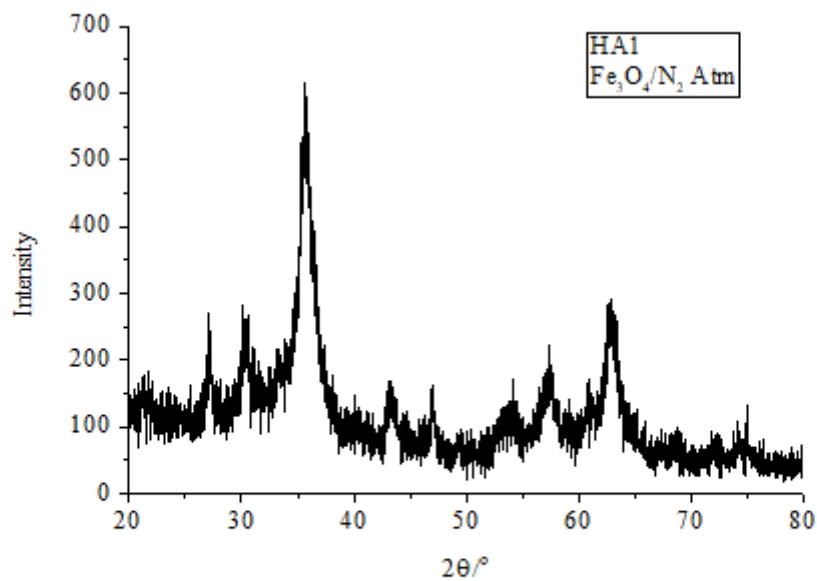


Figure 5.4 XRD pattern of HA1

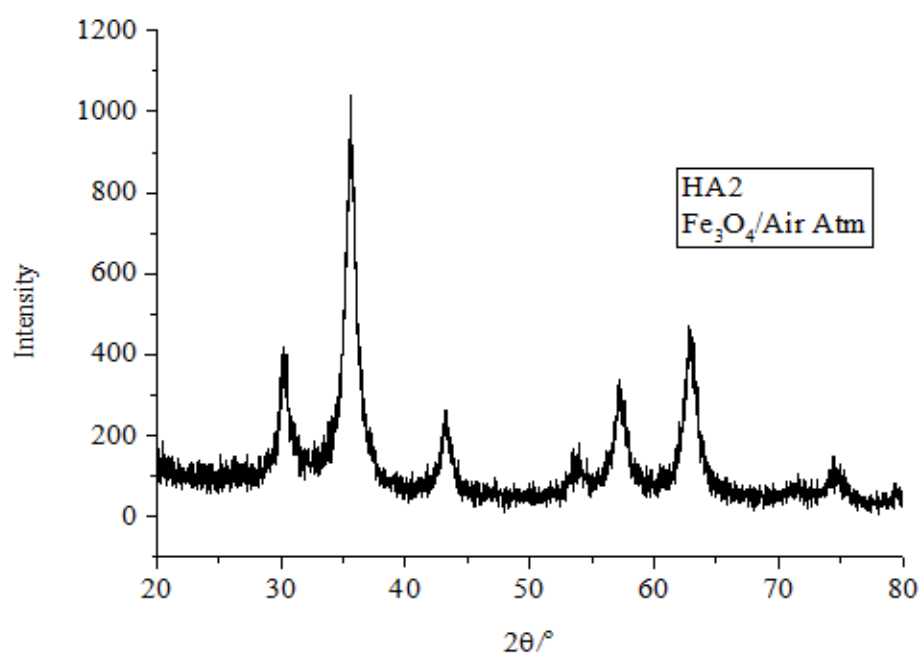


Figure 5.5 XRD pattern of HA2

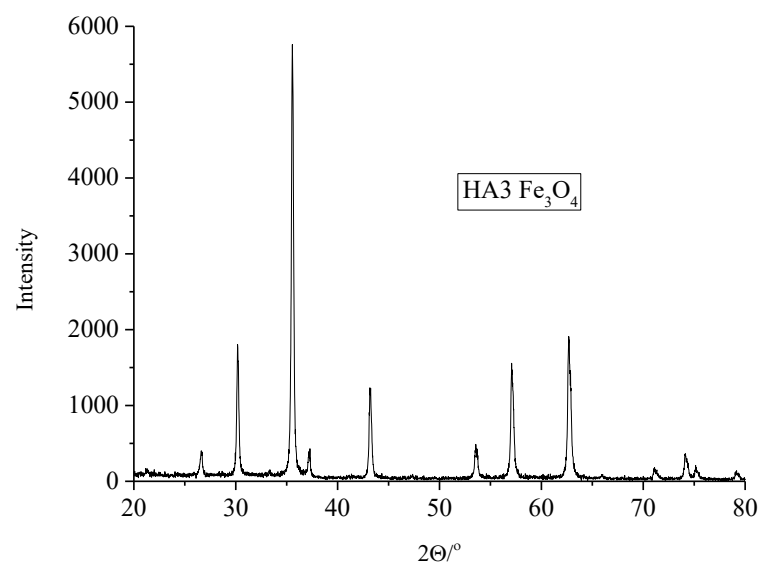


Figure 5.6 XRD pattern of HA3

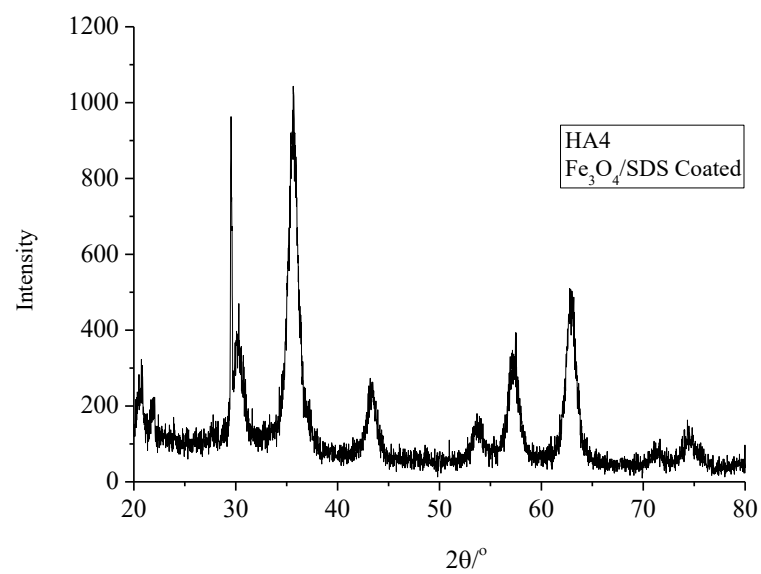


Figure 5.7 XRD pattern of HA4

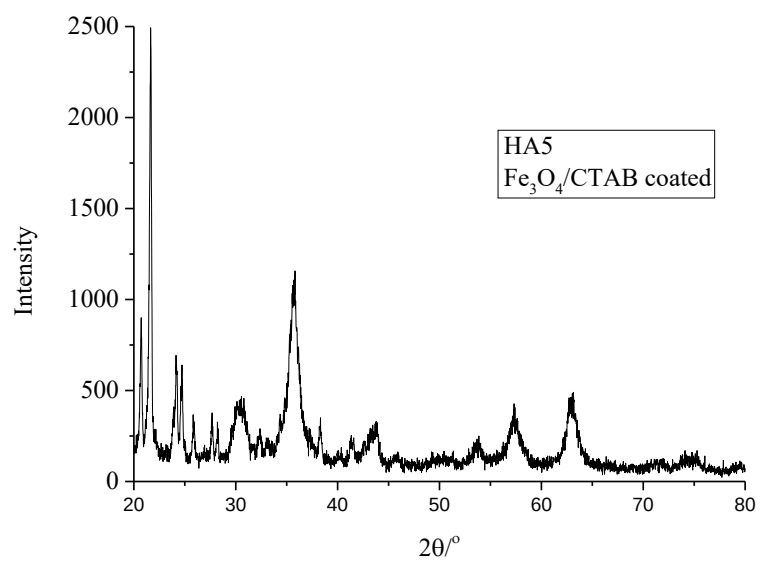


Figure 5.8 XRD pattern of HA5

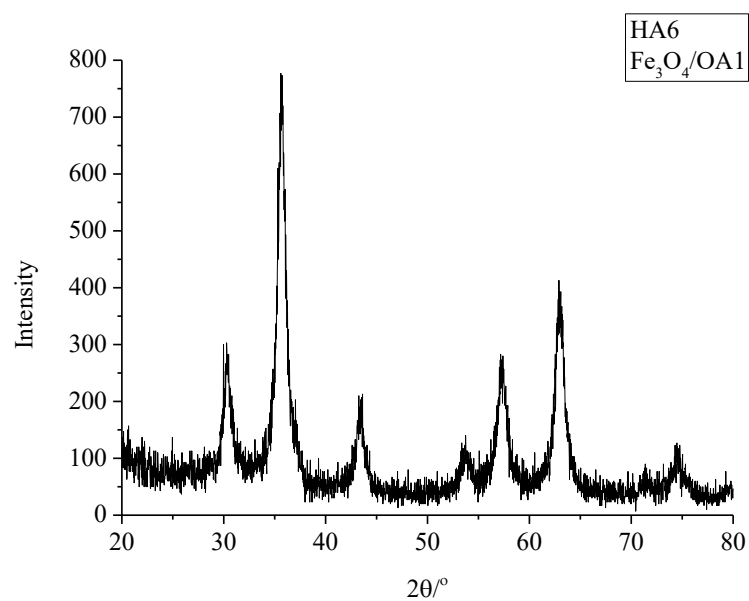


Figure 5.9 XRD pattern of HA6

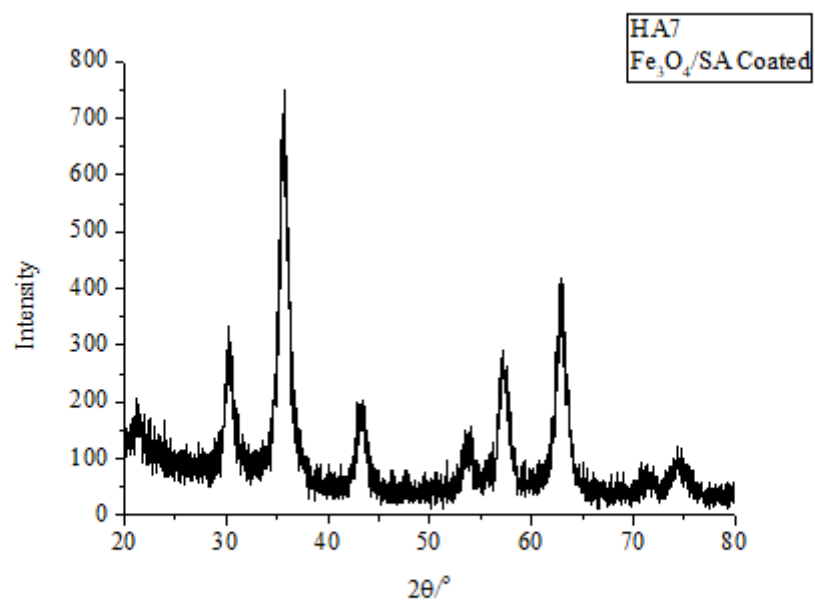


Figure 5.10 XRD pattern of HA7

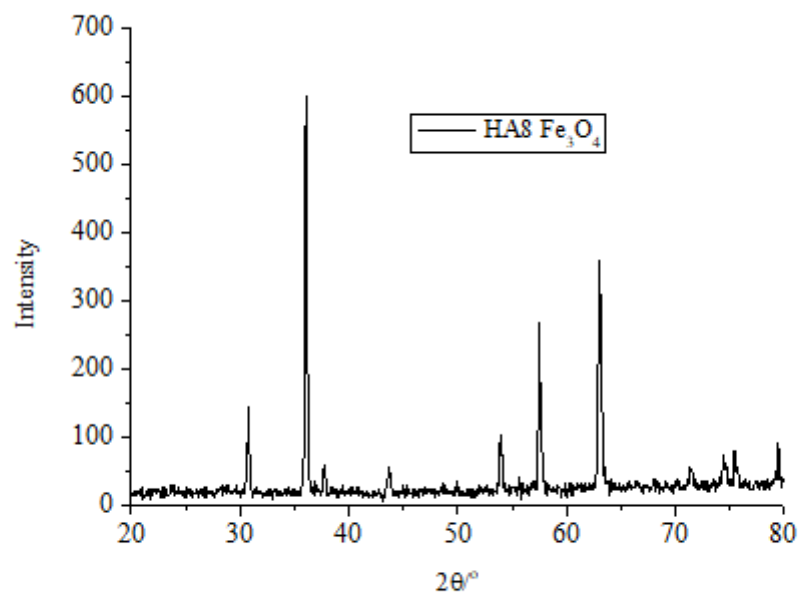


Figure 5.11 XRD pattern of HA8

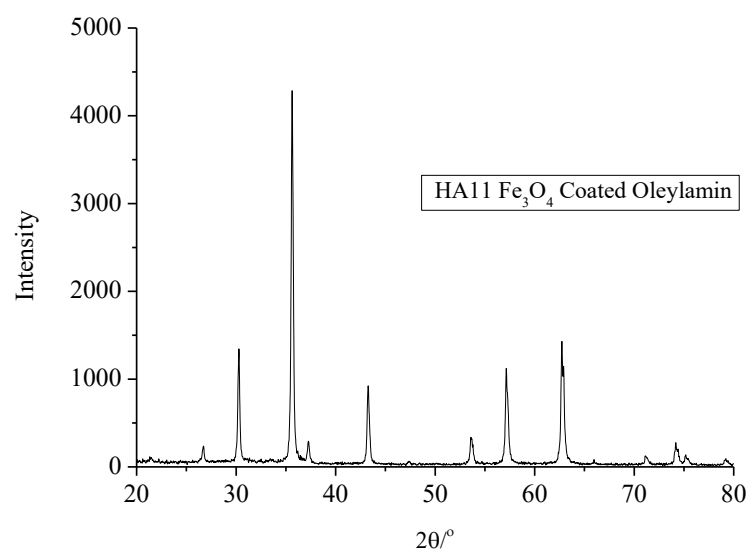


Figure 5.12 XRD pattern of HA11

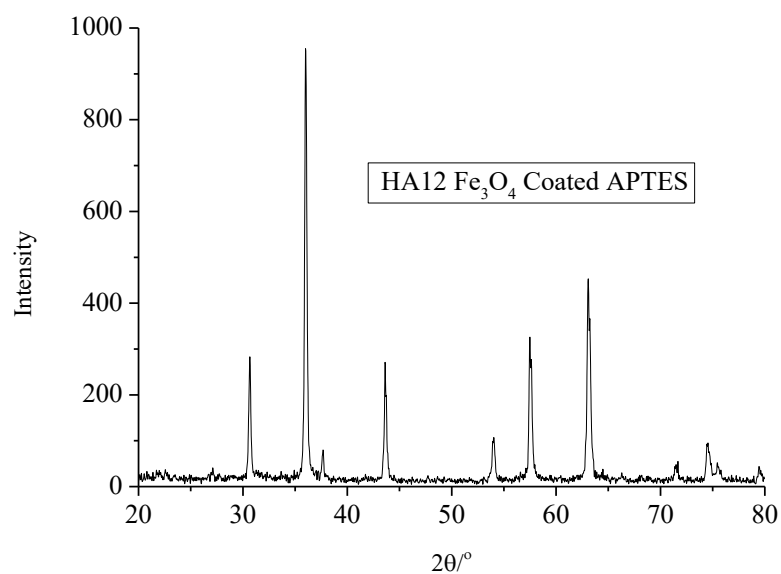


Figure 5.13 XRD pattern of HA12

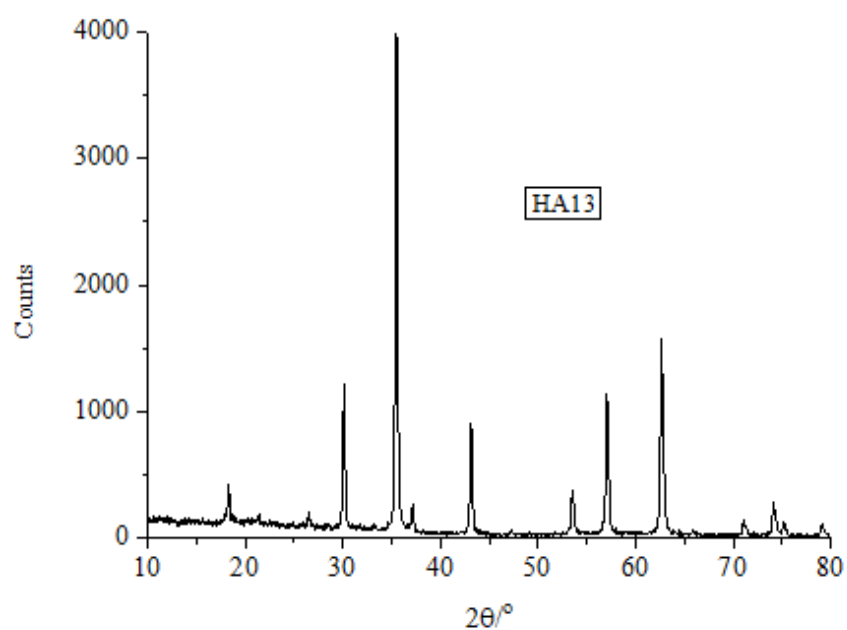


Figure 5.14 XRD pattern of HA13

XRD patterns of Fe_3O_4 NPs and oleic acid, stearic acid, oleylamine, CTAB, SDS, APTES, HDTMS modified Fe_3O_4 NPs were given in Figures 5.4-5.14. XRD analysis

of all of the samples presented in Figure 5.1-5.3 had the same pattern. The patterns coincided with HA3. Coating of the surfaces did not cause any change in the pattern.

5.1.2 Fourier Transform Infrared FT-IR Spectra of the Samples

FTIR spectra of powdered samples were recorded using a Perkin Elmer BX II FTIR spectrometer in a KBr disks, collecting 25 scans in wavenumbers of 400–4000 cm^{-1} range with a resolution of 4 cm^{-1} .

In Figure 5.15 FTIR spectrum of HA3 (Fe_3O_4 Standard) was given in the wavenumbers of 4000-400 cm^{-1} and 800-400 cm^{-1} .

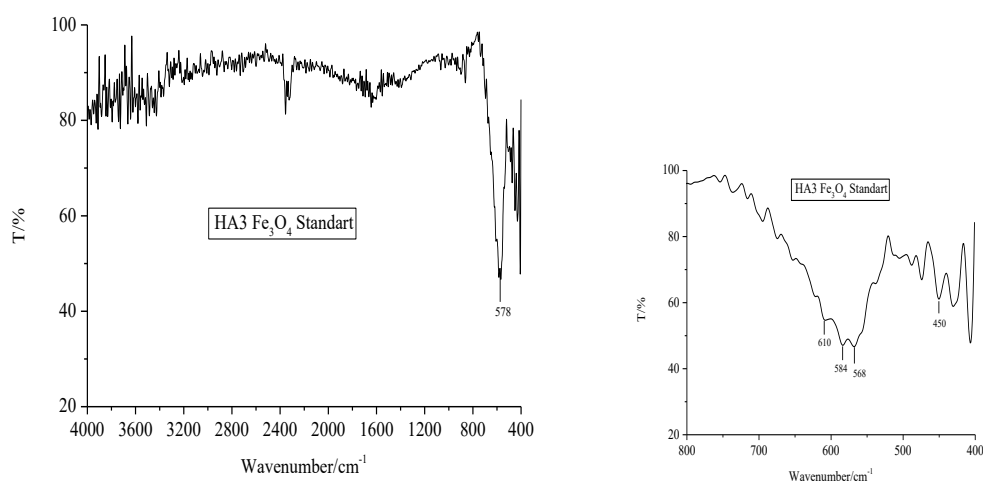


Figure 5.15 FTIR spectra of HA3 (Fe_3O_4 standard)

bands at 610, 584 and 450 cm^{-1} were assigned to Fe–O absorption in magnetite as indicated with the references (Waldron, 1955; Zhang & Misra, 2007).

The strong bands at 584 and 610 cm^{-1} were observed in all spectra which were due to Fe–O stretching vibrational mode of Fe_3O_4 . The band at 540 cm^{-1} was reported for Fe–O (Mahdavi et al., 2013; Chamritski & Burns, 2005).

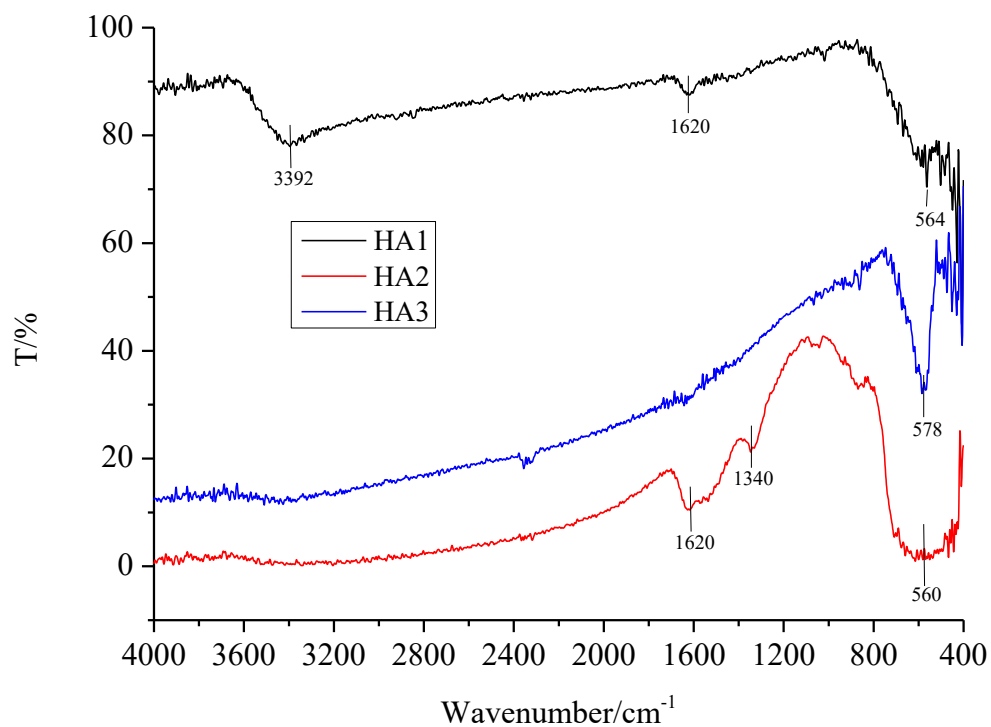


Figure 5.16 FTIR spectra of HA1, HA2 and HA3

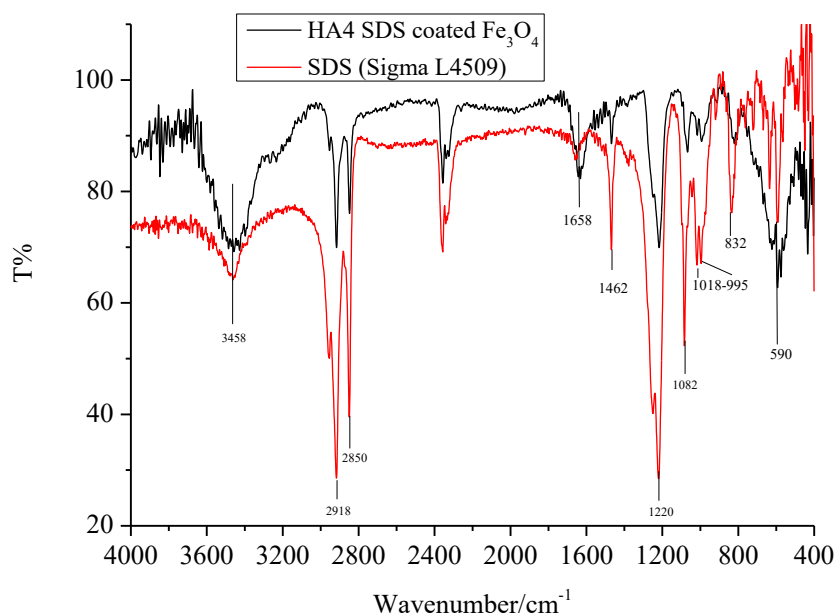


Figure 5.17 FTIR spectra of HA4 and SDS

Sodium Dodecyl Sulfate (SDS)-Coated Magnetite Nanoparticles

Figure 5.17 shows infrared spectra of magnetite nanoparticles coated with SDS and pure SDS. The FT-IR spectrum of pure SDS was also shown for comparison. Magnetite phase is characterized by its main band at $430 - 442 \text{ cm}^{-1}$. On the other hand, the sulfate groups in SDS was estimated by its bands at $998, 1019, 1082 \text{ cm}^{-1}$ and $1223 \text{ cm}^{-1}, 1249 \text{ cm}^{-1}$ for symmetric and asymmetric absorptions, respectively (Dobson, Roddick-Lanzilotta, & McQuillan, 2000). Location and shape/sharpness of the bands changed because of the interaction between the SDS and magnetite nanoparticles. FTIR spectral data of SDS and SDS-coated magnetite was given in details in Table 5.2 (El-kharrag, Amin, & Greish, 2011). Changes in the band position related with bond formation between the sulfate group and the Fe^{2+} and Fe^{3+} ions. (Dobson, Roddick-Lanzilotta, & McQuillan, 2000). This shift was also related with the amounts of SDS (El-kharrag, Amin, & Greish, 2011).

Table 5.2 FTIR spectral data of SDS and SDS-coated magnetite (El-kharrag, Amin, & Greish, 2011).

$\nu_s (-\text{OSO}_3^-)$			$\nu_{as} (-\text{OSO}_3^-)$		
SDS	998	1019	1082	1223	1249
0.2%	1010		***	***	
0.5%	1005		***	1248	
1.0%	969		1063	1242	
2.0%	958		1063	1230	

*** bands were not observed in the FT-IR spectra of these samples

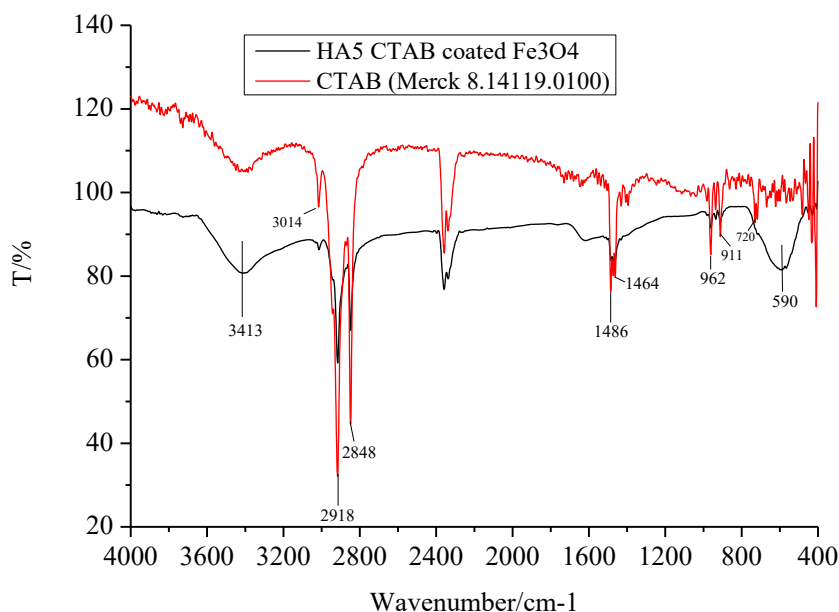


Figure 5.18 FTIR spectra of HA5 and CTAB

FTIR Spectrum of Cetyltrimethylammonium bromide (CTAB)

FTIR spectrum of CTAB was given in Figure 5.18. The bands at about 3420 cm⁻¹ related with N⁺-H vibrations. 2918 and 2848 cm⁻¹ bands were C-H vibration bands of -CH₂ group. The bands at 1486 and 1464 cm⁻¹ related to asymmetric and symmetric stretching vibration of N⁺-CH₃. The band at 962 cm⁻¹ is due to the out-of-plane -C-H vibration of CH₃ (Guivar, Sanches, Magon, & Fernandes, 2015). The band at 720 cm⁻¹ belongs to Br⁻. In the FTIR spectrum of CTAB coated Fe₃O₄ (Figure 5.17), the band at 590 cm⁻¹ was due to Fe-O. On the other hand, broad band at 3413 cm⁻¹ reflected interaction of surface hydroxyl groups of Fe₃O₄ with the ammonium moiety in CTAB (Elfeky, Mahmoud, & Youssef, 2017).

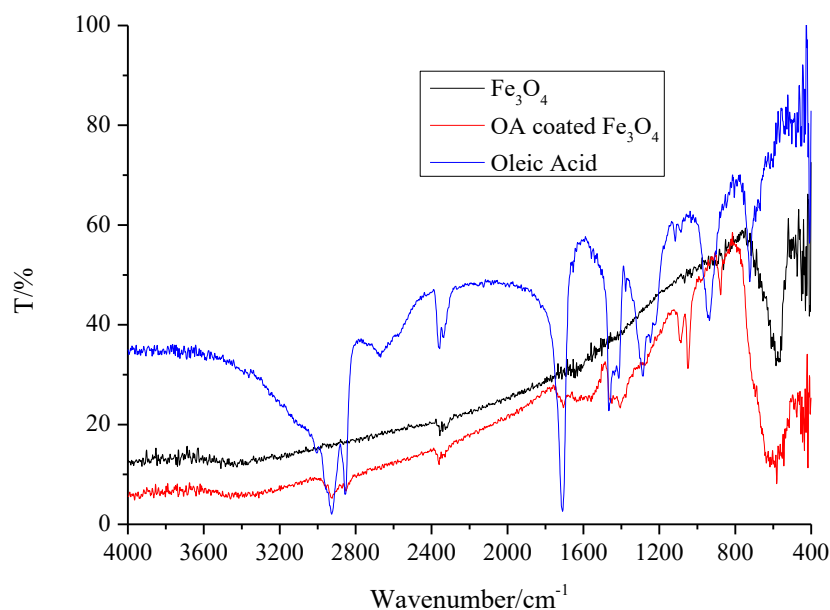


Figure 5.19 FTIR spectra of HA6 and OA

FTIR Spectrum of Oleic Acid

The FTIR spectrum of oleic acid was shown in Figure 5.19. It exhibited the bands related with oleyl group. These bands about 2858 and 2920 cm^{-1} were due to the symmetric and asymmetric CH_2 stretching vibrations. 3002 cm^{-1} band was due to the $\nu(\text{C-H})$ stretching of the C-H bond adjacent double bond of OA. Band at 1648 cm^{-1} was related with $\nu(\text{C=C})$ stretching vibration. In Figure 5.19, the carbonyl group $\nu(\text{C=O})$ of oleic acid was seen at 1709 cm^{-1} . The band at 2670 cm^{-1} was due to $\nu(\text{O-H})$ stretching vibration of dimer form of OA (Shukla et al 2003).

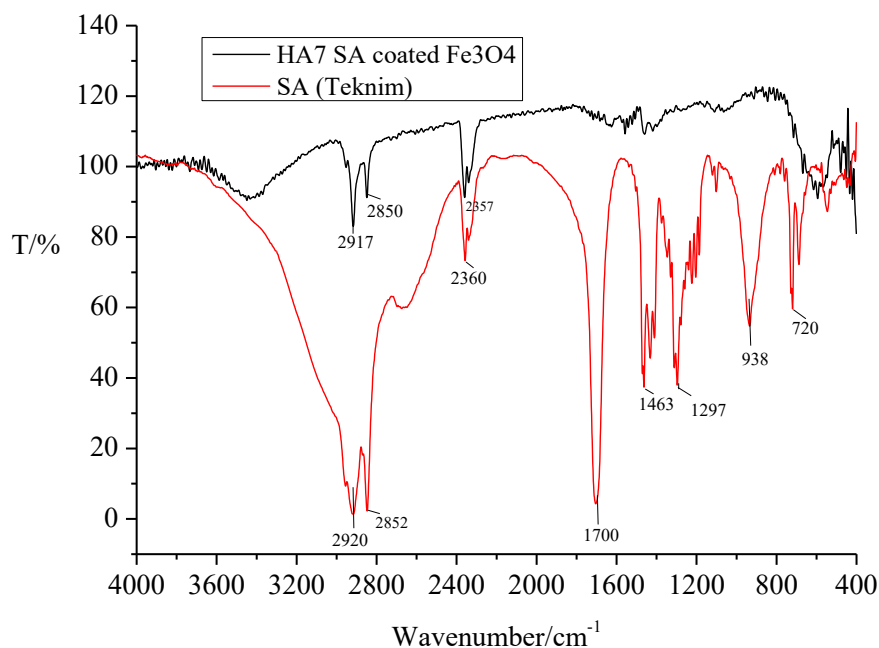


Figure 5.20 FTIR spectra of HA7 and SA

FTIR spectrum of stearic acid was shown in Figure 5.20 as red line. The adsorption bands at about 2920 and 2852 cm^{-1} were related with $-\text{CH}_2-$ asymmetric and symmetric stretching vibrations, respectively (Chen, Li, Hao, Chen, & Kong, 2011; Yang, Zhang, Men, Xu, & Zhu, 2011). In Figure 5.20, band at 1700 cm^{-1} was exposed to $-\text{COOH}$ group of stearic acid. On the other hand, this band disappeared in the spectrum of SA coated Fe_3O_4 . At the same time, the bands of SA, at 1463, 1297, 938 and 720 cm^{-1} were also not observed or very weak in the spectrum of HA7. The results showed that Fe_3O_4 reacted with stearic acid and formed as a thin film (Zhu et al., 2016).

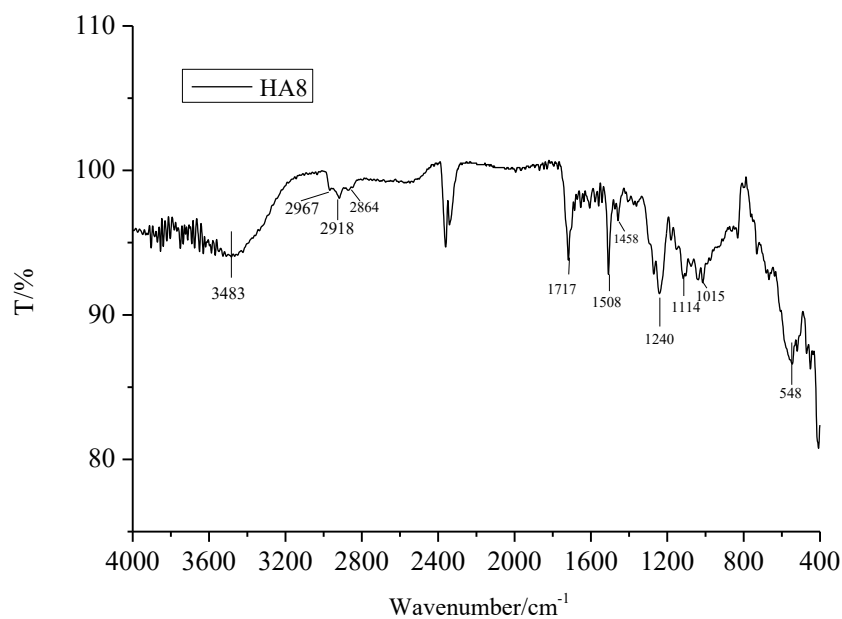


Figure 5.21 FTIR spectra of HA8

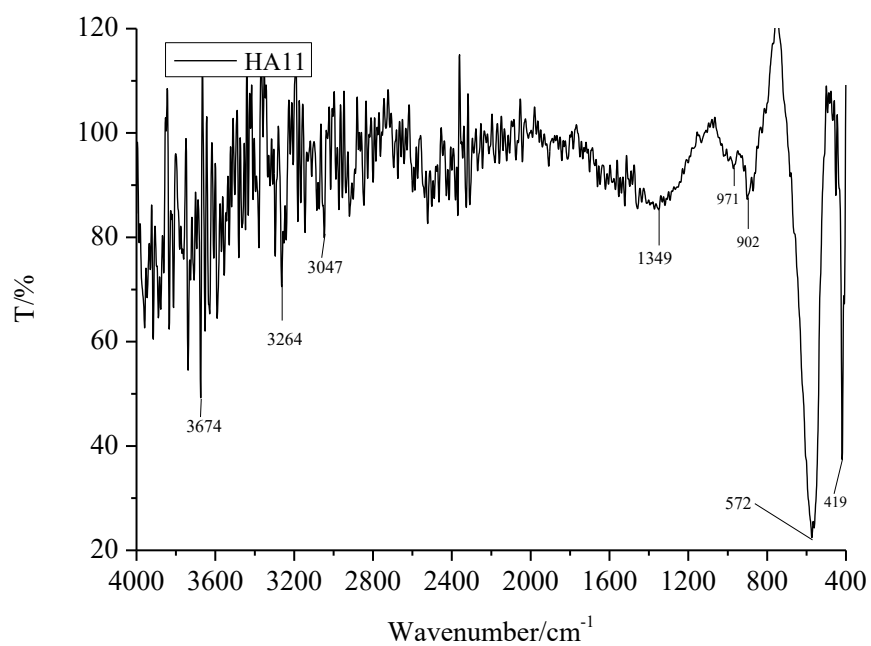


Figure 5.22 FTIR spectra of HA11

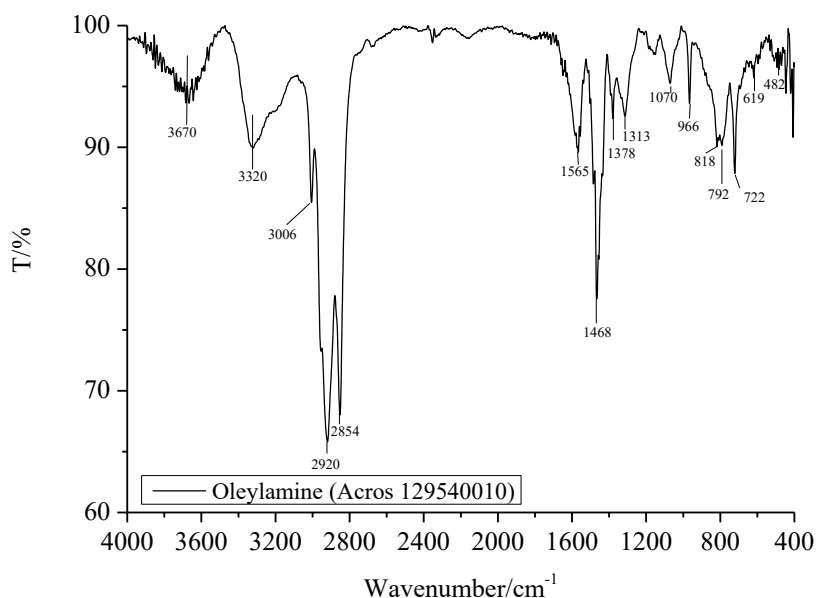


Figure 5.23 FTIR spectra of OAm

FTIR Spectrum of Oleylamine

The spectrum of oleylamine (Figure 5.23) showed the oleyl group bands in the 2850–3000 cm^{-1} region and the $\nu(\text{C}=\text{C})$ stretching band at 1647 cm^{-1} . However, the band at 1593 cm^{-1} was due to the NH_2 . Band at 3300 cm^{-1} was due to the $\nu(\text{N}-\text{H})$. The bands below 1500 cm^{-1} arise from $\nu(\text{C}-\text{C})$, $\nu(\text{C}-\text{O})$ and CH_2 groups. FTIR spectrum of Oam was reported by several researchers and presented as its in Table 5.3. However, FTIR spectrum of Oam coated Fe_3O_4 (Figure 5.22) was not resolved and clear in the wavenumbers range of 4000–1600 cm^{-1} . It is not easy to assign these complex bands. This may be due to the strong interaction between OAm and surface hydroxyl groups of Fe_3O_4 .

Table 5.3 FTIR band assignments of OAm (Shukla, Liu, Jones, & Weller, 2003; Mourdikoudis & Liz-Marzán, 2013)

Vibrational modes	Wavenumbers (cm ⁻¹)	References
$\nu_{as}(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$	3376, 3300	(Erley & Hemminger, 1994)
<i>Trans</i> $\nu(\text{CH=})$	3066	(Sinclair et al. 1952)
<i>Trans</i> $\nu(\text{CH=})$	3035	(Sinclair et al. 1952)
<i>Trans</i> $\nu(\text{CH=})$	3020	(Sinclair et al. 1952)
<i>Cis</i> $\nu(\text{CH=})$	3006	(Lee et al. 2000; Sinclair et al. 1952; Vogel-Weill & Gruger, 1996)
$\nu_a(\text{CH}_2)$	2922	(Lee et al. 2000; Sinclair et al. 1952; Vogel-Weill & Gruger, 1996)
$\nu_s(\text{CH}_2)$	2854	(Lee et al. 2000; Sinclair et al. 1952; Vogel-Weill & Gruger, 1996)
$\nu(\text{OH})$	2670	(Lee & Condrate, 1999; Lee et al. 2000)
$\nu(\text{C=O})$	1709	(Lee & Condrate, 1999; Lee et al. 2000; Sinclair et al. 1952)
$\nu(\text{C=C})$	1647	(Lee & Condrate, 1999; Lee et al. 2000)
$\nu(\text{NH}_2)$	1593	(Erley & Hemminger, 1994)
$\nu(\text{COO})$	1512	(Lee & Condrate, 1999; Lee et al. 2000; Thistlethwaite & Hook, 2000; Liu & Xu, 1995)
<i>Trans</i> $\nu(\text{CH=})$	970	(Sinclair et al. 1952; Vogel-Weill & Gruger, 1996)

ν_s = symmetric stretching vibration; ν_{as} = asymmetric stretching; ν = vibration; δ = bending vibration

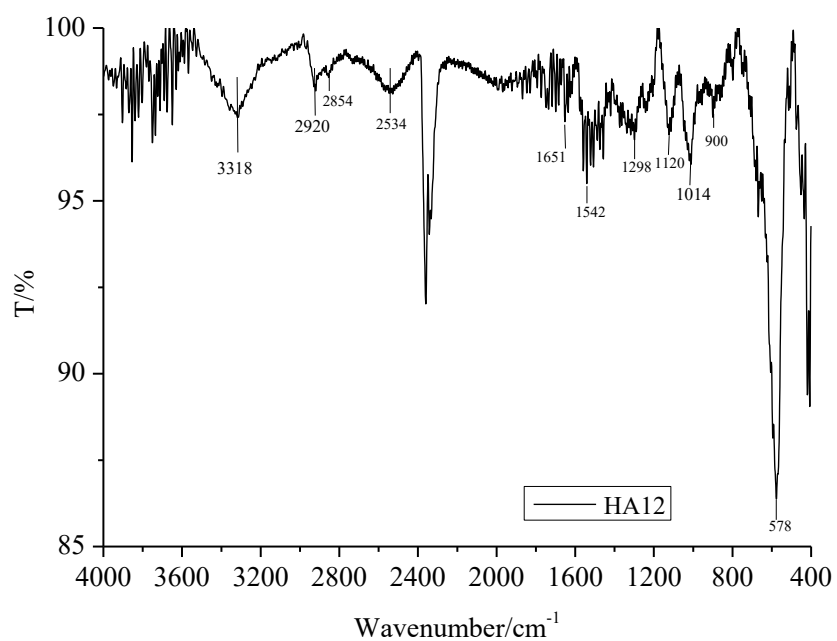


Figure 5.24 FTIR spectrum of HA12

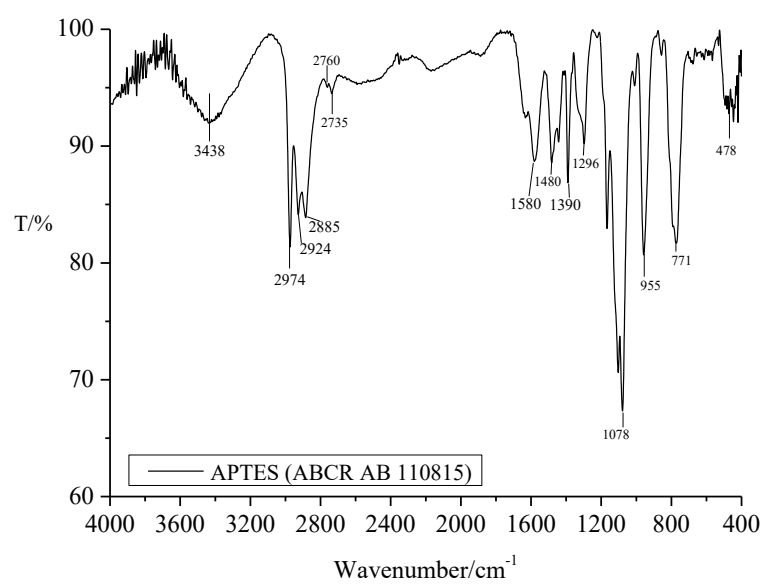


Figure 5.25 FTIR spectrum of APTES

FTIR Spectrum of 3-aminopropyltriethoxysilane (APTES)

FTIR spectra of HA12 (APTES coated sample) and APTES were shown in Figure 5.24 and 5.25, respectively. The interaction between silane, -NH_2 groups of APTES and surface -OH groups of magnetite can be confirmed by FTIR measurements. The schematical presentation of the interaction was also given in Figure 5.26.

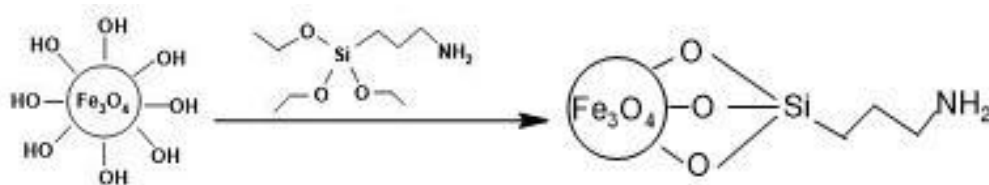


Figure 5.26 Schematic presentation of Interaction of APTES with surface hydroxide groups

The three vibrational bands around 1587 , 1487 , and 1335 cm^{-1} in Figure 5.25 were related with amino groups and C-N in APTES. The symmetric deformation band of CH_3 in ethoxy groups of APTES was observed at 1384 cm^{-1} (Chiang, Ishida, & Koenig, 1980; Pena-Alonso, Rubio, Rubio, & Oteo, 2007). On the other hand, CH_2 stretching band is observed in between $2869\text{-}2927\text{ cm}^{-1}$.

The reaction mechanism was analyzed FTIR spectroscopically. Accordingly, the reaction was evaluated by APTES Si-O and siloxane groups (Si-O-Si) and polymerized APTES related IR bands (Pena-Alonso, Rubio, Rubio, & Oteo, 2007). Some other stretching bands related with -NH_2 groups of APTES film was also reported (Bragaru et al., 2013).

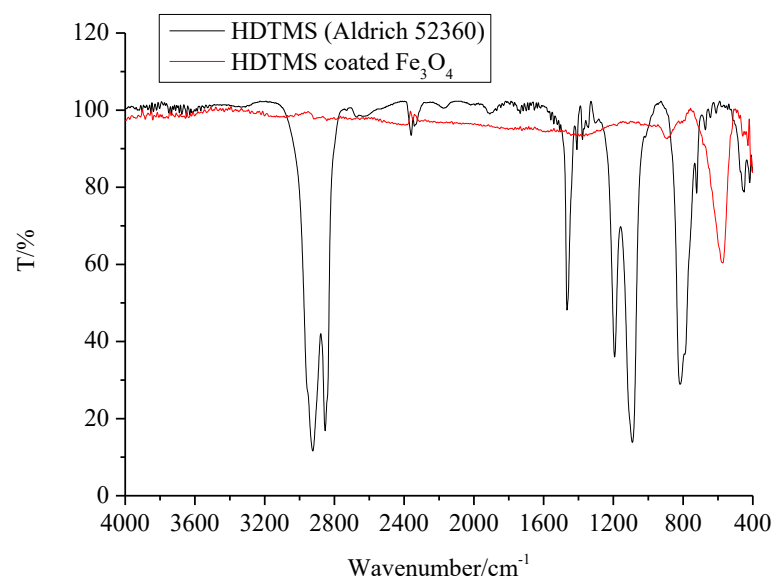


Figure 5.27 FTIR spectrum of HA13 HDTMS

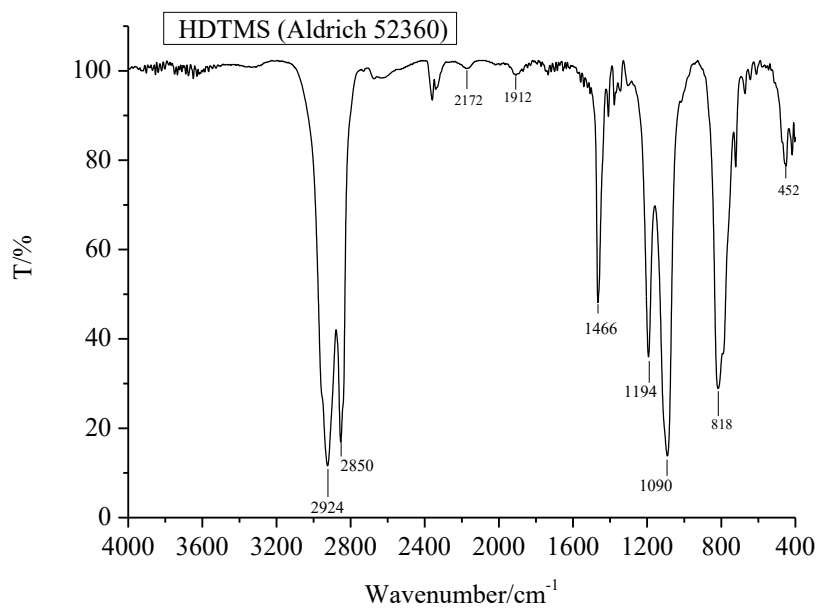


Figure 5.28 FTIR spectrum of HDTMS

FTIR Spectrum of hexadecyltrimethoxysilane (HDTMS)

FTIR spectra of HA13 (HDTMS coated sample) and HDTMS were shown in Figure 5.27 and 5.28, respectively. The covalent bonding between silane -NH_2 group and magnetite -OH groups can be observed by FTIR measurements. The schematical presentation was also given in Figure 5.29.

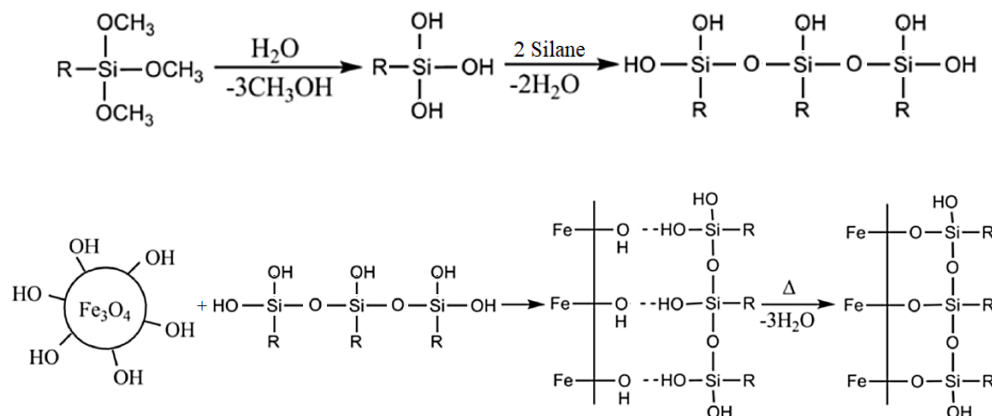


Figure 5.29 Interaction of HDTMS with surface hydroxide groups of Fe_3O_4 (Storozhuk & Iukhymenko, 2019)

The band at 594 cm^{-1} was assigned to Fe-O for magnetite. On the other hand, the bands at 895 , 1047 and 1121 cm^{-1} are related with Fe-OH groups (Nakamoto, 1997). Band at 1642 cm^{-1} was due to water molecules adsorbed on the magnetite surface which is 1630 cm^{-1} for free water molecules as humidity.

HDTMS hydrolysis in aqueous medium. The hydrolysis products formed interact with other silane molecules and concentrate. The formed condensed products interact with the hydroxyl groups on the magnetite and become a film layer. In this way, the hydrophilic magnetite surface becomes hydrophobic. The reaction is shown in Figure 5.28. The reaction mechanism was analyzed FTIR spectroscopically and published. Accordingly, the reaction was evaluated on the IR bands of Fe-O-Si , Si-O-H and Si-O-Si groups (Storozhuk & Iukhymenko, 2019; De Palma et al., 2007). Interaction of HDTMS and magnetite nanoparticles was also investigated and reported (De Palma et al., 2007). Thus, the FTIR spectra in Figure 5.27 (red line) reflected the interaction of HDTMS with magnetite.

5.1.3 Thermogravimetric (TG/DTG) Analysis of the Samples

TGA analyzes of Fe_3O_4 samples were performed with a Perkin-Elmer Diamond TG /DTG analyzer to investigate the thermal stabilities of the samples. Analyzes were performed in platinum vessels under nitrogen gas atmosphere at 30-480 °C and heating rate of 10 °C/min.

TG/DTG thermograms of the samples HA4, HA5, HA6, HA7 and HA8 were given in Figures 5.30-5.34, respectively.

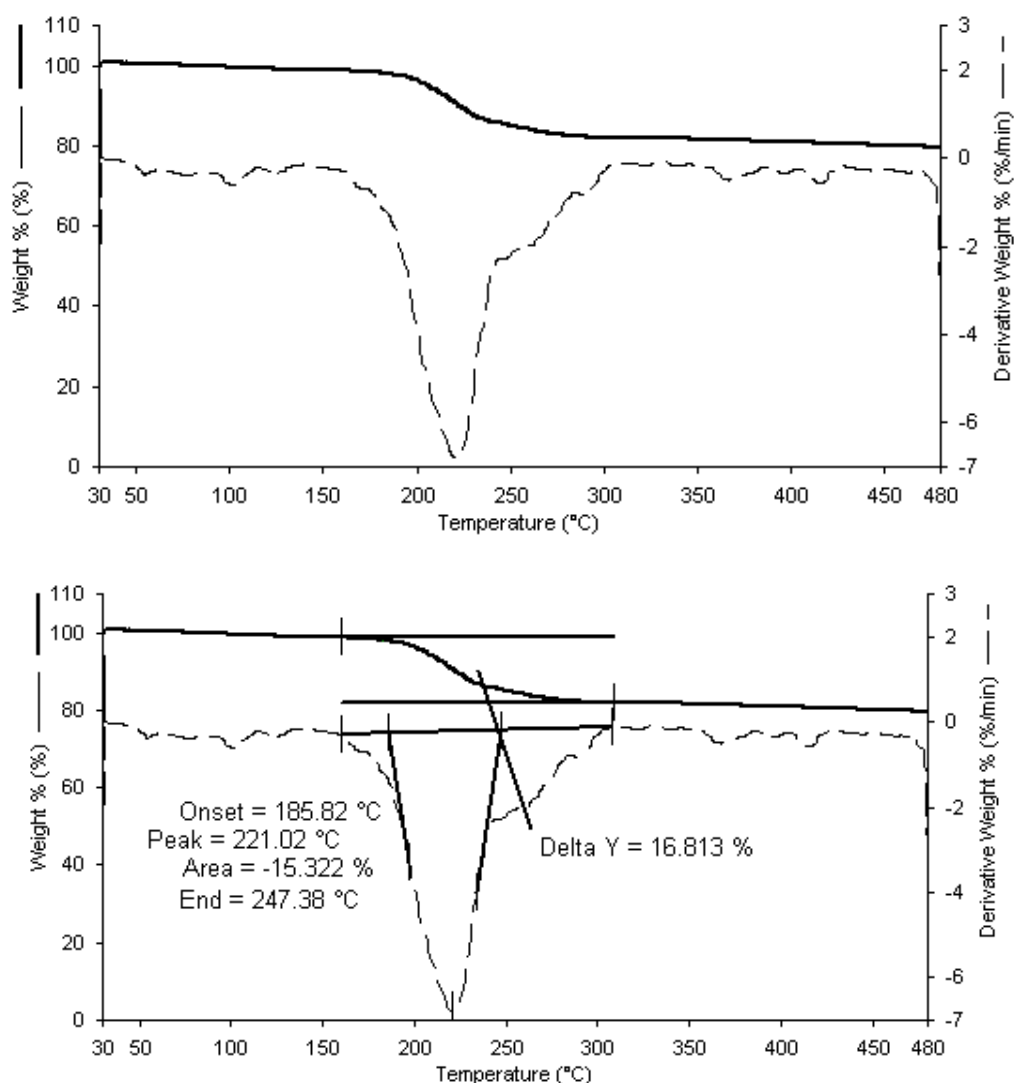


Figure 5.30 TG/DTG thermograms of HA4

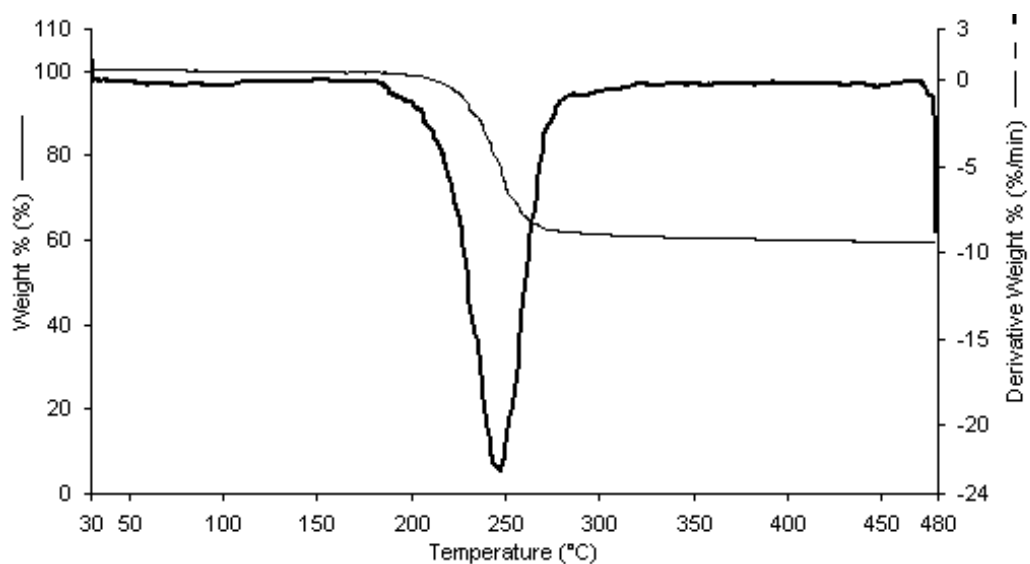
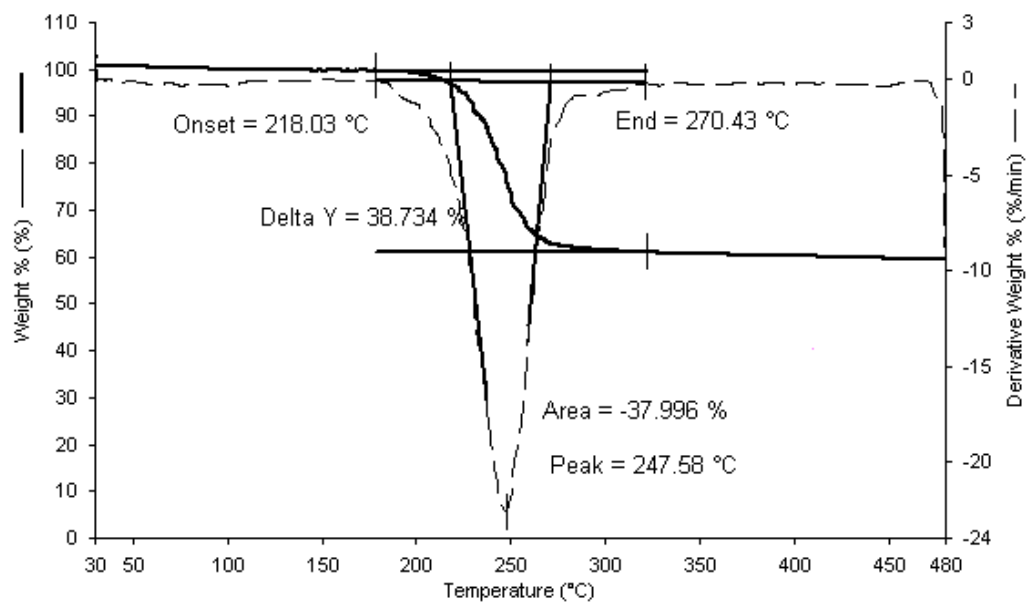


Figure 5.31 TG/DTG thermograms of HA5

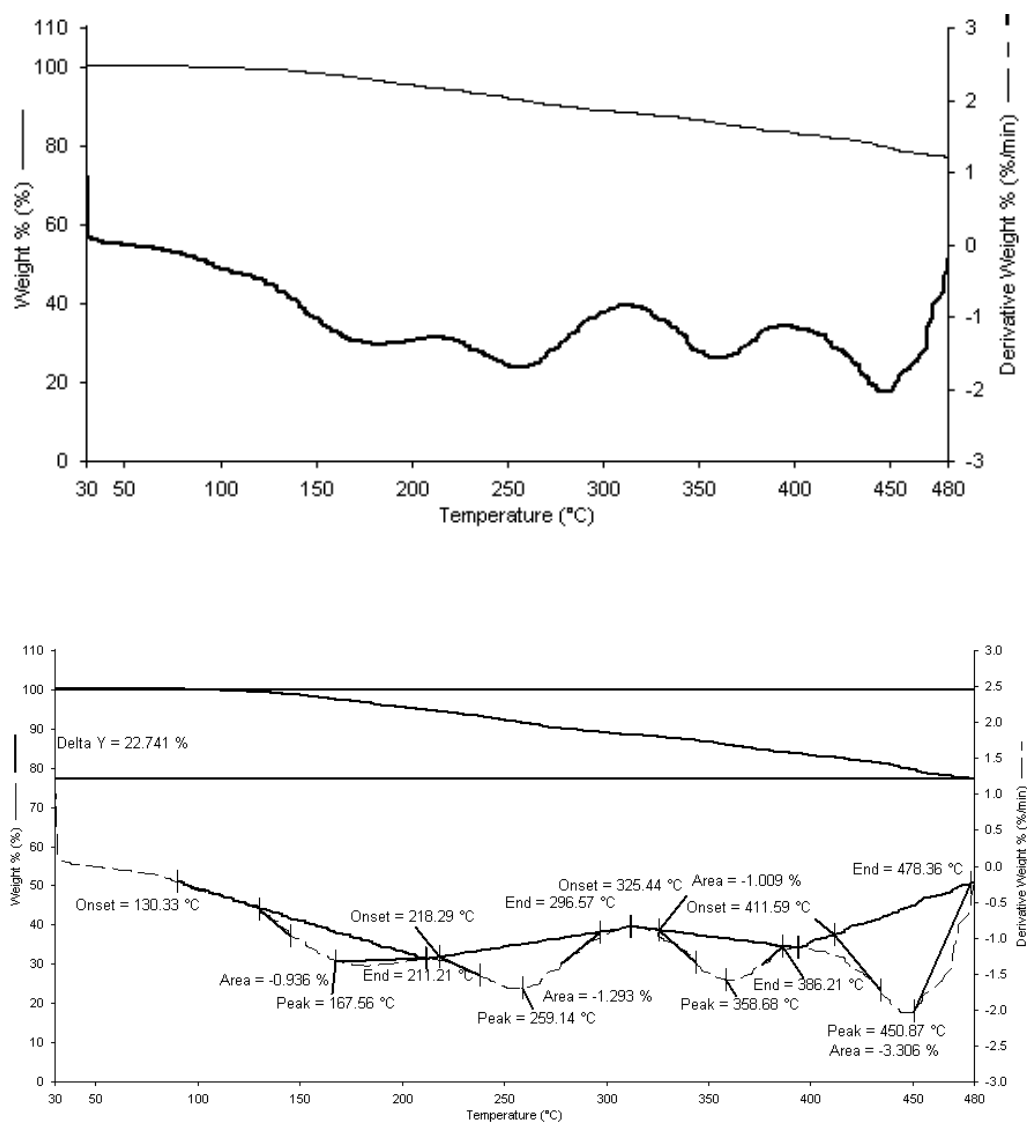


Figure 5.32 TG/DTG thermograms of HA6

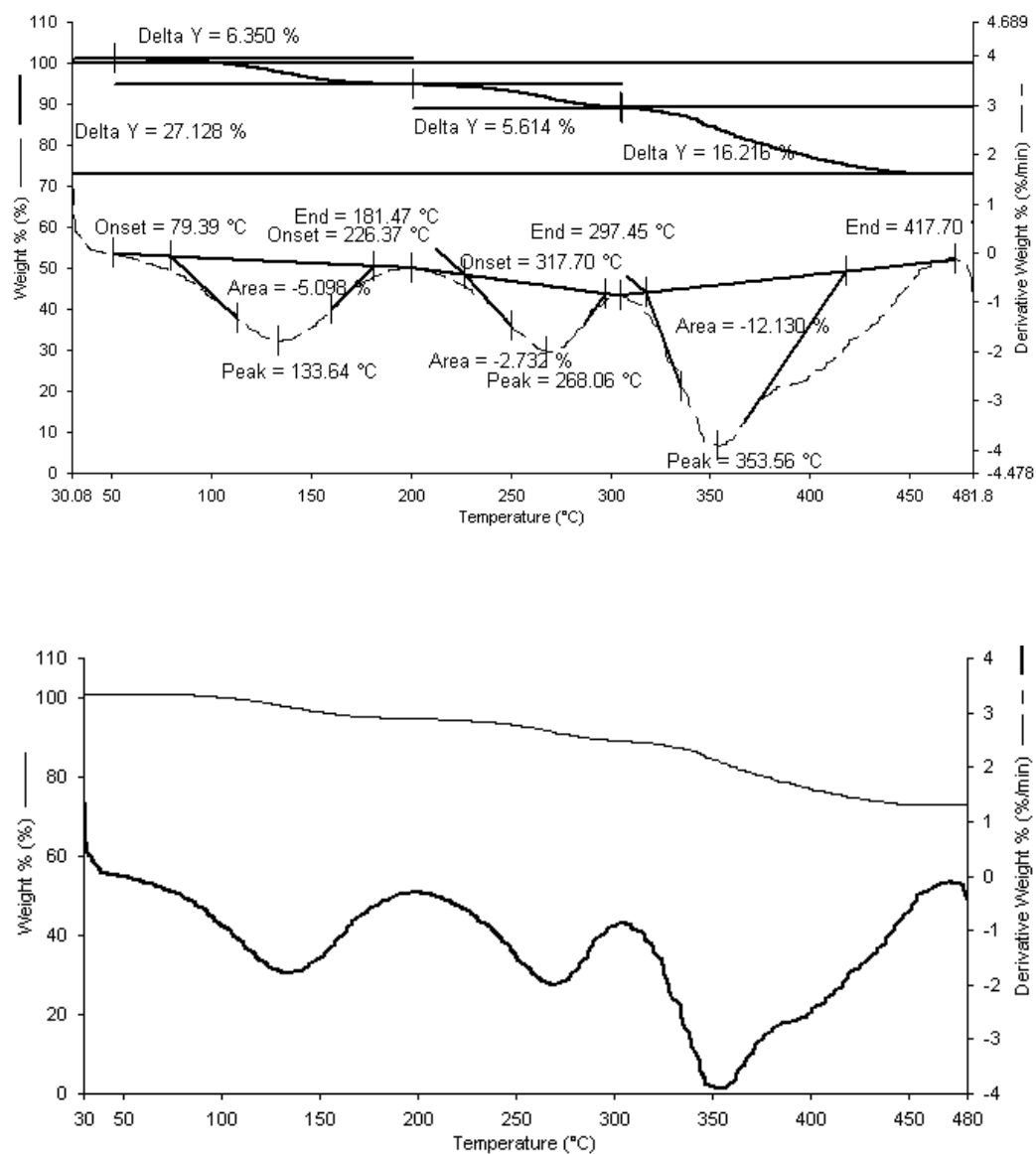


Figure 5.33 TG/DTG thermograms of HA7

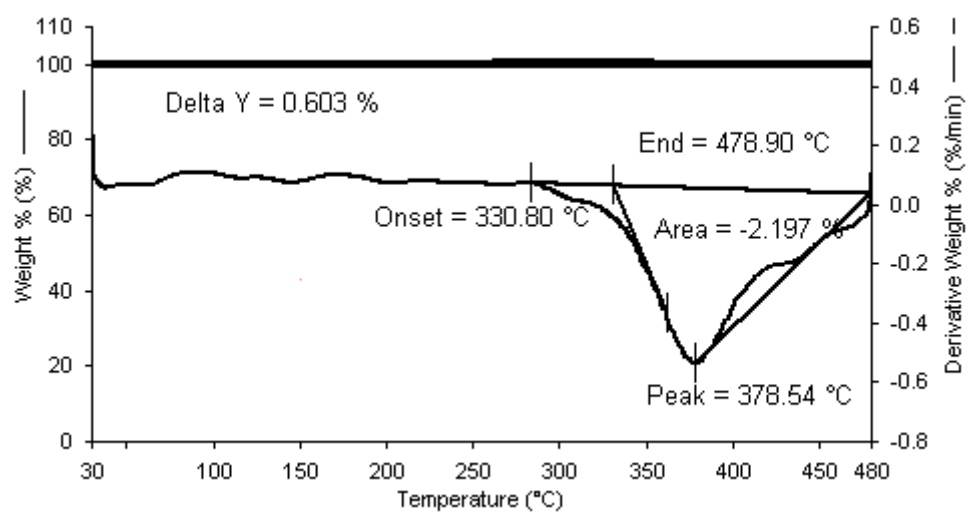
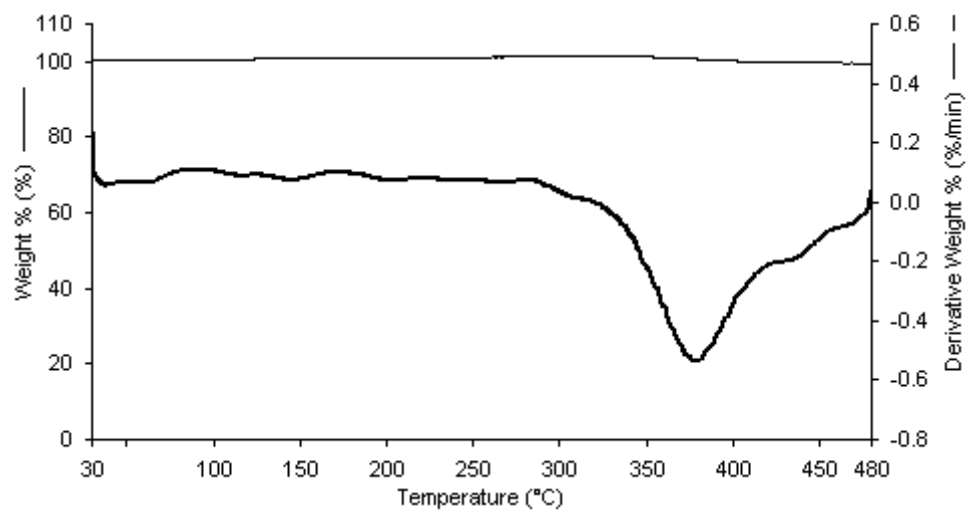


Figure 5.34 TG/DTG thermograms of HA8

Table 5.4 The summary of TG/DTG data of HA4, HA5, HA6, HA7 and HA8

	T _{onset} (°C)	T _{end} (°C)	T _{max} (°C)	Mass Loss (%)	T _{onset} (°C)	T _{end} (°C)	T _{max} (°C)	Mass Loss (%)	T _{onset} (°C)	T _{end} (°C)	T _{max} (°C)	Mass Loss (%)	T _{onset} (°C)	T _{end} (°C)	T _{max} (°C)	Mass Loss (%)	Total Mass Loss (%)
HA4	186	247	221	16.81													16.81
HA5	218	270	248	38.73													38.73
HA6	130	211	168	-	218	297	259	-	325	386	359	-	412	478	451	-	22.74
HA7	79	181	134	6.35	226	297	268	5.61	318	418	354	16.22					27.13
HA8	331	479	379	0.63													0.60

The TGA/DTG profiles presented similar behavior with one main mass loss in the temperature range of 30–480 °C due to the dehydration of adsorbed water as humidity and decomposition of surfactants from 200 to 500 °C (Ramimoghdam, Hussein, & Taufiq-Yap, 2012). Figure 5.30 shows the TGA analysis of HA4 (SDS-coated sample). It has been stated that SDS degraded in one mass loss at a temperature of 180 °C (El-kharrag, Amin, & Greish, 2011). In our case, this step was observed at 186°C and completed at 247 °C with mass loss of 16.81%. TGA curve of HA5 (CTAB coated Fe₃O₄) revealed that CTAB was thermally stable up to 218°C than the degradation process was completed at 270°C with a mass loss of 38.73%.

In the TGA/DTG analysis of SDS and CTAB, thermal degradation was observed as mass losses in two steps between 160–380 °C and 180–340 °C, respectively.

It had been studied that mass loss about 90.8% occurred in a single step between 170-366 °C for OA. However, for OA coated Fe₃O₄, mass loss observed in two steps, between 170-275 °C and 280-470 °C. The first mass loss may be because of free or physically bound OA, while the second loss was due to the chemically bound OA onto surface of Fe₃O₄ nanoparticles (Jadhav et al., 2013). As can be seen from the Figure 5.32 that four steps mass losses were observed between the temperatures of 130-478°C. A mass loss (1–2%) was observed below 130 °C due to water molecules adsorbed onto the Fe₃O₄ particles surfaces. The total of 22.74% of mass losses observed for HA6 as in Table 5.4.

As can be seen from Figure 5.31 for SA coated Fe₃O₄, three steps mass losses were obtained with a total mass loss of 27.13% (Table 5.3). On the other hand, as studied before, No reaction and mass loss from 20 °C to 206 °C were observed for stearic acid. It evaporated rapidly with the rise of temperature and completed at 327 °C with a 2.0% mass loss of residues remained (Chen, Du, Li, Yang, & Lv, 2017).

Furthermore, DTA curves of stearic acid exhibited an endotherm at 67°C, related with its melting point. Then, a broad exothermic peak at the temperature range of 360±380°C, and a small exotherm appeared at 515°C (Jaw, Hsu, & Lee, 2001).

Due to the strong interaction of Fe₃O₄ nanoparticle surfaces with oleic and stearic acids, mass losses spread over a wide temperature range and degradation reactions take a long time. In the case of HA8, the sample was stable up to 330°C and then a single step mass loss was observed with a negligible mass loss (0.60%).

Due to the malfunction of the TG device, analysis of HA1-3, HA11,12 and HA13 samples could not be performed. Therefore, the comments of this section could not be completed.

5.1.4 Scanning Electron Microscopy (SEM) Analysis of the Samples

SEM images were taken at various magnifications at 5 kV on Carl Zeiss 300VP SEM at Research Center of Katip Çelebi University. The samples were coated with Au by using QUORUM Q150 RES device. Their images were shown below.



Figure 5.35 Carl Zeiss 300VP SEM and QUORUM Q150 RES device (IKCU merkeziarařtırmalab, 2020)

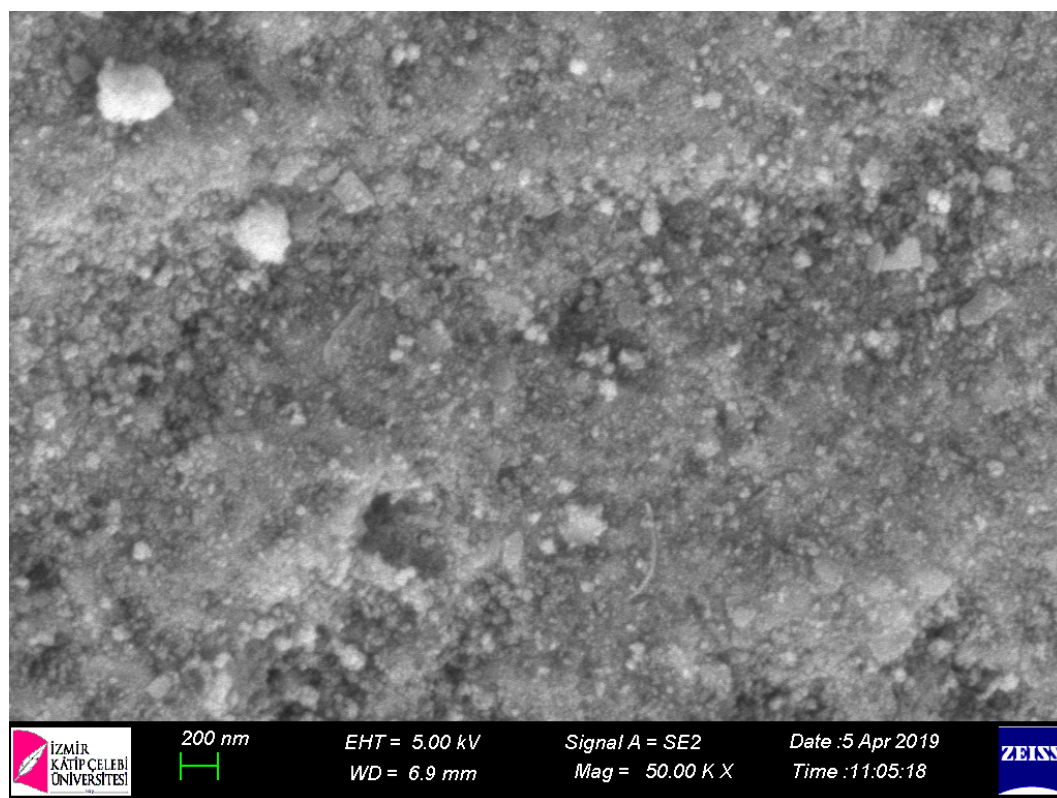


Figure 5.36 SEM Images of HA1 with 50 00 K $\times$ magnifications

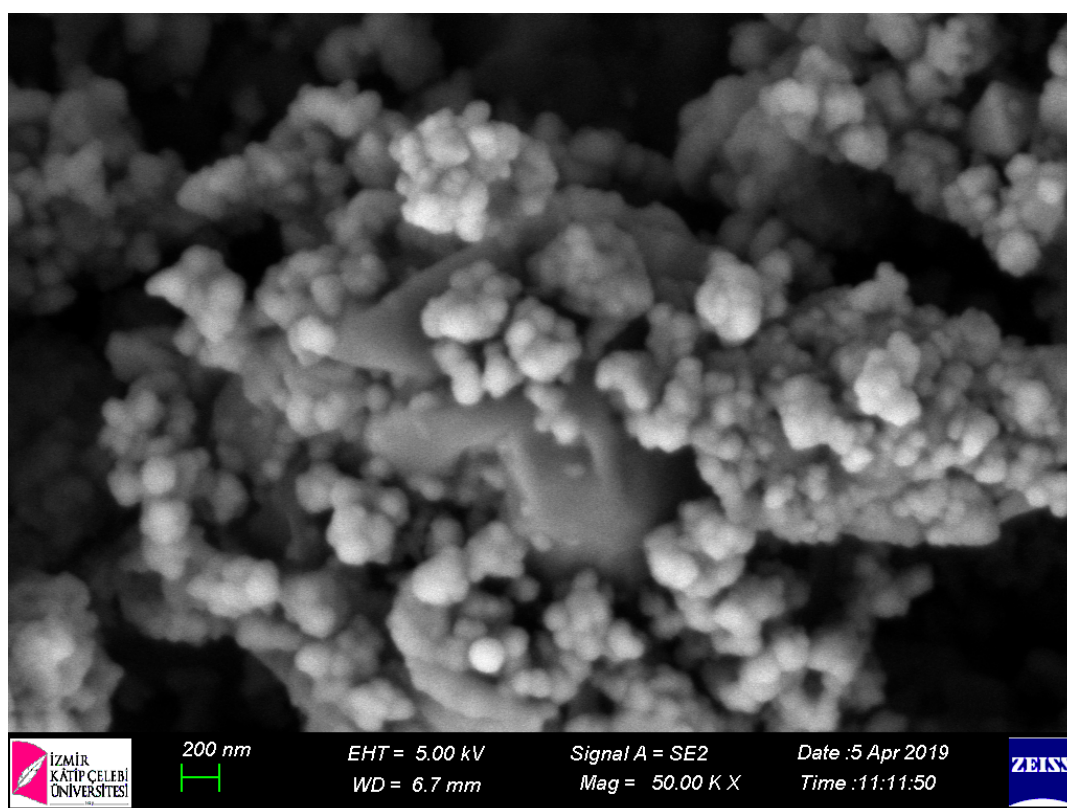


Figure 5.37 SEM Images of HA2 with 50 00 K $\times$ magnifications

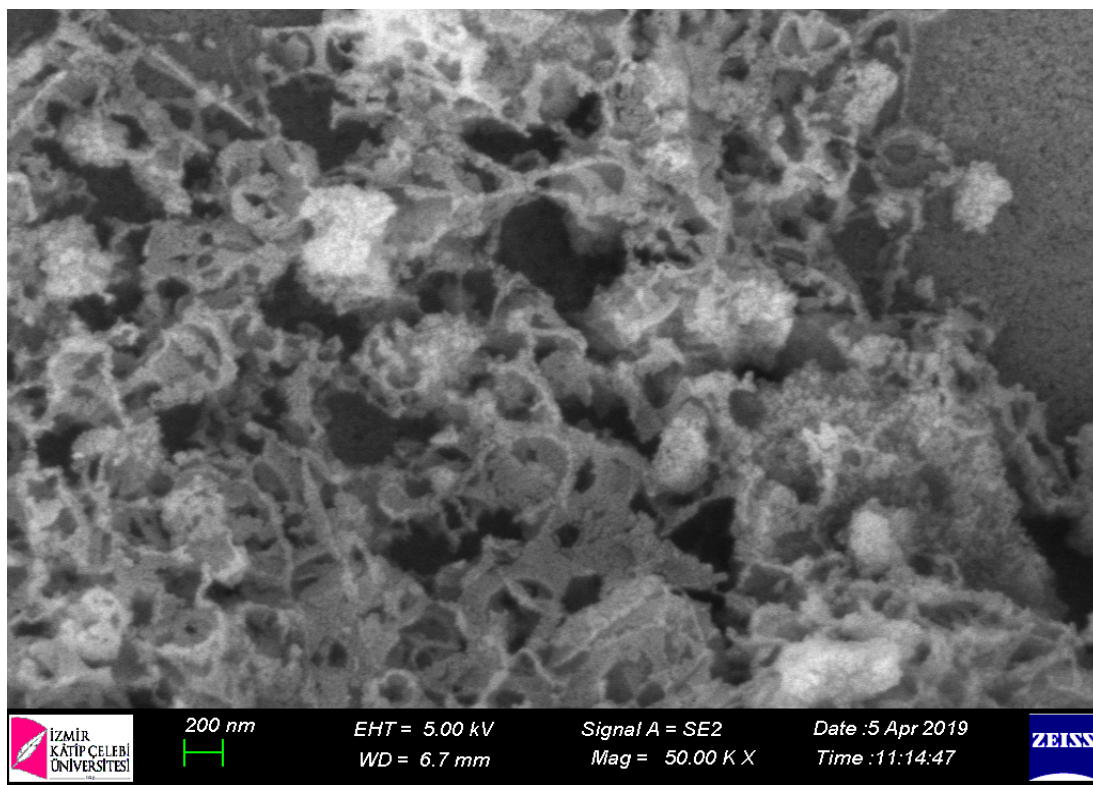


Figure 5.38 SEM Images of HA3 with 50 00 K $\times$ magnifications

SEM images of HA1, HA2 and HA3 were evaluated together due to the different preparation methods. HA1 was prepared in N₂ atmosphere while HA2 was prepared in open air and 60°C. HA3 was standard commercial product. As can be seen from the images that the particles are spherical in shapes and different non homogeneous sizes containing coarse grains. A porous and spongy structure was also observed for HA3 (Figure 5.38).

Other samples, HA4, HA5, HA6 and HA7 were coated with SDS, CTAB, Oleic Acid (OA) and SA, respectively. The dried samples were grinded as coarse particle, sonicated with Ethanol and separated on a glass slide before the SEM Analysis. Their SEM images were given in Figure 5.39-5.42. These pictures show that they are relatively smaller spherical shape particles and size below 100 nm. It was interesting that these samples were coated with surfactants to provide the stability and expected to be relatively coarser particles as compared with HA1, HA2 and HA3.

Among these examples, HA4 and HA5 differ somewhat. In these examples, there are small spherical particles. These particles are homogeneous and combined to some extent with each other. Small and small adherent particles are observed in HA6 and HA7.

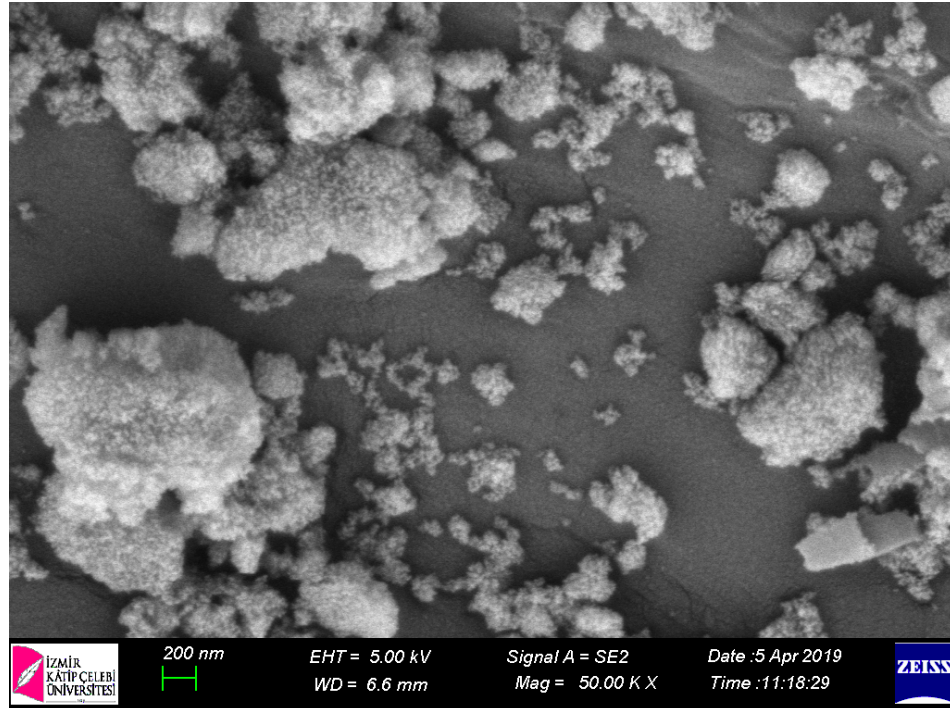


Figure 5.39 SEM Images of HA4 with 50 00 K $\times$ magnifications

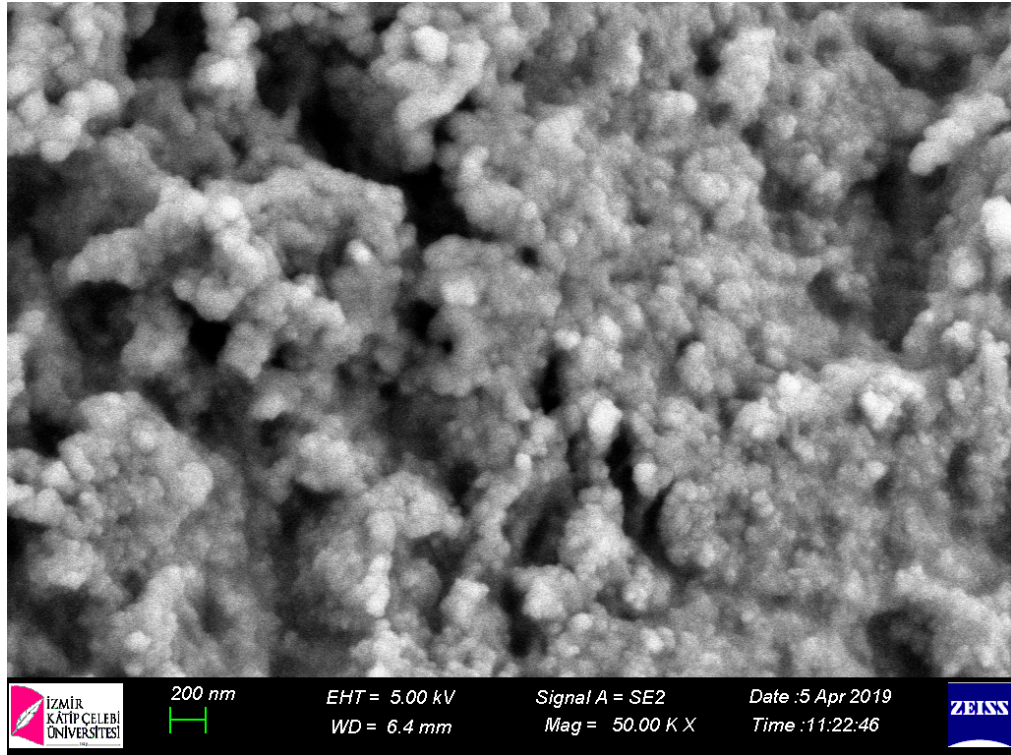


Figure 5.40 SEM Images of HA5 with 50 00 K $\times$ magnifications

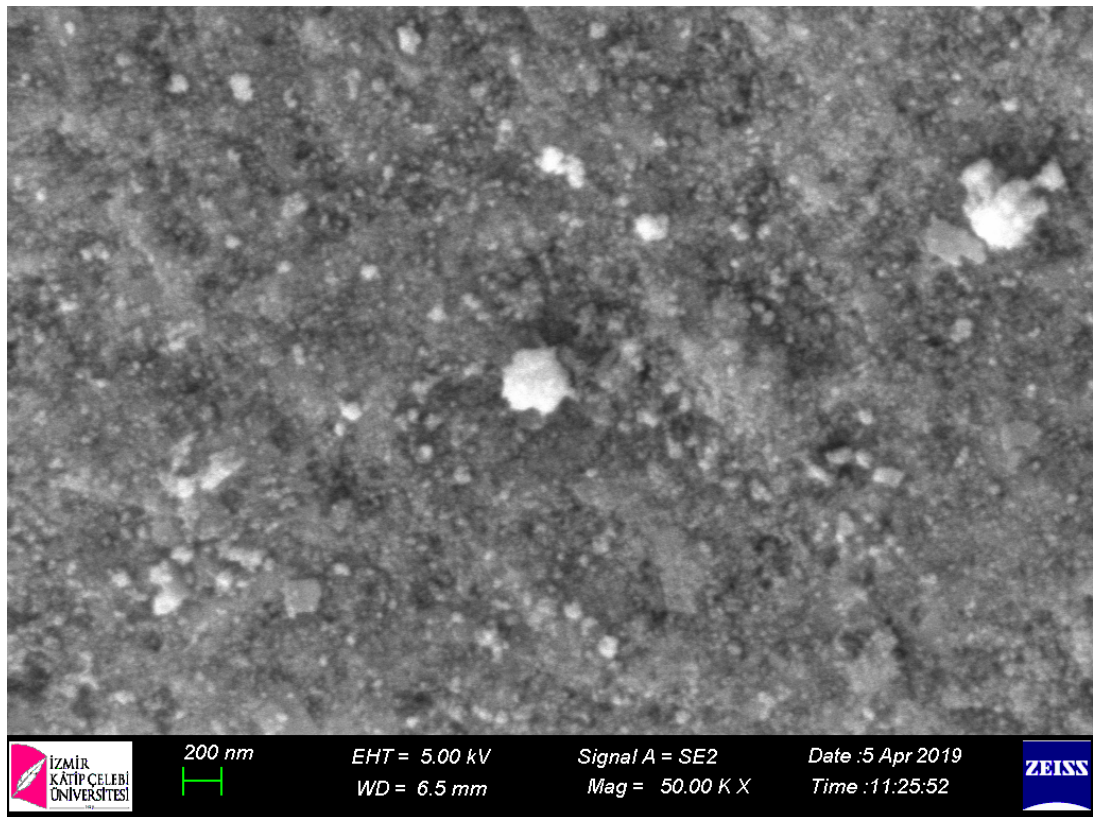


Figure 5.41 SEM Images of HA6 with 50 00 K $\times$ magnifications

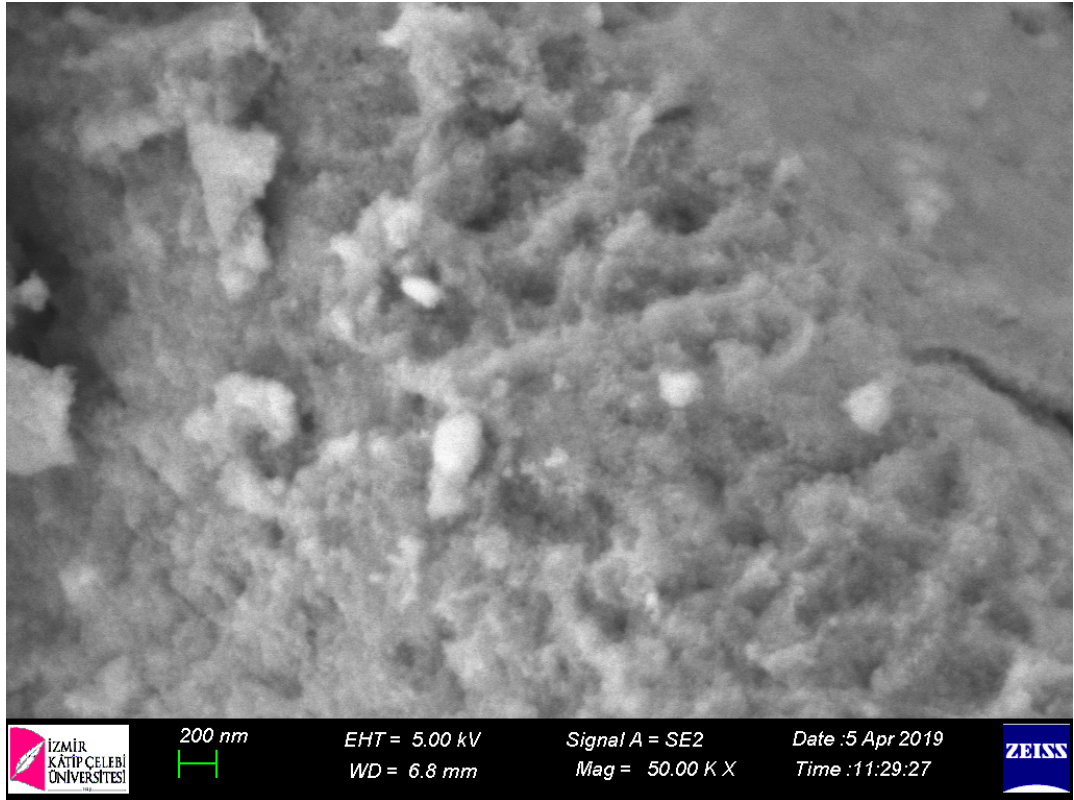


Figure 5.42 SEM Images of HA7 with 50 00 K× magnifications

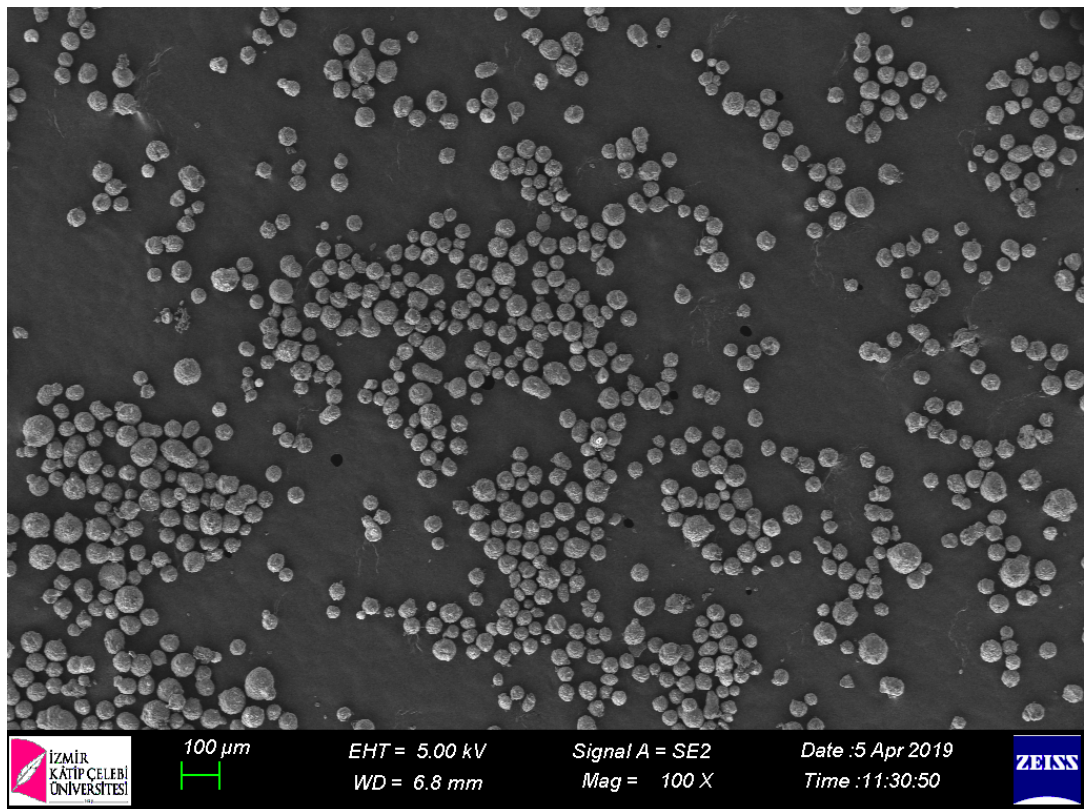


Figure 5.43 SEM Images of HA8 with 100× magnifications

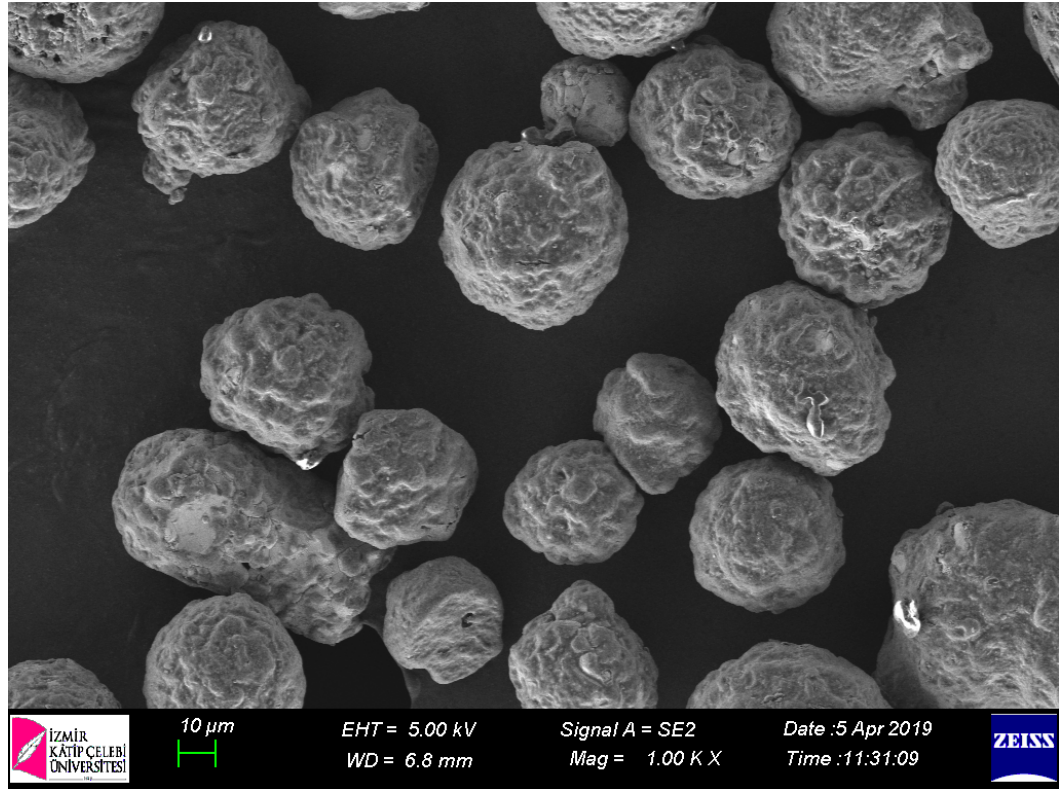


Figure 5.44 SEM Images of HA8 with 1 00 K× magnifications

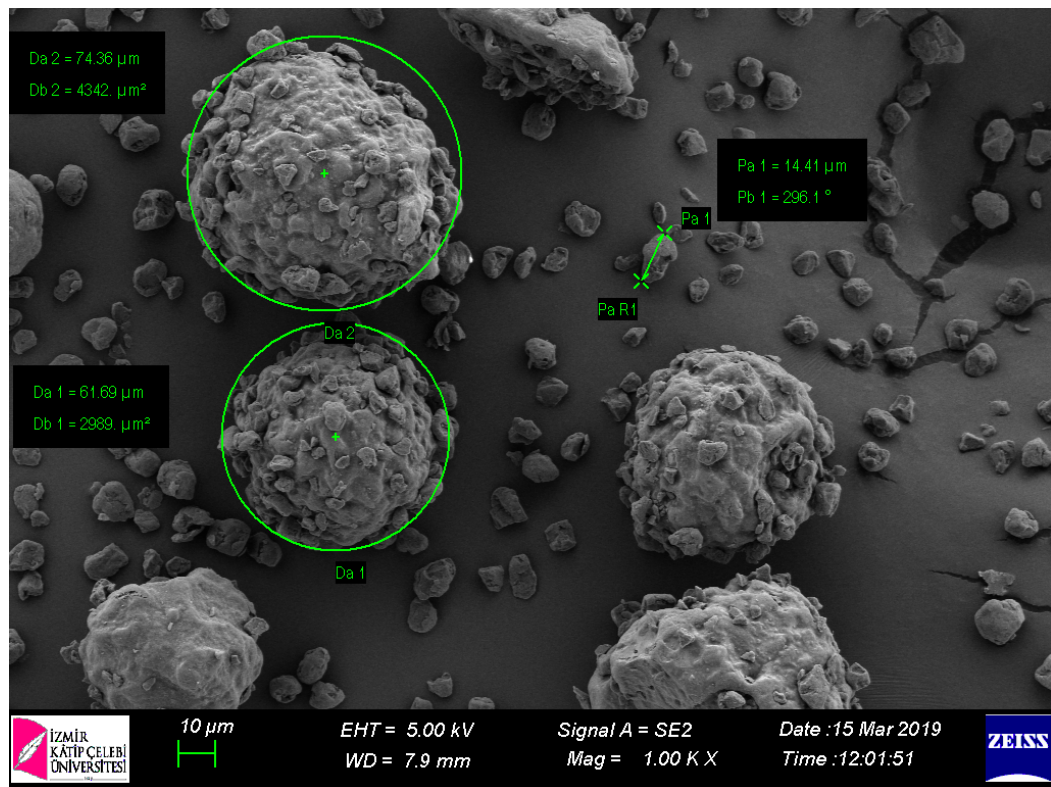


Figure 5.45 SEM Images of HA8 with 1 00 K× magnifications

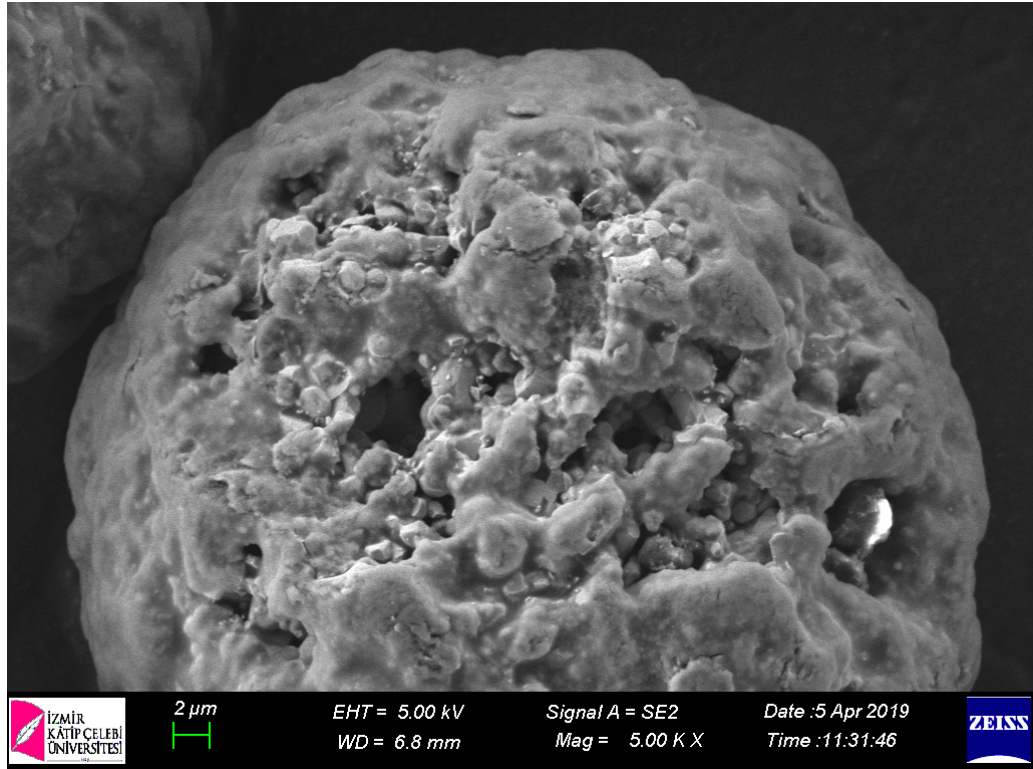


Figure 5.46 SEM Images of HA8 with 5 00 K× magnifications

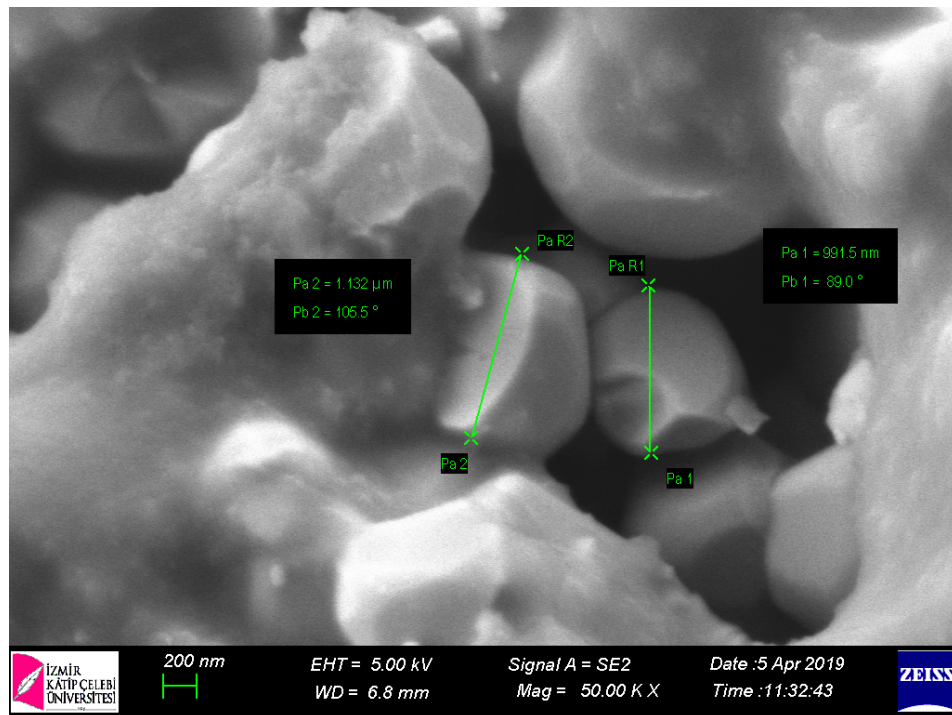


Figure 5.47 SEM Images of HA8 with 50 00 K× magnifications

SEM images of HA8 were presented in Figures 5.43-5.47. As can be seen from Figure 5.45 that Spherical adherent lumpy particles of 14, 62-74 μm in diameter were

observed. On the other hand, in another analysis for HA8 from Figure 5.47 that 1132 μm and 992 nm particles were also seen.

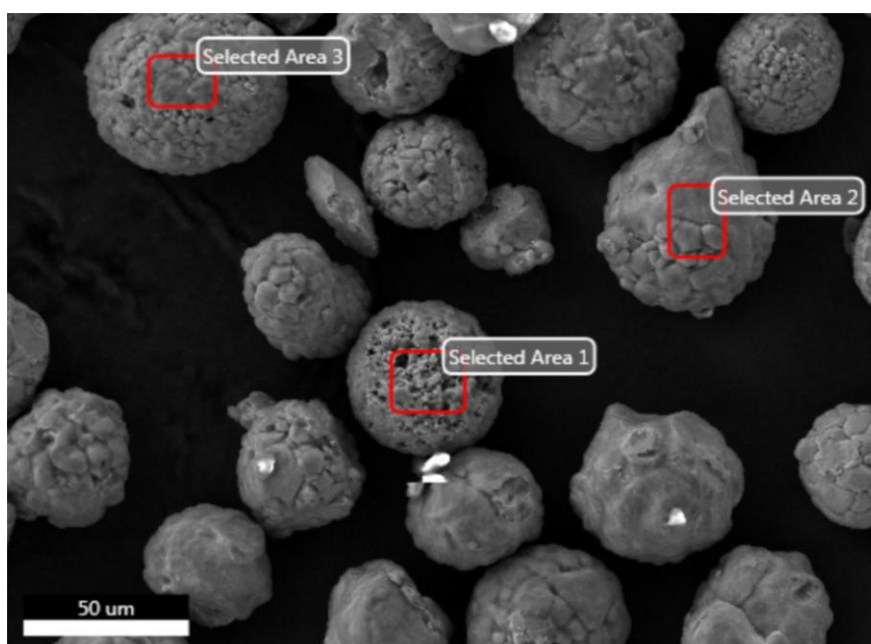


Figure 5.48 SEM EDX Images of HA8 with 50 00 K $\times$ magnifications

In Figure 5.48 SEM EDX Images of HA8 was presented. For this sample, EDX analysis was carried out on the three selected areas in the image.

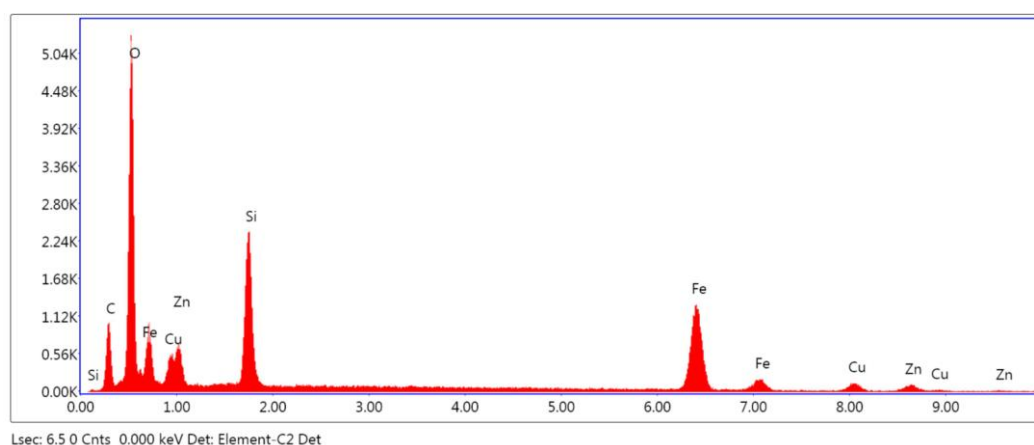


Figure 5.49 SEM EDX Spectrum of HA8 from selected area 1

Evaluation of the elemental analysis from the selected area 1 was presented in Table 5.5.

Table 5.5 EDX Data of HA8 from selected area 1

Element	Weight %	Atomic %	Net Int.	Error %
C K	9.40	22.61	692.73	11.46
O K	20.71	37.39	4648.83	7.49
SiK	10.06	10.35	2939.69	5.79
FeK	41.35	21.39	2742.08	3.52
CuK	8.55	3.89	266.75	11.38
ZnK	9.93	4.39	228.65	12.64

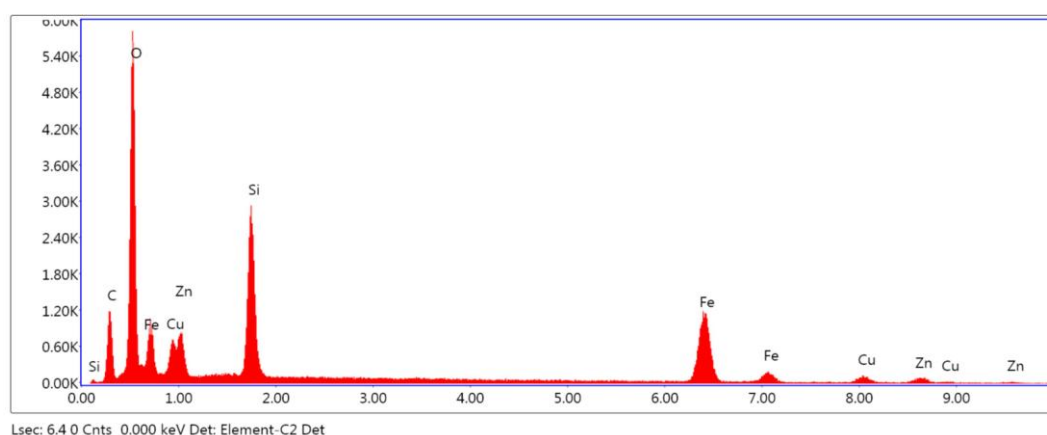


Figure 5.50 SEM EDX Spectrum of HA8 from selected area 2

Evaluation of the elemental analysis from the selected area 2 was presented in Table 5.6.

Table 5.6 EDX Data of HA8 from selected area 1

Element	Weight %	Atomic %	Net Int.	Error %
C K	10.93	24.32	813.33	10.91
O K	23.90	39.95	5287.00	7.53
SiK	11.69	11.13	3534.79	5.51
FeK	37.76	18.08	2501.47	3.61
CuK	7.30	3.07	228.53	14.03
ZnK	8.42	3.44	194.27	14.57

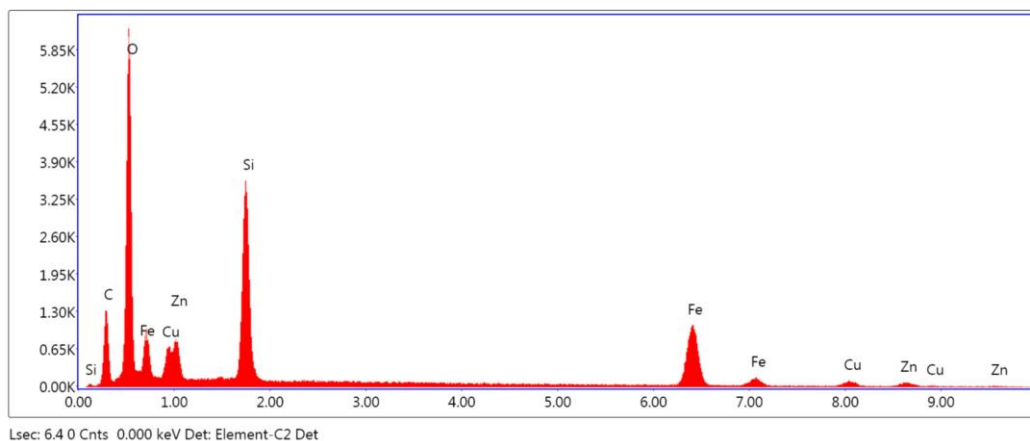


Figure 5.51 SEM EDX Spectrum of HA8 from selected area 3

Evaluation of the elemental analysis from the selected area 1 was presented in Table 5.7.

Table 5.7 EDX Data of HA8 from selected area 1

Element	Weight %	Atomic %	Net Int.	Error %
C K	12.37	25.96	911.50	10.86
O K	25.73	40.54	5567.66	7.63
SiK	14.24	12.78	4471.75	5.21
FeK	34.52	15.58	2294.01	3.67
CuK	6.36	2.52	200.29	14.28
ZnK	6.79	2.62	157.84	16.40

Sample HA8 is a commercial product and used in printers as a toner. For this reason, EDX analysis was also carried out for this sample. As can be seen from the Tables 5-7, the sample contained C, O, Si, Fe, Cu and Zn elements. Fe and O elements came from basically Fe_3O_4 . Si came from the coating materials as silanes. C is due to the sample carrier. Cu and Zn were due to the screening materials.

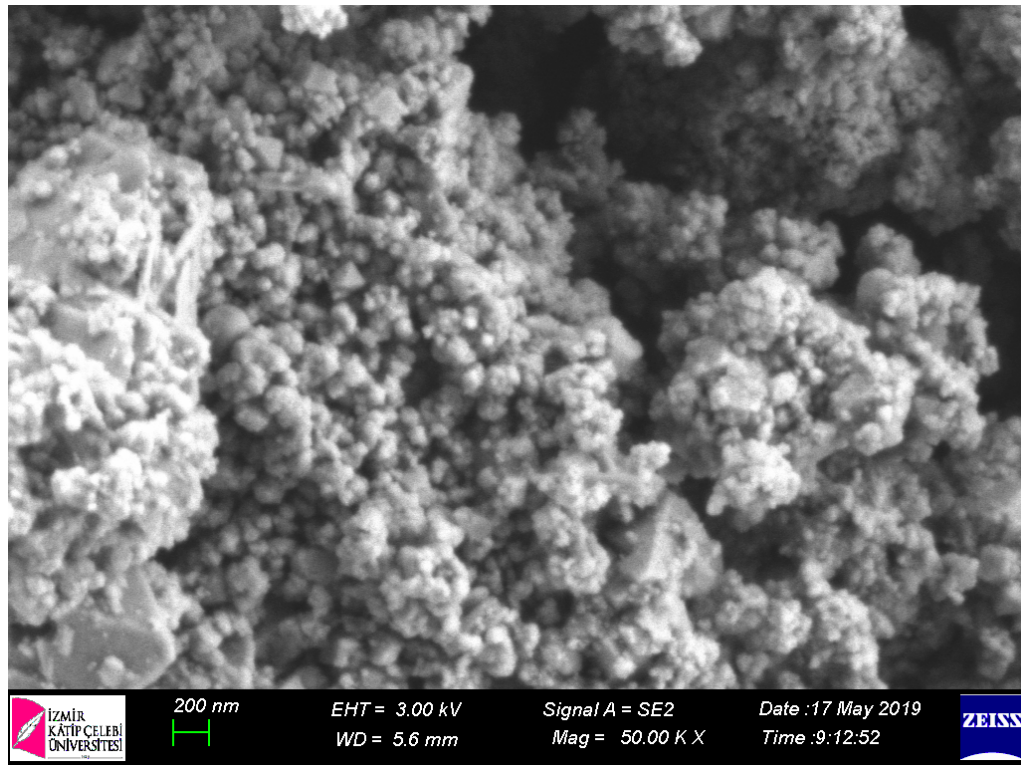


Figure 5.52 SEM Images of HA11 with 50 00 K× magnifications

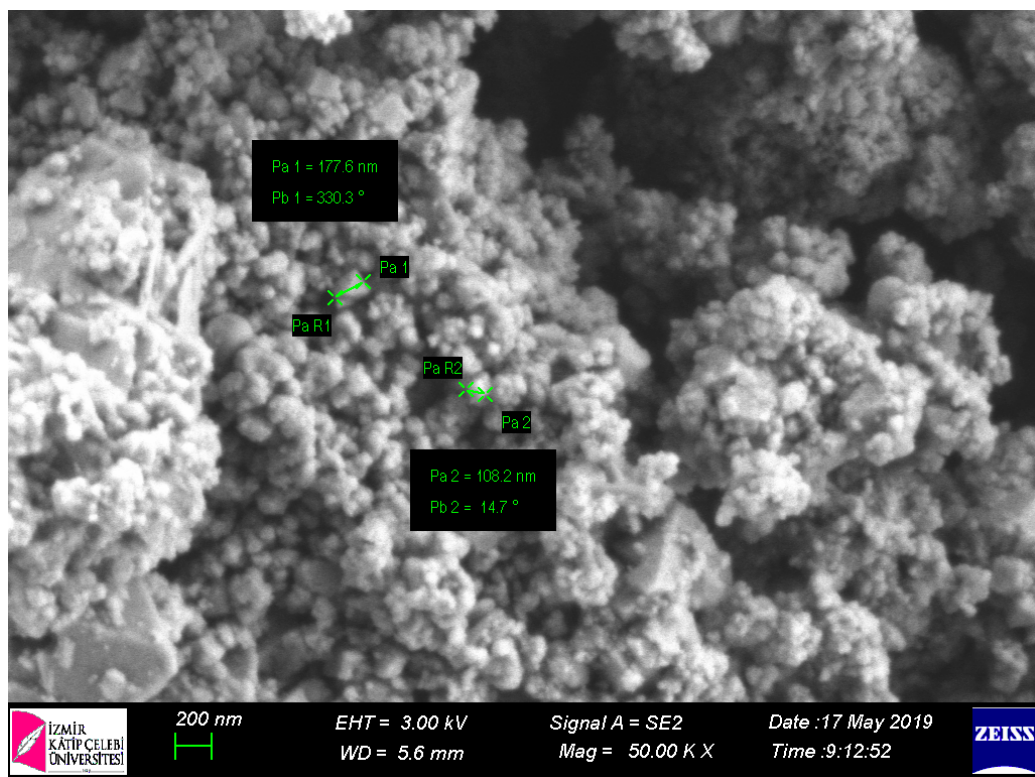


Figure 5.53 SEM Images of HA11 with 50 00 K× magnifications

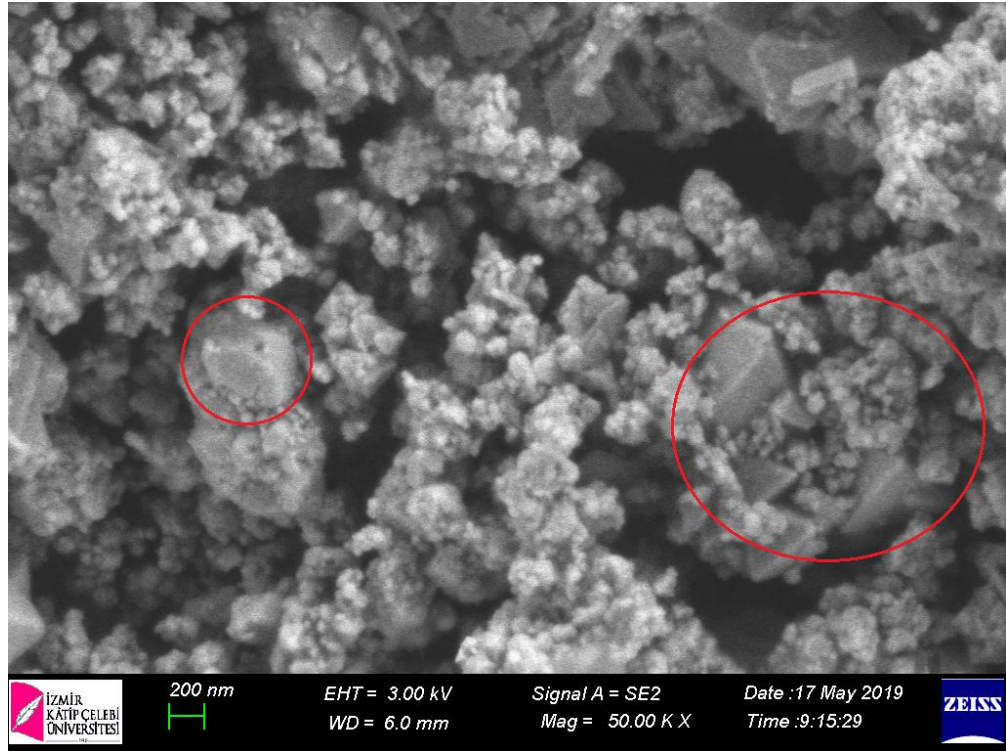


Figure 5.54 SEM Images of HA12 with 50 00 K $\times$ magnifications

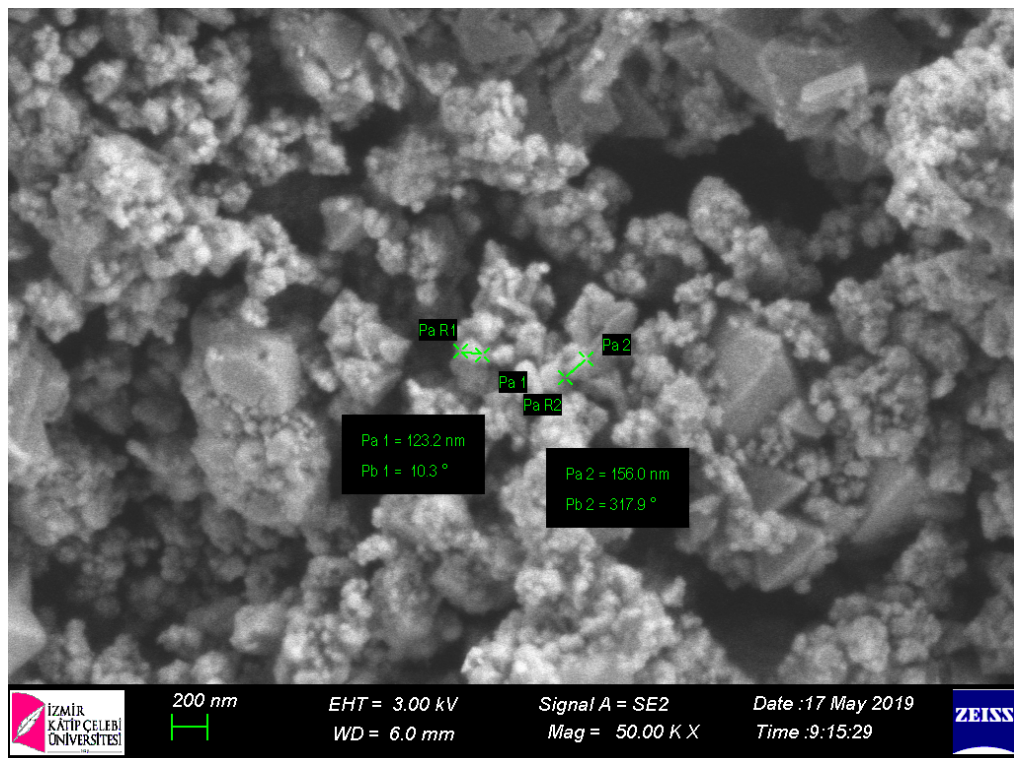


Figure 5.55 SEM Images of HA12 with 50 00 K $\times$ magnifications

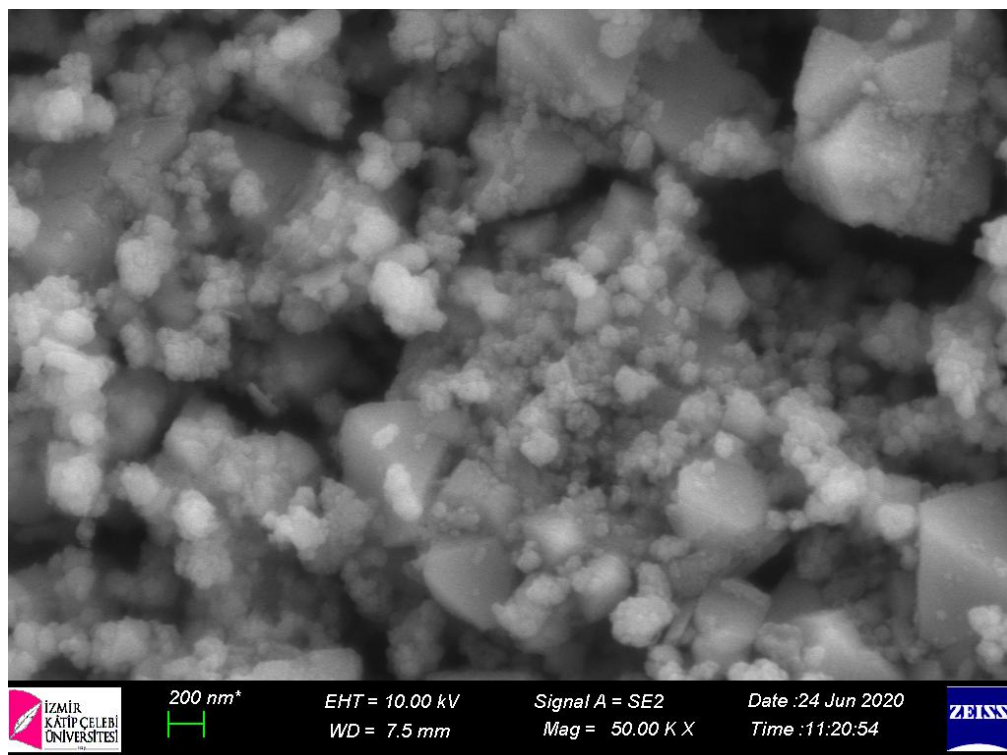


Figure 5.56 SEM Images of HA13 with 50 00 K $\times$ magnification

In Figures 5.52 and 5.53, SEM images of HA11 (coated with Oleyl amine) sample were shown. In Figures 5.54 and 5.55, SEM images of HA12 (coated with APTES) sample were presented. In the HA11 sample, spherical particles with a particle size of 108-178 nm are observed, while in the HA12 sample, particles with a size of 123-156 nm are observed. In addition, in both examples, mainly hexagonal shaped crystalline structure was observed in HA12 and circled in red.

5.1.5 X-ray Photoelectron Spectroscopy (XPS) Analysis of the Samples

XPS can be used for determining the composition and chemical states of the surface of the materials (Briggs, 1990).

XPS analysis of the iron and related oxides were studied and founded that the binding energies related with Fe 2p_{1/2} and Fe 2p_{3/2} depended on oxidation states of Fe (Roosendaal, Van Asselen, Elsenaar, Vredenberg, & Habraken, 1999; Graat &

Somers, 1996,1998; Ruby, Humbert, & Fusy, 2000; Mekki, Holland, McConville, & Salim, 1996; Yamashita & Hayes, 2006).

Fe_3O_4 composed of cubic close packed oxygen sublattice. The Fe^{2+} and Fe^{3+} ions occupy tetrahedral and octahedral sites, respectively. They form a cubic spinel type structure. Fe_3O_4 is also formulated as $\text{FeO Fe}_2\text{O}_3$ with a atomic ratio of 1:2 (Galasso, 1970).

It had been studied that Fe 2p_{3/2} for Fe_3O_4 did not have a satellite peak (Yamashita & Hayes, 2006; Hawn & DeKoven, 1987; Muhler, Schlögl, & Ertl, 1992).

XPS spectrum of Fe_3O_4 was given in Figure 5.57. The binding energies of Fe 2p_{3/2} and Fe 2p_{1/2} are 710.6 and 724.1 eV, respectively.

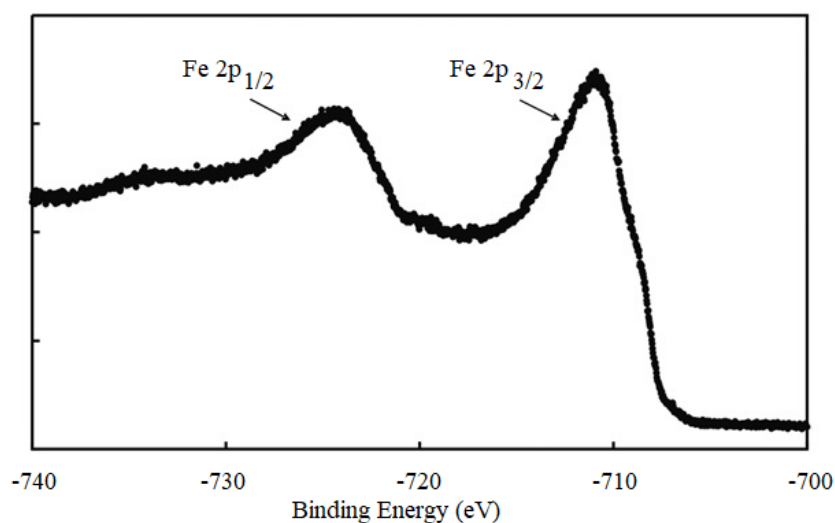


Figure 5.57 The XPS spectrum of Fe2p from the surface of the Fe_3O_4 standard sample (Yamashita & Hayes, 2008)

XPS spectra and related Fe2p analysis data of the samples HA1-HA8 were given in Figures and Tables, respectively.

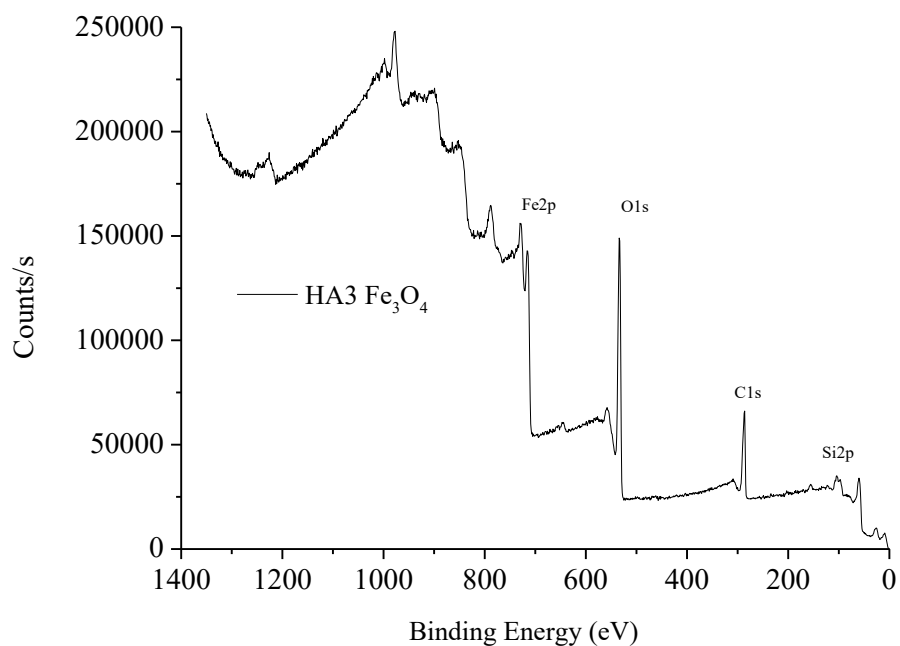


Figure 5.58 XPS analysis of HA3

Table 5.8 XPS Analysis Data Survey Scan for HA3

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
O1s	542.08	533.44	524.58	114794.05	5.87	684456.37	3975.53	34.46
Fe2p	736.92	714.2	706.72	60510.26	7.15	669527.43	913.29	27.63
C1s	295.55	287.03	280.88	39481.37	5.65	223582.61	3139.65	20.43
Si2p	110.08	102.74	91.69	6235.57	14.28	82174.84	1148	17.47

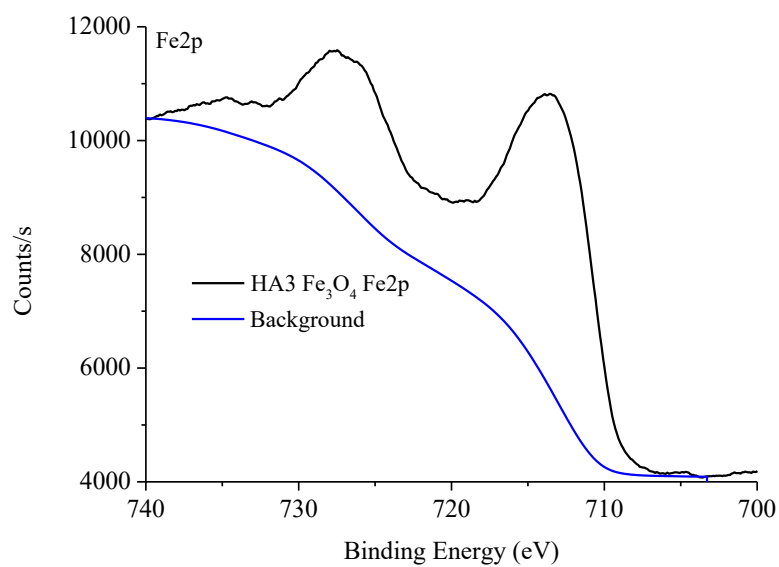


Figure 5.59 XPS analysis of Fe2p for HA3

Table 5.9 XPS Analysis Data of HA3 for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	295.78	286.09	279.08	4618.68	3.75	20526.23	288.06	23.09
O1s	540.28	532.65	525.98	9451.05	5	48757.36	283.02	30.22
Fe2p	740.08	713.14	703.28	5278.32	6.28	59938.44	81.68	30.44
Si2p	110.48	102.34	90.08	511.98	6.79	6202.87	86.64	16.24

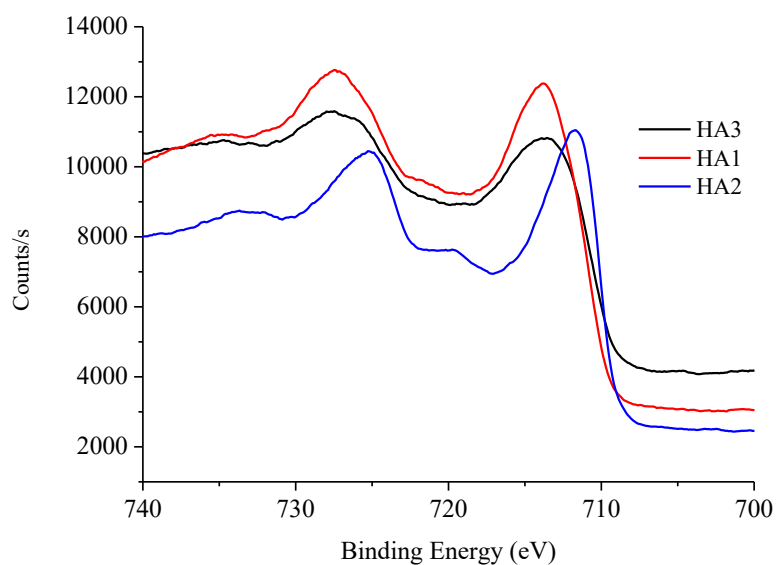


Figure 5.60 XPS Spectra of the samples HA1, HA2 and HA3 for Fe_3O_4 (Fe2p)

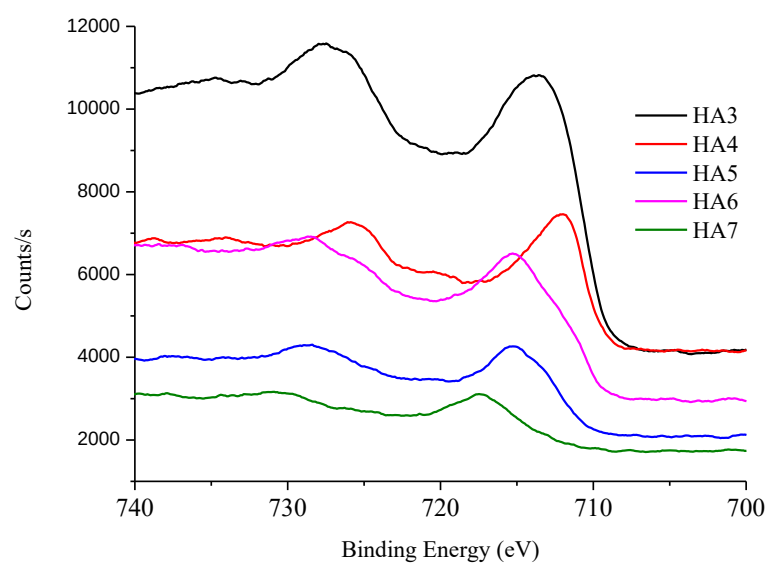


Figure 5.61 XPS Spectra of the samples HA3, HA4, HA5, HA6 and HA7 for Fe_3O_4 (Fe2p)

It has been observed that there was a shift toward a higher binding energy and the peak intensities were also changed. This is due to the oxidation state of Fe as Fe^{2+} or Fe^{3+} .

On the other hand, the peak intensities change mainly because of two reasons: Firstly, the intensity is related with the number of atoms with the respective oxidation state. Secondly, it depends on the depth distribution of the atoms. Here, the sum of the intensity of all peaks of one core level changes. If the atoms diffuse towards the surface, an increase in intensity will be observed, even if they are the same in numbers. And of course, the intensity will decrease, if the atoms diffuse towards the bulk.

The shifts in the XPS peak is related to its oxidation state and higher shift in binding energy corresponds to higher oxidation state. Some times more shift with noise peak is related to the satellite peak or shake up and it is a case for only some metal or its oxide. Before analyzing XPS peak, charging correction by taking the reference binding energy of C1s (284.8 eV) must be done, otherwise it will be difficult to identify the multiple oxidation state.

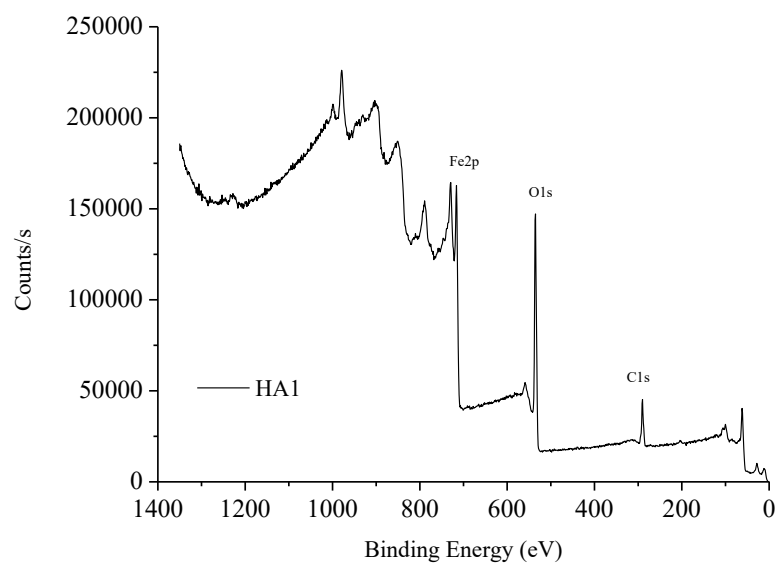


Figure 5.62 XPS Spectrum of HA1

Table 5.10 XPS Analysis Data Survey Scan for HA1

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
O1s	541.58	535.15	523.08	113579.18	4.83	581178.82	3380.23	35.94
Fe2p	740.08	715.88	707.48	91396.91	5.95	1000609.13	1367.11	50.73
C1s	297.58	290.1	282.99	23740.83	4.09	118704.15	1670.18	13.33

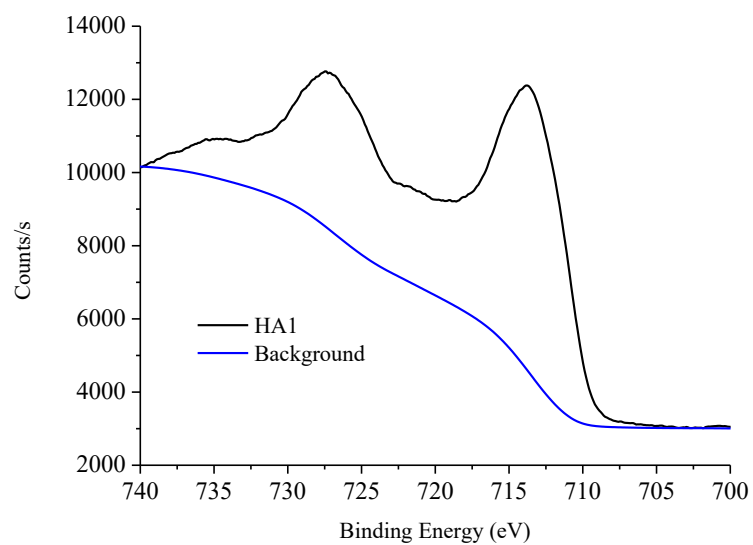


Figure 5.63 XPS Analysis results of HA1 for Fe2p

Table 5.11 XPS Analysis Data of HA1 for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	295.98	287.04	279.38	2275.17	4.22	10752.66	150.99	13.93
O1s	540.18	532.41	523.28	9914.69	4.25	43547.04	252.73	31.07
Fe2p	742.08	713.57	698.08	7721.26	6.04	94013.82	128.17	55

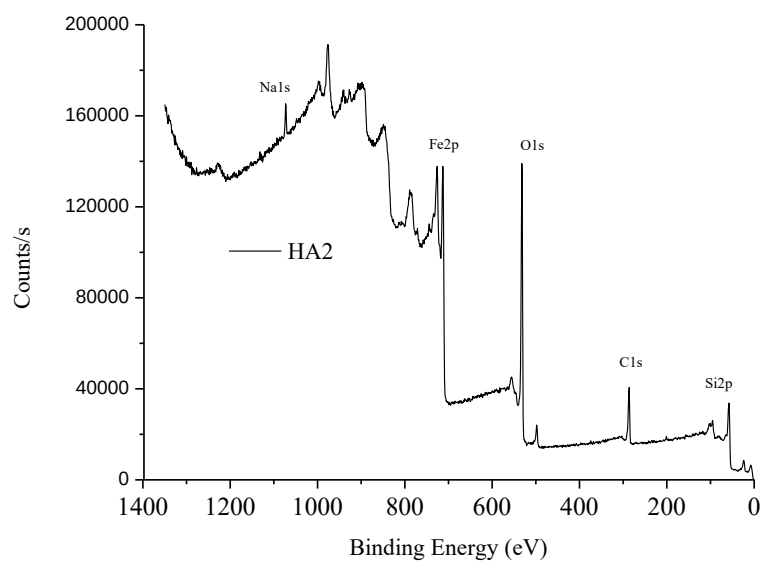


Figure 5.64 XPS Spectrum of HA2

Table 5.12 XPS Analysis Data Survey Scan for HA2

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
O1s	540.58	531.92	524.58	111047.12	3.6	442220.67	2565.46	26.98
Fe2p	740.08	712.8	705.21	84515.85	5.34	941387.1	1282.41	47.07
C1s	293.9	286.54	282.79	22700.57	2.34	94126.55	1321.35	10.43
Na1s	1078.08	1072.93	1069.44	13085.81	3.1	46233.57	133.3	2.01
Si2p	108	95.33	90.11	6282.44	3.13	52566.69	731.33	13.5

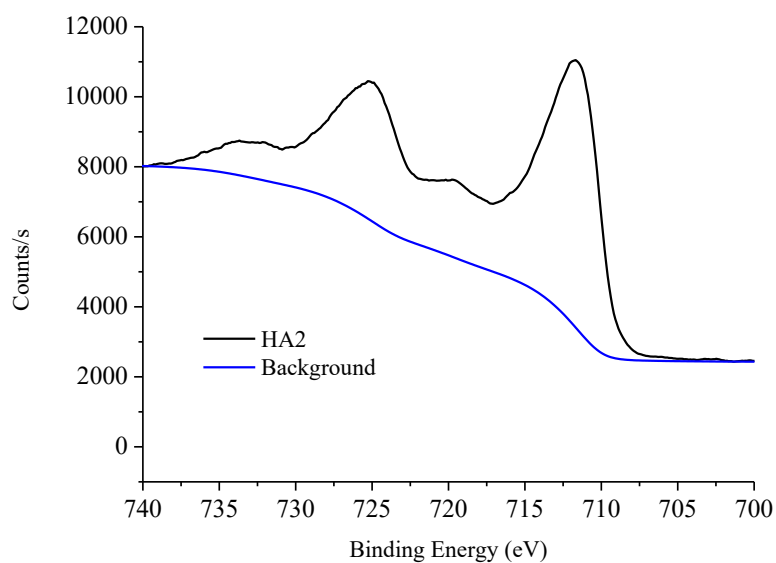


Figure 5.65 XPS Analysis results of HA2 for Fe2p

Table 5.13 XPS Analysis Data of HA2 for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	295.28	285.69	281.18	2943.61	2.07	7863.22	110.32	10.68
O1s	539.98	530.81	522.08	11680.12	2.45	33124.88	192	24.76
Fe2p	740.08	711.72	699.28	7627.35	4.43	75147.24	102.26	46.03
Na1s	1076.88	1072.12	1067.28	1621.72	1.89	3722.96	10.72	1.99
Si2p	112.08	94.48	88.98	659.82	3.67	5259.3	73.13	16.55

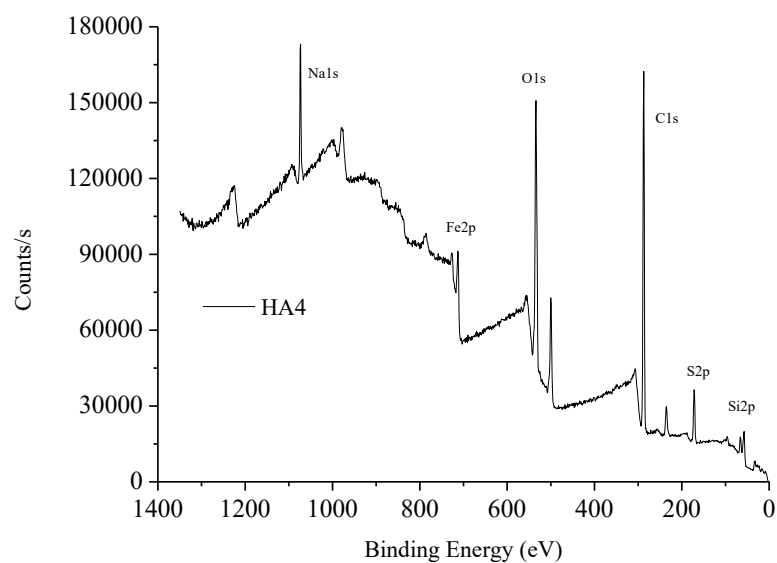


Figure 5.66 XPS Spectrum of HA4

Table 5.14 XPS Analysis Data Survey Scan HA4

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	293.58	287.29	278.08	138693.11	3.43	511814.39	7188.34	47.71
O1s	542.08	534.04	527.76	100947.9	4.78	503220.07	2924.25	25.86
Na1s	1079.08	1073.42	1066.82	51500.55	2.96	189802.72	547.7	6.96
Fe2p	729.93	712.34	706.82	24464.96	3.97	147786.7	201.24	6.21
S2p	175.08	171.6	166.08	19318.85	3.72	75102.59	522.32	9.26
Si2p	108.99	95.99	92.03	2859.89	1.3	18556.65	258.26	4.01

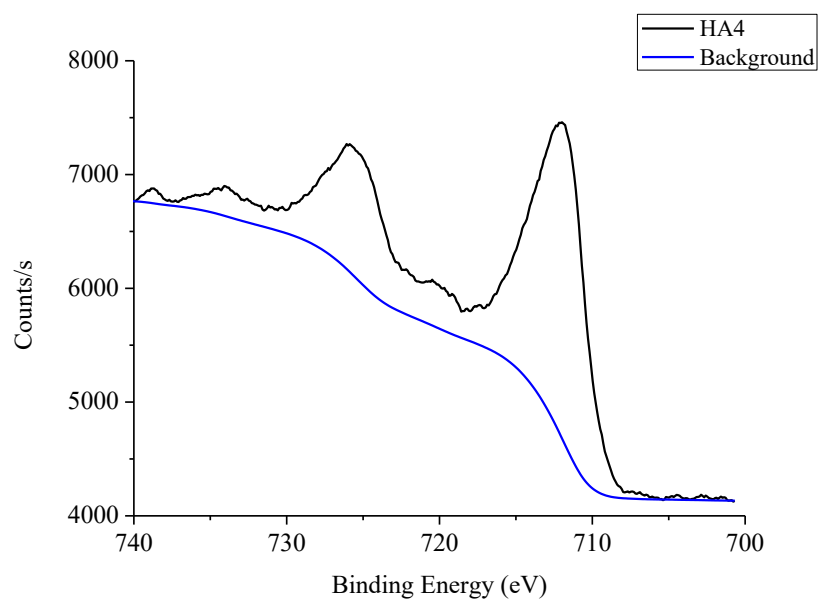


Figure 5.67 XPS Analysis results of HA4 for Fe2p

Table 5.15 XPS Analysis Data of HA4 for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	293.18	286.71	279.08	12225.14	2.78	35992.75	505.32	41.4
O1s	541.28	533.79	522.38	8871.64	4.63	40215.4	233.65	25.5
Fe2p	740.48	711.97	700.68	2777.76	3.94	20920.19	28.48	10.85
Na1s	1080.38	1073.25	1062.08	6086.13	2.22	15718.16	45.34	7.11
S2p	177.08	171.07	160.08	1902.25	2.96	6317.73	43.92	9.61
Si2p	111.98	94.85	90.38	288.36	3.79	2081.64	28.95	5.55

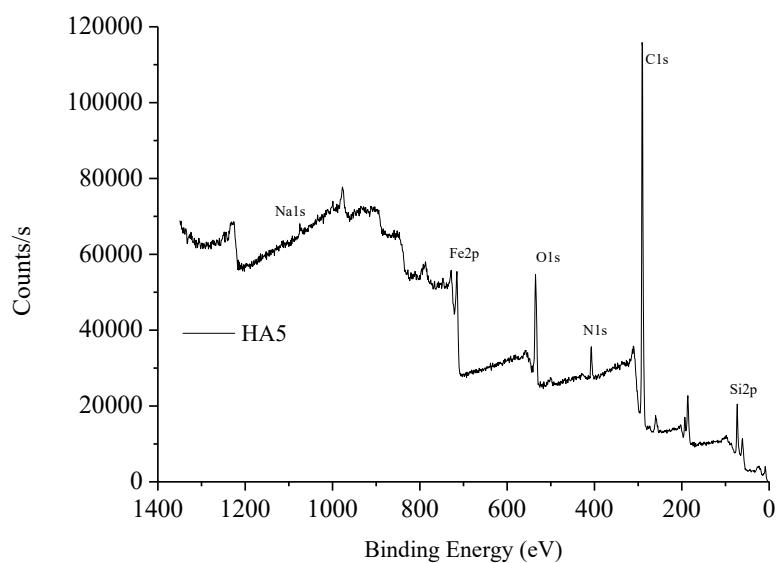


Figure 5.68 XPS Spectrum of HA5

Table 5.16 XPS Analysis Data Survey Scan HA5

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	296.08	290.28	280.08	95510.91	3.31	377880.56	5317.46	62.36
O1s	544.08	534.65	525.58	26431.62	4.84	141095.72	820.31	12.82
Fe2p	737.58	714.86	702.08	19131.15	5.29	181366.46	247.56	13.5
N1s	410.08	407.22	396.08	7880.07	3.33	33817.73	307.18	4.2
Na1s	1077	1074.7	1064	2145.87	0.96	10501.36	30.37	0.68
Si2p	109.83	98.33	90.17	1625.05	6.28	16855.23	234.89	6.44

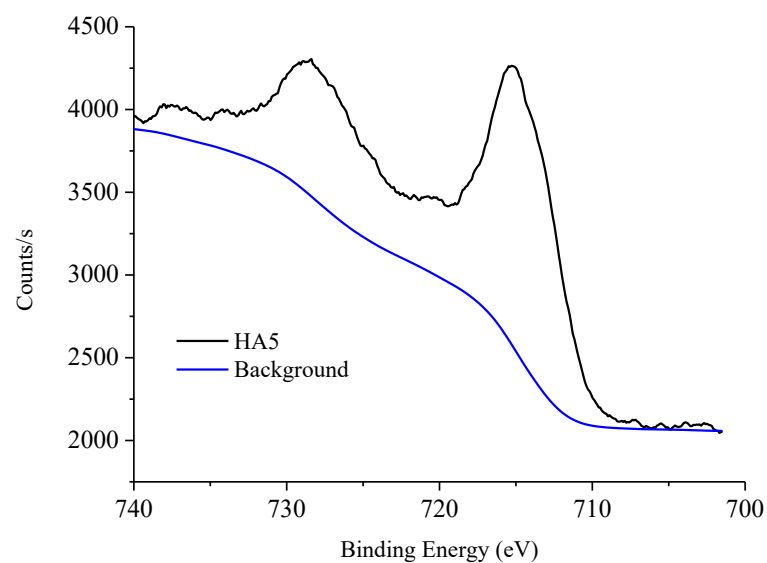


Figure 5.69 XPS Analysis results of HA5 for Fe2p

Table 5.17 XPS Analysis Data of HA5 for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	296.08	290.33	280.08	8707.77	2.62	27942.38	393.21	58.67
O1s	540.08	534.44	524.38	1979.25	4.62	9942.28	57.79	11.49
Fe2p	742.08	714.74	701.48	1682.09	5.34	18340.82	25.03	17.36
Na1s	1081.18	1074.38	1065.18	169.98	4.36	996.11	2.88	0.82
N1s	412.08	407.31	392.08	648.87	2.54	2535.47	23.03	4.01
Si2p	110.68	98.58	90.88	165.69	7.87	1573.29	21.93	7.65

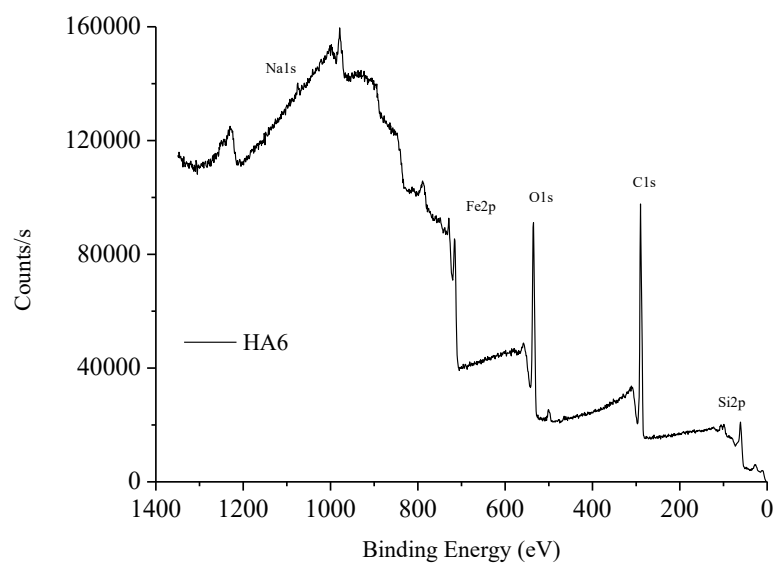


Figure 5.70 XPS Spectrum of HA6

Table 5.18 XPS Analysis Data Survey Scan HA6

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	297.08	289.71	278.58	76032.89	3.28	398359.49	5603.57	54.05
O1s	542.08	535.13	523.58	61616.62	5.45	356114.37	2071.18	26.61
Fe2p	740.08	714.8	705.08	26752.05	5.34	220939.55	301.55	13.52
Na1s	1077	1074.79	1064	2986.99	1.98	12421	35.92	0.66
Si2p	109.1	98.96	94.83	1943.65	4.69	16364.03	228.13	5.15

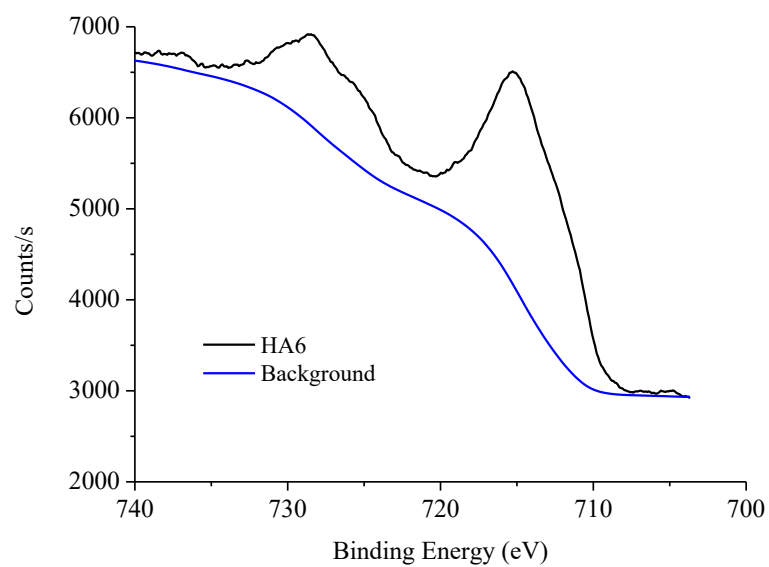


Figure 5.71 XPS Analysis results of HA6 for Fe2p

Table 5.19 XPS Analysis Data of HA6 for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	295.88	289.4	280.88	5691.58	3.67	29568.51	415.85	45.9
O1s	540.98	534.85	522.08	4648.84	6.06	27497.75	159.89	23.51
Fe2p	742.08	714.44	703.68	2348.16	6.57	24471.82	33.39	17.14
Na1s	1078.28	1074.09	1063.08	323.12	5.46	2067.8	5.97	1.26
Si2p	112.08	97.77	90.48	283.67	12.82	3389.63	47.22	12.19

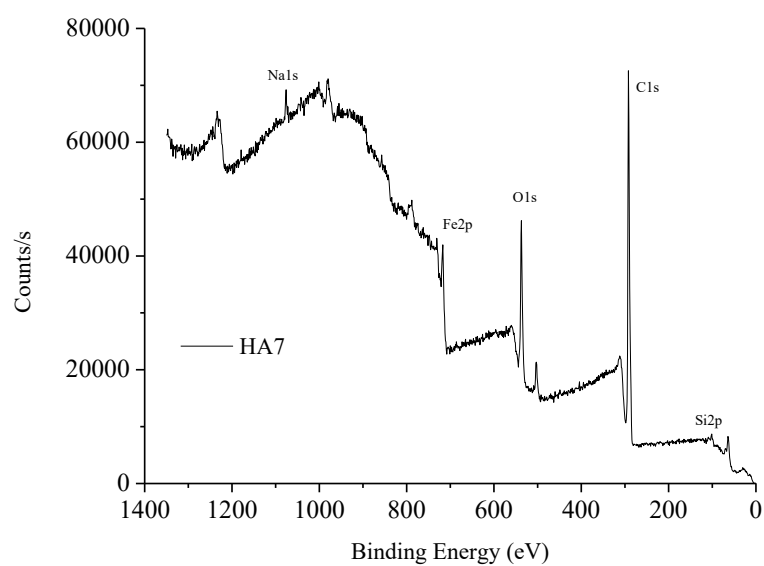


Figure 5.72 XPS Spectrum of HA7

Table 5.20 XPS Analysis Data Survey Scan HA7

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	298.08	291.69	281.08	60582.52	4.12	292060.57	4113.53	68.81
O1s	544.08	537.1	523.08	26061.59	4.4	140159.96	816.45	18.19
Fe2p	740.08	716.79	708.08	10031.7	4.95	79527.89	108.75	8.46
Na1s	1079.08	1076.05	1070.08	4589.11	3.97	21677.07	62.82	2.01
Si2p	108	101	96	1035.01	2.61	4638.92	64.74	2.53

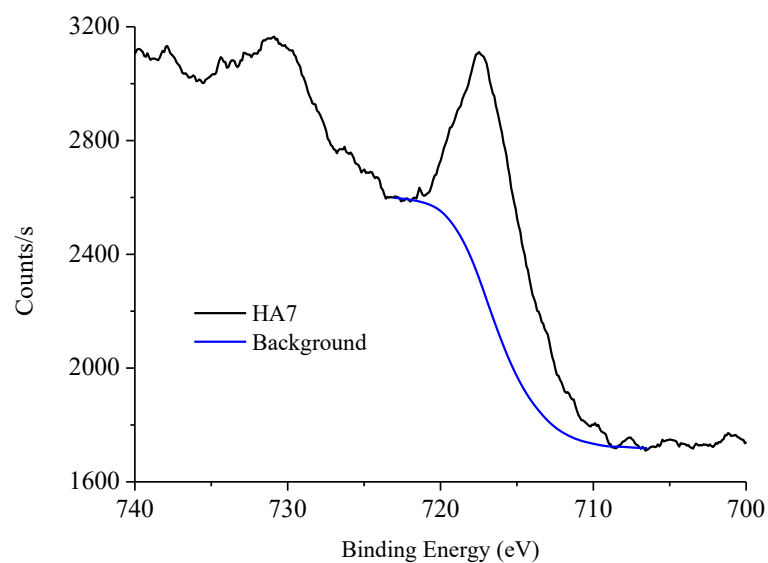


Figure 5.73 XPS Analysis results of HA2 for Fe2p

Table 5.21 XPS Analysis Data of HA7 for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
C1s	297.68	291.5	277.08	5254.12	3.36	22311.2	314.2	68.24
O1s	543.48	536.9	524.18	2142.99	3.87	10071	58.66	16.97
Fe2p	723.08	716.77	706.48	814.41	4.79	4434.21	6.06	6.12
Na1s	1080.08	1076.56	1063.18	617.03	3.29	2627.45	7.62	3.17
Si2p	111.28	100.57	91.38	97.93	5.05	775.04	10.81	5.49

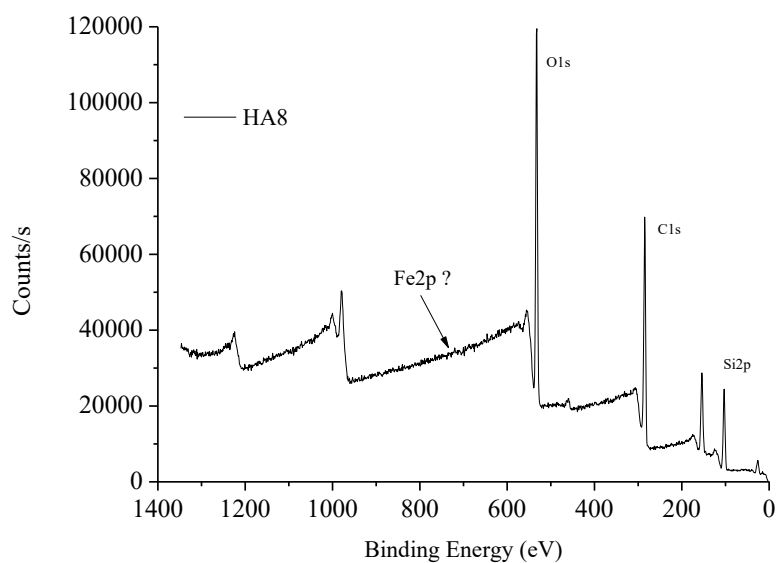


Figure 5.74 XPS Spectrum of HA8

Table 5.22 XPS Analysis Data Survey Scan HA8

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
O1s	539.08	532.43	523.08	95410.45	4.46	455852.35	2645.61	32.66
C1s	292.08	284.87	277.08	55186.46	4.66	273440.77	3834.47	35.54
Si2p	110.08	103.11	94.08	20759.9	4.7	105015.04	1467.39	31.8

In XPS spectrum of HA8 (Figure 5.74), any significant peaks were observed for the Fe2p peak. This may be due to the amount of Fe much smaller below the sensitivity or resolution limit of the XPS which can not detect XPS. It could be tried to search for the Fe3p at about 60 eV, although the cross section with normal XPS is very low. Another way for Fe is to search for the Auger lines. the Fe LMM lines are between 780 and 880eV (using Al-Ka).

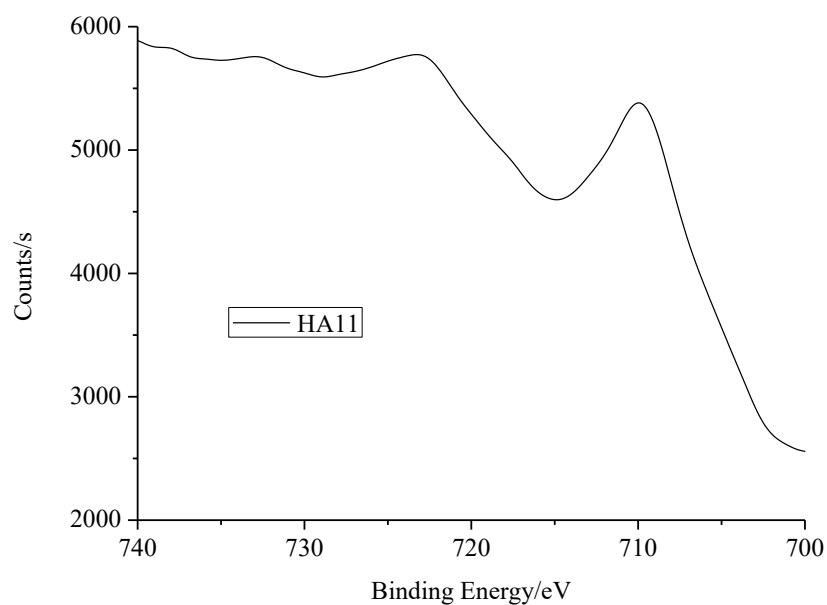


Figure 5.75 XPS Analysis results of HA11 for Fe2p

Table 5.23 XPS Analysis Data Survey Scan for HA11

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
O1s	534.58	529	519.76	37429.75	5.1	228269.37	1321.21	31.92
C1s	289.89	284.26	274.04	30452.53	4.61	185179.65	2595.76	47.08
Fe2p	738.08	708.85	699.08	17247.24	6.24	175303.72	237.91	20.06
N1s	408	399.31	394	1321.85	2.48	4893.08	44.2	0.93

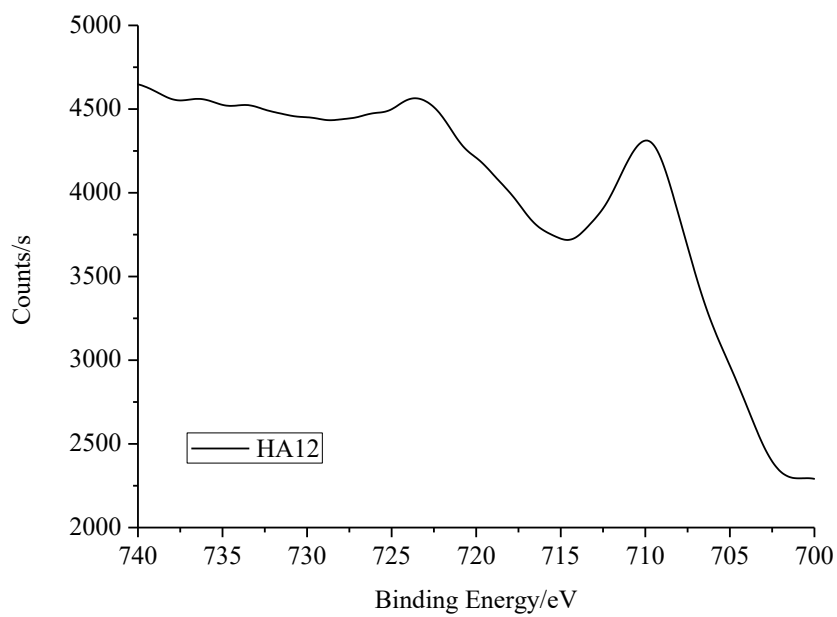


Figure 5.76 XPS Analysis results of HA12 for Fe2p

Table 5.24 XPS Analysis Data of HA12 for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
Si2p	106.08	101.78	93.28	196.91	4.12	961.56	13.43	6.81
C1s	290.78	284.9	275.18	2479.61	4.39	15680.41	219.89	47.72
N1s	403.98	398.91	391.68	229.57	5.71	1337.32	12.08	3.06
O1s	534.88	529.22	520.28	3010.38	5.92	18440.36	106.75	30.86
Fe2p	739.63	709	698.28	1161.3	5.9	8437.96	11.45	11.56

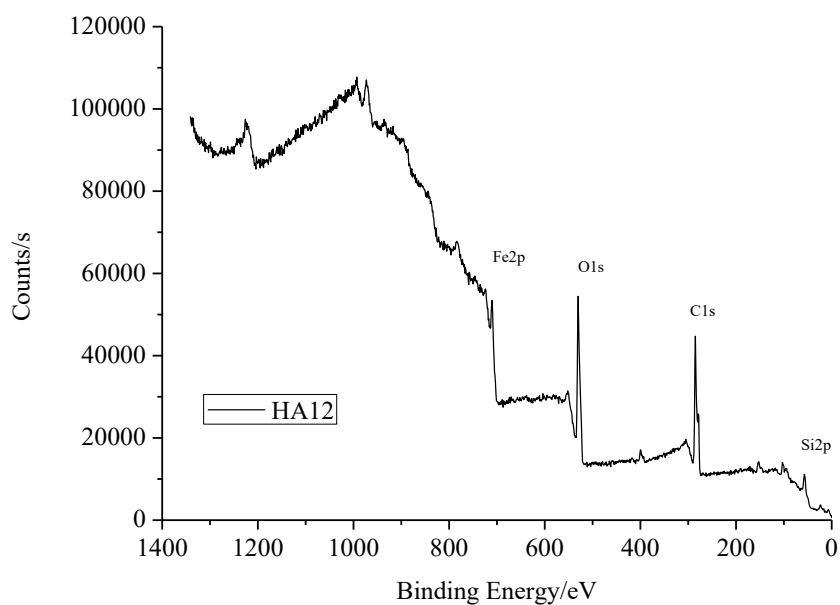


Figure 5.77 XPS Spectrum of HA12

Table 5.25 XPS Analysis Data Survey Scan for HA12

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
O1s	534.58	529.82	520.08	34125.09	3.76	214520.82	1242.43	28.5
C1s	290.08	284.88	273.83	29538.43	4.64	187944.66	2635.56	45.38
Fe2p	738.58	709.39	698.08	12439.12	6.36	116825.25	158.63	12.7
N1s	410.08	399.79	390.58	3182.28	3.25	24803.73	224.13	4.5
Si2p	106.58	102.21	93.08	2567.41	4.62	15880.36	221.79	8.93

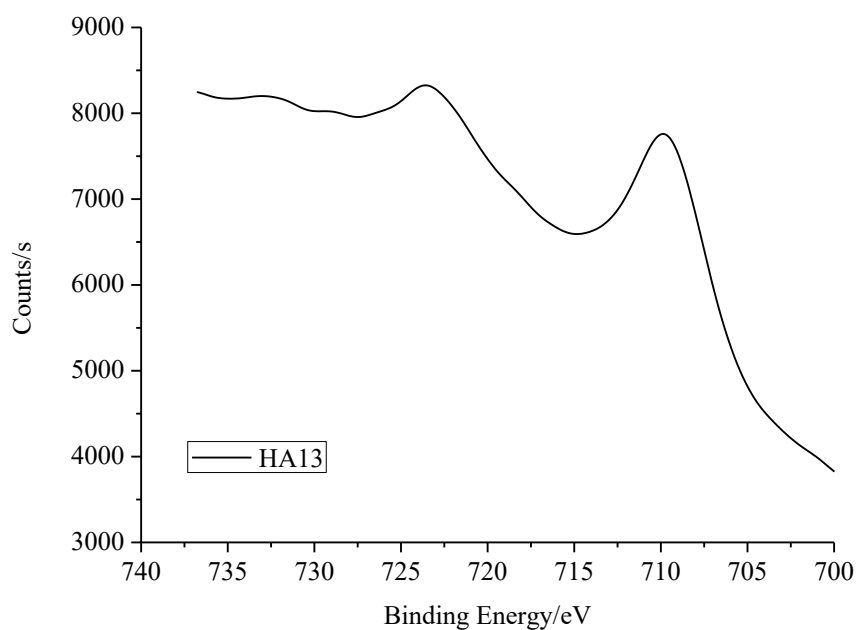


Figure 5.78 XPS Analysis results of HA13 for Fe2p

Table 5.26 XPS Analysis Data of HA13 for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
Si2p	106.78	102	91.88	365.15	3.85	1999.84	27.93	9.03
C1s	290.88	284.59	271.88	4353.19	3.67	21569.69	302.42	41.82
N1s	409.18	400.22	391.88	35.68	4.34	348.65	3.15	0.51
O1s	536.88	529.71	516.88	5366.99	4.2	29399.67	170.26	31.36
Fe2p	736.73	709.13	698.88	2423.38	5.19	19790.69	26.87	17.27

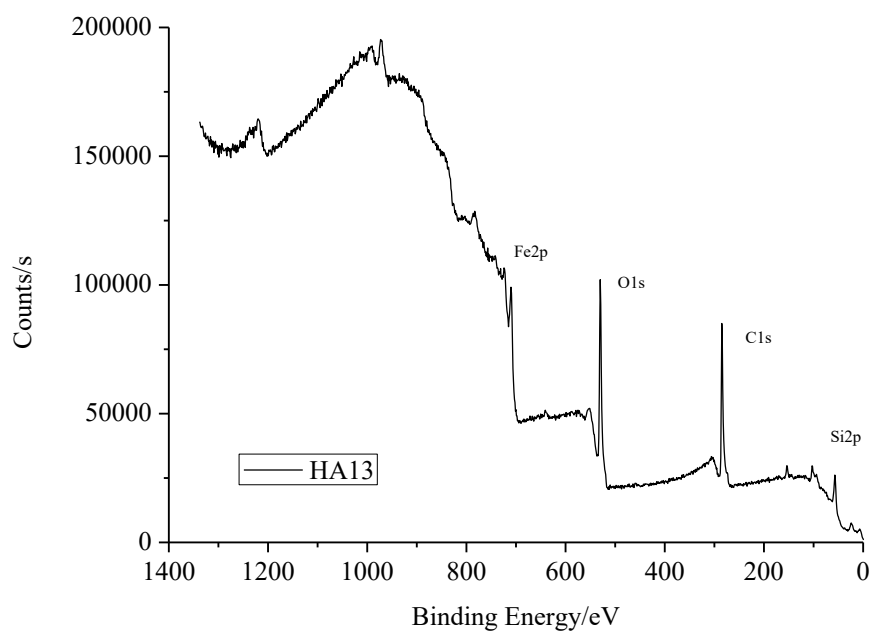


Figure 5.79 XPS Spectrum of HA13

Table 5.27 XPS Analysis Data Survey Scan for HA13

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
O1s	535.16	529.8	517	68774.41	4.14	369294.2	2138.81	30.64
C1s	289.58	284.63	272.17	56475.67	2.33	269493.84	3778.54	40.64
Fe2p	735.08	709.21	698.08	29658.64	5.53	286840.03	389.42	19.47
Si2p	107.58	102.71	93.08	5199.24	2.41	25490.73	356.11	8.96
N1s	408.79	403.24	393.59	533.96	0.83	2501.31	22.66	0.28

When we look at all of the Tables for the XPS peak of C1s which is used as a reference appearing in between 285-290 eV instead of constant 284.8 eV. Due to this fact all the other elements were shifted accordingly. It is most probable because of charging which can be checked by using a conductive sample such as a piece of aluminium foil and grounded with the XPS instrument. By taking a spectrum and the looking the peak positions, whether correct or not then the energy scale needs adjustment. On the other hand, For example, its thickness can also be effective.

Too many C1s data are available in the NIST database, the standard one is selected to make the correction. The "adventurous" carbon commonly used to calibrate XPS in air-exposed samples refers to C-C hydrocarbon bonds. The binding energy of the C-C property is 284.5 - 285.0 eV, depending on who you ask; It is different for inorganic surface studies. The C-O types occur at higher binding energies, so if your C 1s feature consists of more than one peak, you should use the peak in the lowest binding energy for calibration to adventurous carbon. It depends on your application. For example, if your sample has been exposed to air, there will be hydrocarbon contamination, which is generally thought to be at 285 eV binding energy. The two peaks will probably appear as a broad symmetrical peak.

After making the best estimate at the C1s main peak, comparisons are made with other known peaks in F1s or other spectra such as Si2p, so you can increase the confidence that you have correctly assigned the C1s peak for each peak you control.

If you are dealing with a properly grounded or insulating sample, you can go astray by making such a multi-point reference. If the sample is charged differently during analysis, you can see that various peaks have changed and expanded, and the job is more complex.

.

Table 5.28 XPS Data Analysis of The Samples for Fe2p

Peak Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Weight %
HA1	740.08	715.88	707.48	91396.91	5.95	1000609.13	1367.11	50.73
HA2	740.08	711.72	699.28	7627.35	4.43	75147.24	102.26	46.03
HA3	740.08	713.14	703.28	5278.32	6.28	59938.44	81.68	30.44
HA4	740.08	711.72	699.28	7627.35	4.43	75147.24	102.26	46.03
HA5	742.08	714.74	701.48	1682.09	5.34	18340.82	25.03	17.36
HA6	742.08	714.44	703.68	2348.16	6.57	24471.82	33.39	17.14
HA7	723.08	716.77	706.48	814.41	4.79	4434.21	6.06	6.12
HA11	740.98	709.07	699.98	1608.56	6.05	12422.32	16.86	16.44
HA12	739.63	709	698.28	1161.3	5.9	8437.96	11.45	11.56
HA13	736.73	709.13	698.88	2423.38	5.19	19790.69	26.87	17.27

O1s peak for Fe₃O₄ was observed at 529.9 eV. On the other hand, the peak at 531.9 eV related with –OH oxygen on the surface of Fe₃O₄ (Gong et al., 2012; Chandra et al., 2010).

5.1.6 Vibrating-Sample Magnetometer (VSM) Analysis of Samples

Vibrating Sample Magnetometer (VSM) is used for the determination of magnetic properties of materials such as solids, single crystals, powders, liquids even thin films as a function of magnetic field, temperature, and time. The characteristics of any magnetic material are defined by VSM curves.

Definition of Magnetic Parameters

For a magnetic material, the relation between magnetization (M) and applied field (H) is defined as hysteresis loop (red line, S type curve). It is shown schematically in Figure 5.80.

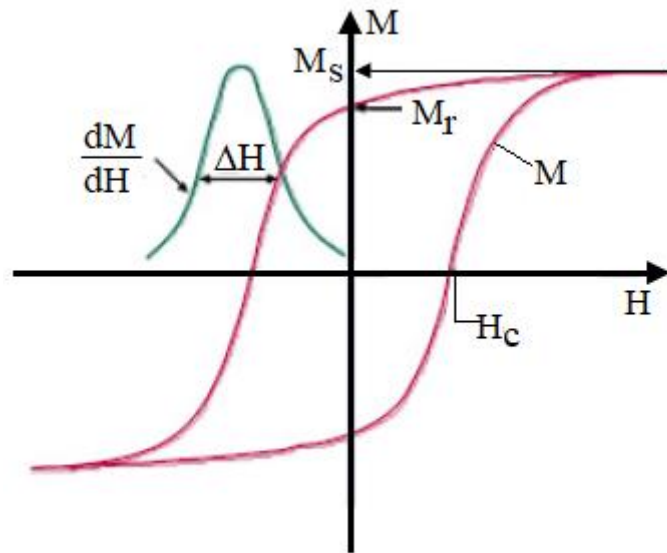


Figure 5.80 The relationship between magnetization M and the applied field H (Measuring magnetic media using a vsm, 2019)

In Figure 5.80, M_s , M_r , H_c , SQR and SFD are the parameters of saturation of magnetization, remanence, coercivity, squareness ratio (M_r/M_s), and switching field distribution ($\Delta H/H_c$), respectively. H_c is defined as field required to reduce magnetization to zero after saturation. It depends on shape and dimensions of the crystallite. The squareness ratio determines the hysteresis loop. Its magnitude is to determine whether the material is suitable for the recording medium. of how square

the hysteresis loop is. large SQR values are desired for recording medium.” (Measuring magnetic media using a vsm, 2019).

The magnetic properties of the bulk Fe_3O_4 had been investigated by several Authors and estimated as saturation magnetization (M_s) of $\sim 92 \text{ emu g}^{-1}$ and H_c of 323 Oe (Cullity, 1972; Long et al., 2011; Jiles, 2015; Goya, Berquo, Fonseca, & Morales, 2003; Ghosh et al., 2011). For magnetite nanopowders, the coercivity and the saturation magnetization values were also measured as 114 Oe and 3.7 emu/g , respectively (Kim, Kim, Lee, Maeng, & Kim, 2008).

Determination of Magnetic Properties

The magnetic parameters of the samples were determined by vibrating-sample magnetometer (VSM) in powder form. VSM analysis results of the prepared samples (HA1-HA8) are given in Figure 5.81-5.85.

.

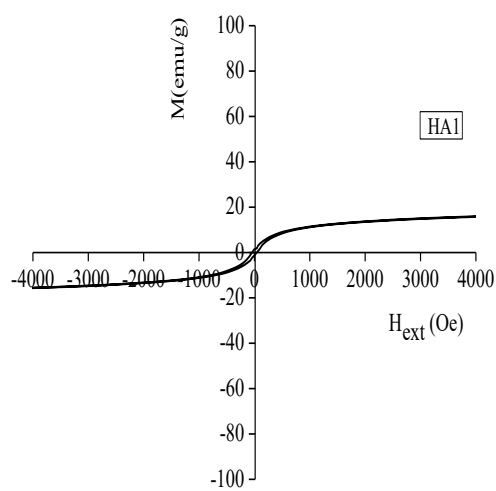


Figure 5.81 Magnetization curve of the sample HA1 at 298 K

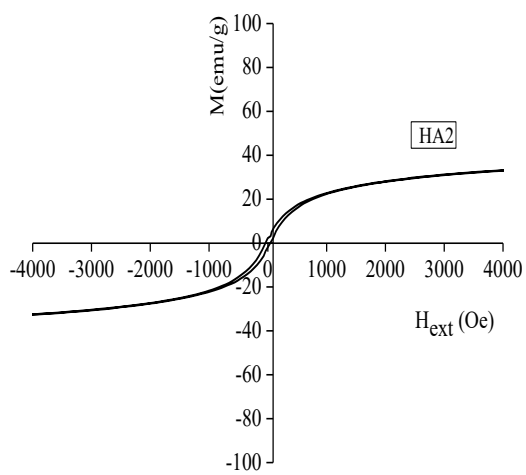


Figure 5.82 Magnetization curve of the sample HA2 at 298 K

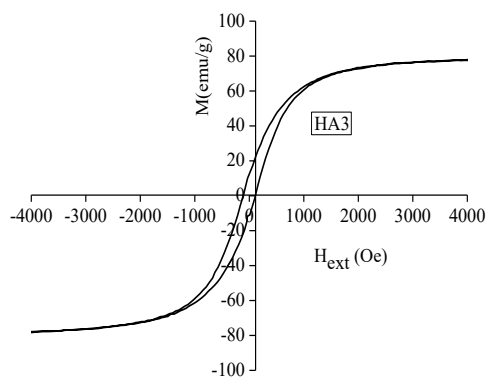


Figure 5.83 Magnetization curve of the sample HA3 at 298 K

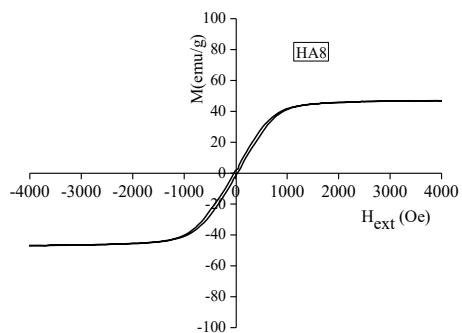


Figure 5.84 Magnetization curves of the sample HA8 at 298 K

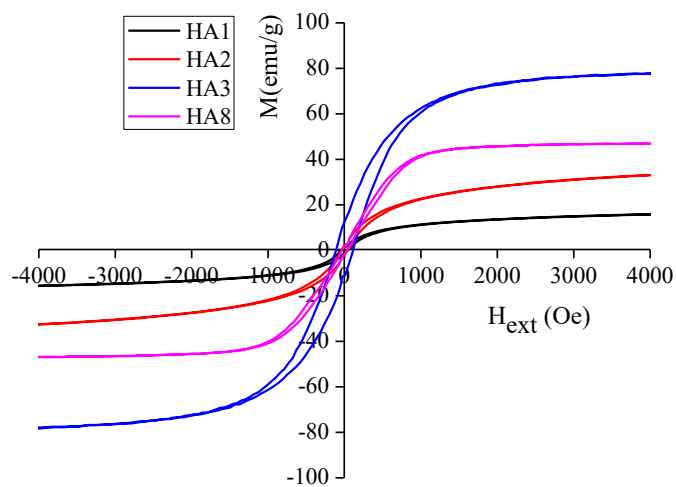


Figure 5.85 Magnetization curves of the samples (HA1-3 and HA8) at 298 K

Table 5.29 Magnetization parameters of the Fe₃O₄ samples at 298 K

Sample Code	M _s (emu/g)	M _r (emu/g)	M _r /M _s	Properties
HA1	16.89	1.39	0.082	Fe ₃ O ₄ N ₂ atm, 25°C
HA2	35.19	2.26	0.064	Fe ₃ O ₄ Air, 60°C
HA3	78.87	12.52	0.159	Fe ₃ O ₄ Standart
HA8	47.32	1.81	0.038	Ricoh 55μ HA1

The HA8 sample is used as a commercial sample. Saturation magnetization values of synthesized samples in N₂ (HA1) and open environment (HA2) are below standard HA3 and HA8. The sample synthesized at 60°C and open medium (HA2) appears to be closer to the commercial sample. S-type M–H curves were obtained with an immeasurable coercivity and remanence.

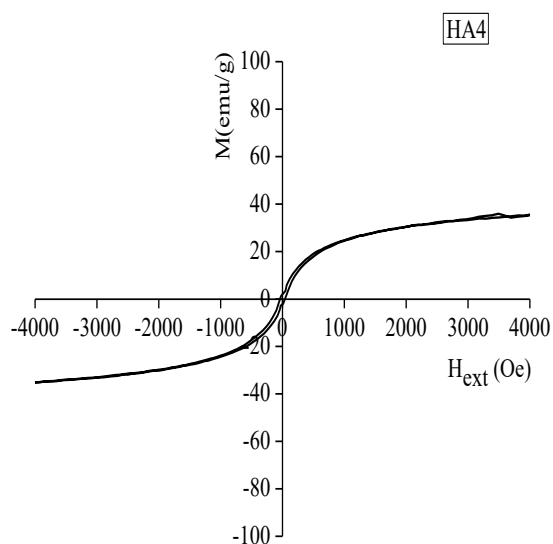


Figure 5.86 Magnetization curve of the sample HA4 at 298 K

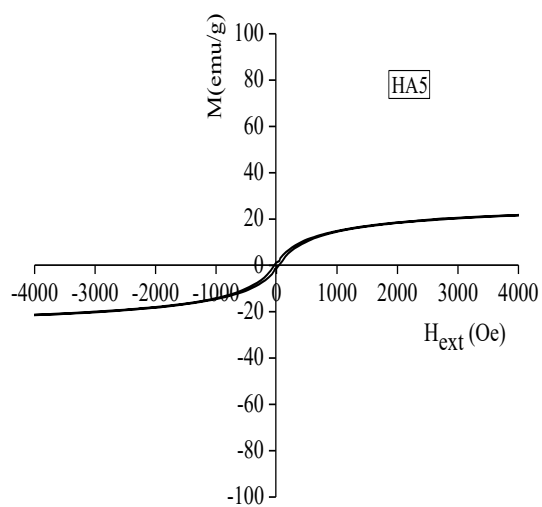


Figure 5.87 Magnetization curve of the sample HA5 at 298 K

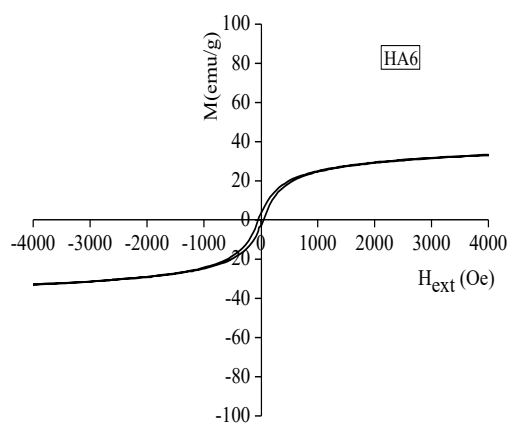


Figure 5.88 Magnetization curve of the sample HA6 at 298 K

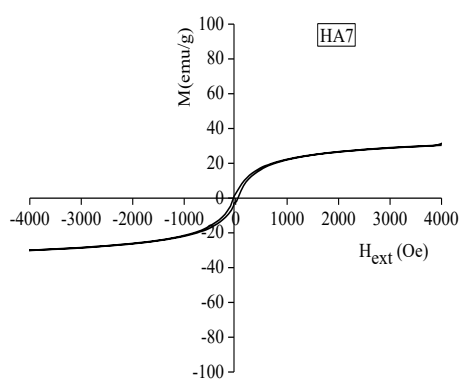


Figure 5.89 Magnetization curve of the sample HA7 at 298 K

The parameters obtained from the magnetization curves of the samples (HA1-HA8) were summarized and given in Table 5.30

Table 5.30 Magnetization parameters of the samples at 298 K

Sample Code	M_s (emu/g)	M_r (emu/g)	M_r/M_s	Properties
HA3	78.87	12.52	0.159	Fe ₃ O ₄ Standart
HA4	39.65	1.94	0.049	Fe ₃ O ₄ SDS Coated
HA5	22.91	1.27	0.055	Fe ₃ O ₄ CTAB Coated
HA6	34.67	3.24	0.094	Fe ₃ O ₄ OA Coated
HA7	35.06	2.57	0.073	Fe ₃ O ₄ SA Coated

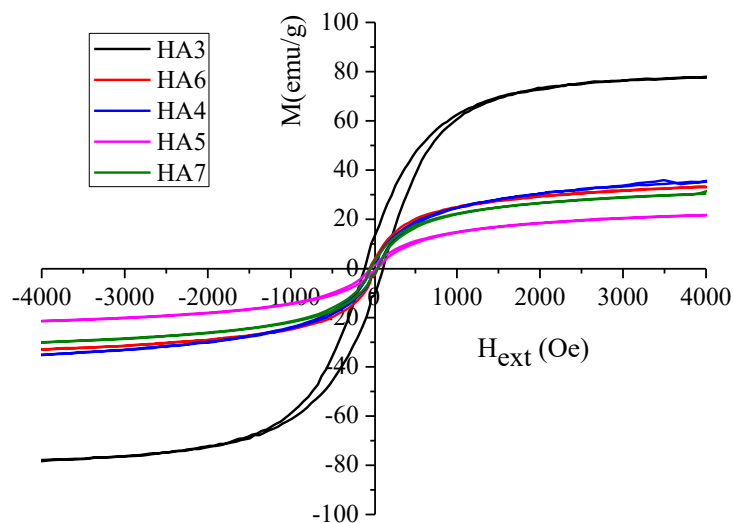


Figure 5.90 Magnetization curves of the samples (HA3-HA7) at 298 K

VSM analysis results obtained for the samples are given in the Table 5.30. M_s value for HA3, standard Fe_3O_4 was determined to be about 79 emu/g. Saturation magnetization values of 35-40 emu/g for other samples (HA4-HA7) and 22 emu/g for HA5 were also determined. These values show a significant reduction in bulk Fe_3O_4 (92 emu/g) and HA3 (79 emu/g). This is due to the coating of the particle surfaces with non-magnetic surfactants SDS, CTAB, OA and SA. It shows that the treatment with CTAB is highly effective and reduces saturation magnetization properties by 27.5% based on HA3. The effects of other surfactants are 50%. The determined squareness ratio (M_r/M_s) values were low. The S-shape of M-H curves of the samples exhibited zero coercivity and permanence indicating its superparamagnetism.

It is seen that the results obtained with magnetic properties are in agreement with the literature data (Batlle & Labarta, 2002; Kodama, Berkowitz, McNiff Jr, & Foner, 1996). Especially the VSM data of HA3, for example, was close to the commercial product (HA8) values.

It had been stated that the magnetic properties of Fe_3O_4 nanoparticles was sensitive to the crystallinity and particle size (López-Quintela & Rivas, 1993). Any decrease in size means decrease in M_s value. It has been also suggested that modifications with surfactants decrease in M_s (Pan, Gao, & Gu, 2005; Si et al., 2005).

The magnetic properties of the SDS coated sample (HA4) were close to the VSM results of the commercial sample (HA8).

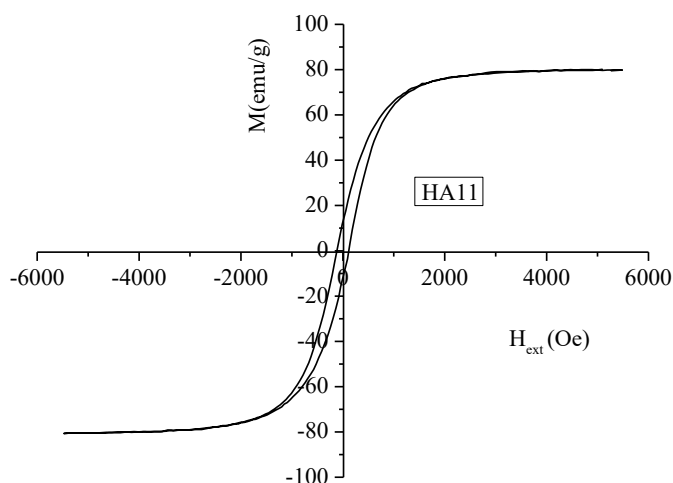


Figure 5.91 Magnetization curve of HA11 at 298 K

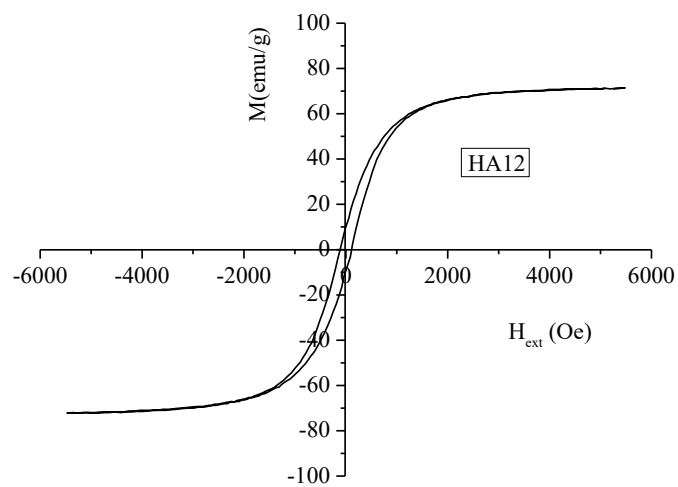


Figure 5.92 Magnetization curve of HA12 at 298 K

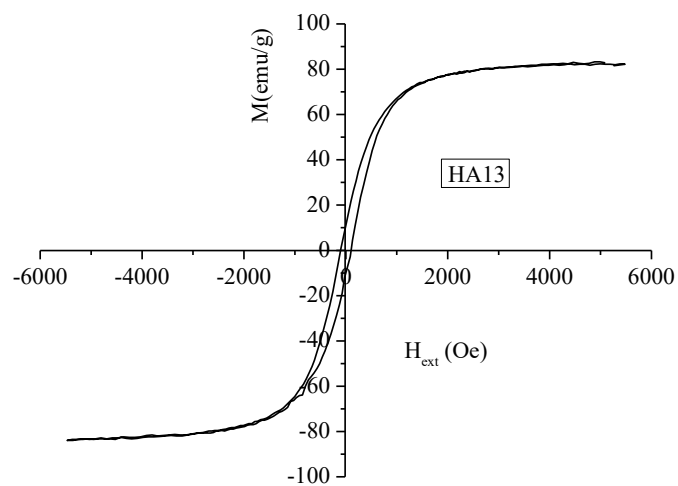


Figure 5.93 Magnetization curve of HA13 at 298 K

Table 5.31 Magnetization parameters of the Fe₃O₄ samples at 298 K

Sample Code	M _s (emu/g)	M _r (emu/g)	M _r /M _s	Properties
HA3	78.87	12.52	0.159	Fe ₃ O ₄ Standart
HA11	80.18	12.79	0.160	Fe ₃ O ₄ coated with Oam
HA12	71.46	10.01	0.140	Fe ₃ O ₄ coated with APTES
HA13	83.26	10.90	0.131	Fe ₃ O ₄ coated with HDTMS

As can be seen from Table 5.31 that there were a good correlation about the magnetic properties of HA3 (standard), HA11, HA12 and HA13.

CHAPTER SIX

CONCLUSIONS AND PERSPECTIVES

In this thesis, magnetite nanoparticles were synthesized in three stages by co-precipitation method. The experiments were carried out with the 2:1 ($\text{Fe}^{3+}/\text{Fe}^{2+}$) ratio and pH=8 at 80 °C. The products were then characterized by FTIR, XRD, SEM, TG / DTG, XPS and VSM methods in comparison with the commercially purchased Fe_3O_4 sample.

Surfaces of the particles were coated with OA, SA, SDS, CTAB, APTES, OAm and HDTMS. Their physico-chemical properties were compared with standard Fe_3O_4 . These products are characterized by the same methods. The properties of all the products obtained were compared with those of a commercial toner sample.

The XRD patterns of the samples were shown in Figure 5.4-5.14. All diffraction patterns were evaluated based on the magnetite data. In Figure 5.4 and Figure 5.5, eight peaks were observed in all diffraction patterns, $2\theta / ^\circ$: 26.61, 30.20 °, 35.56 °, 43.21 °, 53.60 °, 57.13 °, 62.73 °, 74.14 °, and Miller indices of reflection planes are determined as (220), (311), (222), The (400), (422), (511), (440), (533), respectively. It is understood that the main mineral structure fits Magnetite Fe_3O_4 inverted cubic spinel structure (JCPDS card: 89-691). The particles were pure Fe_3O_4 coincided with JCPDS, PDF No. 65-3107. It can be said from the results that the modification of the Fe_3O_4 with surfactants did not affect the crystal structure.

By using XRD data, the crystallite size was calculated by using the Debye-Scherrer Formula for all peaks in the diffractograms. At the same time, the strongest peak for all samples was about 35.5° for (311) reflections. Crystallite size was also calculated for this peak. The results were summarized in Table 5.1. The crystallite sizes were 6-29 nm. There was a good correlation for the standard sample HA3, commercial product HA8, HA11 and HA12 samples.

On the other hand, FTIR spectra of the samples were given in Figure 5.15- Figure 5.28. Bands at 610, 584 and 450 cm^{-1} were related with Fe–O as indicated with the references. In the case of, modification of the surfaces with OA, SA, SDS, CTAB, APTES, OAm and HDTMS did not changed practically the bands of Fe–O. On the other hand, some changes were occurred in the band assignments of the coating precursors. The bands between 850-1200 cm^{-1} were related with Fe–OH groups. The interaction between silane and magnetite was evaluated as covalent bonding and confirmed by FTIR measurements for APTES and HDTMS coated magnetite samples as in Figure 5.24 and 5.28, respectively.

TG/DTG thermograms of the samples HA4, HA5, HA6, HA7 and HA8 were given in Figures 5.30-5.34, respectively. The analysis were not carried out for HA11, HA12 and HA13 samples due to the fact that the problems in TG/DTG Apparatus.

The TGA/DTG curves were presented in Figure 5.30 and 5.34. The profiles had two step mass losses in the temperature range of 30–500 °C which covered the dehydration of physically adsorbed water or humidity from 30–200 °C and surfactant decomposition from 200 °C to 500 °C. The data was summarized in Table 5.4.

SEM images of HA1, HA2 and HA3 were evaluated together due to the different preparation methods (Figures 5.36-5.38). These images showed that the particles are spherical in shapes and different non homogeneous sizes containing coarse grains. Porous and spongy structure was seen for HA3 as standard. In Figures 5.39-5.42, for HA4, HA5, HA6 and HA7 were coated with SDS, CTAB, Oleic Acid (OA) and SA, respectively. These pictures show that they are relatively smaller spherical shape particles and size below 100 nm. It was interesting that these samples were coated with surfactants to provide the stability and expected to be relatively coarser particles as compared with HA1, HA2 and HA3. SEM images of the commercial product, HA8 were presented in Figures 5.43-5.47. Spherical adherent lumpy particles of 14, 62-74 μm in diameter were observed. On the other hand, in another analysis for HA8 from Figure 5.47 that 1132 μm and 992 nm particles were also seen.

In Figure 5.48, SEM EDX Images of HA8 was presented. For this sample, EDX analysis was carried out on the three selected areas in the image. As can be seen from the Tables 5.5-5.7, the sample contained C, O, Si, Fe, Cu and Zn elements. Fe and O elements came from basically Fe_3O_4 . Si came from the coating materials as silanes. C is due to the sample carrier. Cu and Zn were due to the screening materials.

In Figures 5.52 and 5.53, SEM images of HA11 (coated with Oleyl amine) sample were shown. In Figures 5.54 and 5.55, SEM images of HA12 (coated with APTES) sample were presented. In these samples, spherical particles with 100-180 nm size were observed. In addition, in both examples, mainly hexagonal shaped crystalline structure was also observed in some respect.

XPS analysis of the samples were studied and the binding energies of $\text{Fe}2p_{1/2}$ and $\text{Fe}2p_{3/2}$ related with the oxidation states of Fe. These peaks may be used for the determination of the ionic states of iron. It has been observed that there was a shift toward a higher binding energy and the peak intensities were also changed. The peak shift in XPS is related with the oxidation state of Fe as Fe^{2+} or Fe^{3+} . From the Figure 5.74 and Table 5.22 for HA8, no significant peaks were observed for the Fe2p peak. This may be due to the amount of Fe much smaller below the sensitivity or resolution limit of the XPS which can not detect XPS. When we look at all of the Tables for the XPS peak of C1s which is used as a reference appearing in between 285-290 eV instead of constant 284.8 eV. Due to this fact all the other elements were shifted accordingly. In XPS Data Analysis of all of the samples for Fe2p was given. Peak started binding energies, maxima of binding energies and end of the peak binding energies of all samples were founded as 740-742, 709-716 and 698-707 eV, respectively. The peak about 530 eV is O1s in Fe_3O_4 . Meanwhile, binding energy of surface hydroxyl groups O1s around at 532 eV confirmed the presence of Fe_3O_4 .

The magnetic parameters were determined by VSM device. The hysteresis loops of the samples, which were measured in the powder state, were shown in Figure 5.80. The magnetic properties of the bulk Fe_3O_4 had been estimated as M_s value of $\sim 92 \text{ emu g}^{-1}$ and H_c of 323 Oe. VSM analysis results obtained for the samples are

given in the Table 5.29-5.30. M_s value of HA3 as standard Fe_3O_4 was determined to be about 79 emu/g. Saturation magnetization values of 35-40 emu/g for other samples (HA4-HA7) and 22 emu/g for HA5 were also determined. This is due to the coating of the particle surfaces with non-magnetic surfactants SDS, CTAB, OA and SA. It shows that the treatment with CTAB is highly effective and reduces saturation magnetization properties by 27.5% based on HA3. The effects of other surfactants are 50%. The determined squareness ratio (M_r/M_s) values were low. It was also seen that M_s value of Fe_3O_4 is closely related with crystallinity and size of the particles. When the size decreased, decrease in M_s was observed. There is a good correlation with the crystallite sizes determined from XRD data. The magnetic properties of the SDS coated sample (HA4) were close to the VSM results of the commercial sample (HA8). In Table 5.31, there was a good relationship between the magnetic properties of HA3, HA11, HA12, and HA13.

In the light of these studies, it is recommended to use the synthesized substances since it is understood that they have sufficient magnetic properties and quality for the toner. It is believed that HA11, HA12 and HA13 may be more suitable, given that the hydrophobic surface properties are provided with silane compounds and include is recommended to measure the zeta potentials of the magnetite samples synthesized for future studies and to determine the surface contact angles. In addition, it will be extremely useful to take Raman spectra and support them with FTIR results.

REFERENCES

- Abd, A., Latif, D., & Wasna'a, M. (2016). Synthesis and some physical properties of magnetite (Fe_3O_4) nanoparticles. *Synthesis*, 2(3), 341-345.
- Al-Ghamdi, A., Al-Hazmi, F., Al-Tuwirqi, R., Alnowaiser, F., Al-Hartomy, O., El-Tantawy, F., & Yakuphanoglu, F. (2013). Synthesis, magnetic and ethanol gas sensing properties of semiconducting magnetite nanoparticles. *Solid State Sciences*, 19, 111-116.
- Ali, S., Khan, S., Eastoe, J., Hussaini, S., Morsy, M., & Yamani, Z. (2018). Synthesis, characterization, and relaxometry studies of hydrophilic and hydrophobic superparamagnetic Fe_3O_4 nanoparticles for oil reservoir applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 543, 133-143.
- Alp, E., & Aydogan, N. (2016). A comparative study: synthesis of superparamagnetic iron oxide nanoparticles in air and N_2 atmosphere. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 510, 205-212.
- Asenath Smith, E., & Chen, W. (2008). How to prevent the loss of surface functionality derived from aminosilanes. *Langmuir*, 24(21), 12405-12409.
- Barick, K., & Bahadur, D. (2006). Assembly of Fe_3O_4 nanoparticles on SiO_2 monodisperse spheres. *Bulletin of Materials Science*, 29(6), 595-598.
- Battle, X., & Labarta, A. (2002). Finite-size effects in fine particles: magnetic and transport properties. *Journal of Physics D: Applied Physics*, 35(6), R15-R42.
- Bear, J., Yu, B., Blanco-Andujar, C., McNaughton, P., Southern, P., Mafina, M., . . . Parkin, I. (2015). A low cost synthesis method for functionalised iron oxide nanoparticles for magnetic hyperthermia from readily available materials. *Faraday Discussions*, 175, 83-95.

- Berger, P., Adelman, N., Beckman, K., Campbell, D., Ellis, A., & Lisensky, G. (1999). Preparation and properties of an aqueous ferrofluid. *Journal of Chemical Education*, 76(7), 943-948.
- Bindu, P., & Thomas, S. (2014). Estimation of lattice strain in ZnO nanoparticles: X-ray peak profile analysis. *Journal of Theoretical and Applied Physics*, 8(4), 123-134.
- Black Iron Oxide Pigments*, (n.d.). Retrieved April 10,2020 from <https://images.app.goo.gl/HaoJWB6DDqYoHzxs5>.
- Bragaru, A., Kusko, M., Radoi, A., Danila, M., Simion, M., Craciunoiu, F., . . . Ignat, T. (2013). Microstructures and growth characteristics of polyelectrolytes on silicon using layer-by-layer assembly. *Open Chemistry*, 11(2), 205-214.
- Briggs, D. (1990). *Practical Surface Analysis second edition Vol. 1, Auger and X-ray Photoelectron Spectroscopy*. New York.:John Wiley & Sons Ltd.
- Cabrera, L., Gutierrez, S., Menendez, N., Morales, M., & Herrasti, P. (2008). Magnetite nanoparticles: electrochemical synthesis and characterization. *Electrochimica Acta*, 53(8), 3436-3441.
- Can, K., Ozmen, M., & Ersoz, M. (2009). Immobilization of albumin on aminosilane modified superparamagnetic magnetite nanoparticles and its characterization. *Colloids and Surfaces B: Biointerfaces*, 71(1), 154-159.
- Cao, H., He, J., Deng, L., & Gao, X. (2009). Fabrication of cyclodextrin functionalized superparamagnetic Fe₃O₄/Amino-Silane core-shell nanoparticles via layer-by-layer method. *Applied Surface Science*, 255, 7974-7980.
- Chaki, S., Malek, T., Chaudhary, M., Tailor, J., & Deshpande, M. (2015). Magnetite Fe₃O₄ nanoparticles synthesis by wet chemical reduction and their characterization. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 6(3), 03500.

- Chamritski, I., & Burns, G. (2005). Infrared-and Raman-active phonons of magnetite, maghemite, and hematite: a computer simulation and spectroscopic study. *The Journal of Physical Chemistry B*, 109(11), 4965-4968.
- Chandra, V., Park, J., Chun, Y., Lee, J., Hwang, I., & Kim, K. (2010). Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal. *American Chemical Society Nano*, 4(7), 3979-3986.
- Chang, C., Hon, M., & Leu, I. (2010). Preparation of ZnO nanorod arrays with tailored defect-related characteristics and their effect on the ethanol gas sensing performance. *Sensors and Actuators B: Chemical*, 151(1), 15-20.
- Chen, Y., Zhang, X., Wang, B., Lv, M., Zhu, Y., & Gao, J. (2017). Fabrication and characterization of novel shape-stabilized stearic acid composite phase change materials with tannic-acid-templated mesoporous silica nanoparticles for thermal energy storage. *Royal Society of Chemistry Advances*, 7(26), 15625-15631.
- Chen, Z., Du, Y., Li, Z., Yang, K., & Lv, X. (2017). Controllable synthesis of magnetic Fe₃O₄ particles with different morphology by one-step hydrothermal route. *Journal of Magnetism and Magnetic Materials*, 426, 121-125.
- Chen, Z., Li, F., Hao, L., Chen, A., & Kong, Y. (2011). One-step electrodeposition process to fabricate cathodic superhydrophobic surface. *Applied Surface Science*, 258(4), 1395-1398.
- Chiang, C., Ishida, H., & Koenig, J. (1980). The structure of γ -aminopropyltriethoxysilane on glass surfaces. *Journal of Colloid and Interface Science*, 74(2), 396-404.
- Chiarakorn, S., Areerob, T., & Grisdanurak, N. (2007). Influence of functional silanes on hydrophobicity of MCM-41 synthesized from rice husk. *Science and Technology of Advanced Materials*, 8(1-2), 110-115
- Color Paint Red/ Yellow/ Black Pigments Factory Iron Oxide, (n.d.). Retrieved April 10, 2020 from <https://images.app.goo.gl/UniJyyLyCrDH9gvd7>.

- Cullity, B. (1972). *Introduction to Magnetic Materials*. London: Addison-Wesley Publishing Company.
- Dai, Z., Liang, T., & Lee, J. (2019). Gas sensors using ordered macroporous oxide nanostructures. *Nanoscale Advances*, 1(5), 1626-1639.
- De Palma, R., Peeters, S., Van Bael, M., Van de Rul, H., Bonroy, K., Laureyn, W., . . . Maes, G. (2007). Silane ligand exchange to make hydrophobic superparamagnetic nanoparticles water-dispersible. *Chemistry of Materials*, 19(7), 1821-1831.
- Ding, Y., Hu, Y., Zhang, L., Chen, Y., & Jiang, X. (2006). Synthesis and magnetic properties of biocompatible hybrid hollow spheres. *Biomacromolecules*, 7(6), 1766-1772.
- Dobson, K., Roddick-Lanzilotta, A., & McQuillan, A. (2000). An in situ infrared spectroscopic investigation of adsorption of sodium dodecylsulfate and of cetyltrimethylammonium bromide surfactants to TiO₂, ZrO₂, Al₂O₃, and Ta₂O₅ particle films from aqueous solutions. *Vibrational Spectroscopy*, 24(2), 287-295.
- Du, G., Lu, Q., Xia, X., Jia, L., & Yao, K. (2006). Fe₃O₄/CdSe/ZnS magnetic fluorescent bifunctional nanocomposites. *Nanotechnology*, 17(12), 2850-2854
- Dutra, G., Araujo, O., Neto, W., Garg, V., Oliveira, A., & Junior, A. (2017). Obtaining superhydrophobic magnetic nanoparticles applicable in the removal of oils on aqueous surface. *Materials Chemistry and Physics*, 200, 204-216.
- Dutz, S., & Hergt, R. (2014). Magnetic particle hyperthermia a promising tumour therapy. *Nanotechnology*, 25(45), 452001.
- Dutz, S., Hergt, R., Mürbe, J., Müller, R., Zeisberger, M., Andra, W., . . . Bellemann, M. (2007). Hysteresis losses of magnetic nanoparticle powders in the single domain size range. *Journal of Magnetism and Magnetic Materials*, 308(2), 305-312.
- El Ghandoor, H., Zidan, H., Khalil, M., & Ismail, M. (2012). Synthesis and some physical properties of magnetite (Fe₃O₄) nanoparticles. *International Journal of Electrochemical Science*, 7(6), 5734-5745.

- Elfeky, S., Mahmoud, S., & Youssef, A. (2017). Applications of CTAB modified magnetic nanoparticles for removal of chromium (VI) from contaminated water. *Journal of Advanced Research*, 8(4), 435-443.
- El-kharrag, R., Amin, A., & Greish, Y. (2011). Synthesis and characterization of mesoporous sodium dodecyl sulfate-coated magnetite nanoparticles. *Journal of Ceramic Science and Technology*, 2, 203-210.
- Erley, W., & Hemminger, J. (1994). Spectroscopic identification of an HCNH species on Pt (111). *Surface Science*, 316(1-2), L1025-L1030.
- Fahlepy, M. R., & Tiwow, V. (2018). Characterization of magnetite (Fe₃O₄) minerals from natural iron sand of Bonto Kanang Village Takalar for ink powder (toner) application. In *Journal of Physics: Conference Series*, 997,(1), 012036.
- Ferreira, R., Pereira, I., Cavalcante, L., Gamarra, L., Carneiro, S., Amaro, E., . . . Andrade, A. (2009). Synthesis and characterization of silica-coated nanoparticles of magnetite. In *LACAME 2008* (265-274). Berlin, Heidelberg: Springer.
- Galasso, F. (1970). *Structure and properties of inorganic solids: International series of monographs in solid state physics*, 7(1st ed.), 211. Oxford: Pergamon Press.
- Gao, J., Gu, H., & Xu, B. (2009). Multifunctional magnetic nanoparticles: design, synthesis, and biomedical applications. *Accounts of Chemical Research*, 42(8), 1097-1107.
- Ghosh, R., Pradhan, L., Devi, Y., Meena, S., Tewari, R., Kumar, A., . . . Ningthoujam, R. (2011). Induction heating studies of Fe₃O₄ magnetic nanoparticles capped with oleic acid and polyethylene glycol for hyperthermia. *Journal of Materials Chemistry*, 21(35), 13388-13398.
- Gong, J., Wang, X., Shao, X., Yuan, S., Yang, C., & Hu, X. (2012). Adsorption of heavy metal ions by hierarchically structured magnetite-carbonaceous spheres. *Talanta*, 101, 45-52.

- Gong, P., Li, H., He, X., Wang, K., Hu, J., Tan, W., ... (2007). Preparation and antibacterial activity of Fe₃O₄@Ag nanoparticles. *Nanotechnology*, 18(28), 285604.
- Goya, G., Berquo, T., Fonseca, F., & Morales, M. (2003). Static and dynamic magnetic properties of spherical magnetite nanoparticles. *Journal of Applied Physics*, 94(5), 3520-3528.
- Graat, P., & Somers, M. (1996). Simultaneous determination of composition and thickness of thin iron-oxide films from XPS Fe2p spectra. *Applied Surface Science*, 100, 36-40.
- Graat, P., & Somers, M. (1998). Quantitative analysis of overlapping XPS peaks by spectrum reconstruction: determination of the thickness and composition of thin iron oxide films. *Surface and interface analysis: An international journal devoted to the development and applications of techniques for the analysis of surfaces, interfaces and thin films*, 26(11), 773-782. London: John Wiley & Sons, Ltd.
- Guan, D., Gao, Z., Yang, W., Wang, J., Yuan, Y., Wang, B., . . . Liu, L. (2013). Hydrothermal synthesis of carbon nanotube/cubic Fe₃O₄ nanocomposite for enhanced performance supercapacitor electrode material. *Materials Science and Engineering: B*, 178(10), 736-743.
- Guivar, J., Sanches, E., Magon, C., & Fernandes, E. (2015). Preparation and characterization of cetyltrimethylammonium bromide (CTAB)-stabilized Fe₃O₄ nanoparticles for electrochemistry detection of citric acid. *Journal of Electroanalytical Chemistry*, 755, 158-166.
- Guo, W., Fu, Z., Zhang, Z., Wang, H., Liu, S., Feng, W., . . . Giesy, J. (2020). Synthesis of Fe₃O₄ magnetic nanoparticles coated with cationic surfactants and their applications in Sb(V) removal from water. *Science of The Total Environment*, 710, 136302.
- Gupta, A., & Gupta, M. (2005). Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. *Biomaterials*, 26(18), 3995-4021.

- Hawn, D., & DeKoven, B. (1987). Deconvolution as a correction for photoelectron inelastic energy losses in the core level XPS spectra of iron oxides. *Surface and Interface Analysis*, 10(2-3), 63-74.
- Herrera, A., Barrera, C., & Rinaldi, C. (2008). Synthesis and functionalization of magnetite nanoparticles with aminopropylsilane and carboxymethyldextran. *Journal of Materials Chemistry*, 18(31), 3650-3654.
- Hong, R., Pan, T., & Li, H. (2006). Microwave synthesis of magnetic Fe₃O₄ nanoparticles used as a precursor of nanocomposites and ferrofluids. *Journal of Magnetism and Magnetic Materials*, 303(1), 60-68.
- Hong, S., Lee, J., Lee, J., Kim, H., Park, J., Cho, J., . . . Han, D. (2011). Subtle cytotoxicity and genotoxicity differences in superparamagnetic iron oxide nanoparticles coated with various functional groups. *International Journal of Nanomedicine*, 6, 3219-3231.
- IKCU merkezıarařtırmalab. (2020). Carl Zeiss 300VP SEM Carl Zeiss 300VP SEM and QUORUM Q150 RES device. 20 Mart 2020, <https://merkeziarařtırmalab.ikcu.edu.tr/S/15260/sem>.
- Iron(II) oxide, (n.d.). Retrieved April 10,2020 from <https://images.app.goo.gl/htks6vxYbPELqQph8>.
- Israel, L., Galstyan, A., Holler, E., & Ljubimova, J. (2020). Magnetic iron oxide nanoparticles for imaging, targeting and treatment of primary and metastatic tumors of the brain. *Journal of Controlled Release*,45-62
- Issa, B., Obaidat, I., Albiss, B., & Haik, Y. (2013). Magnetic nanoparticles: surface effects and properties related to biomedicine applications. *International Journal of Molecular Sciences*, 14(11), 21266-21305.
- Jadhav, N., Prasad, A., Kumar, A., Mishra, R., Dhara, S., Babu, K., . . . Vatsa, R. (2013). Synthesis of oleic acid functionalized Fe₃O₄ magnetic nanoparticles and studying their interaction with tumor cells for potential hyperthermia applications. *Colloids and Surfaces B: Biointerfaces*, 108, 158-168.

- Jagadeesan, D., Mansoori, U., Mandal, P., Sundaresan, A., & Eswaramoorthy, M. (2008). Hollow spheres to nanocups: tuning the morphology and magnetic properties of single-crystalline α -Fe₂O₃ nanostructures. *Angewandte Chemie International Edition*, 47(40), 7685-7688.
- Jaw, K., Hsu, C., & Lee, J. (2001). The thermal decomposition behaviors of stearic acid, paraffin wax and polyvinyl butyral. *Thermochimica Acta*, 367, 165-168.
- Jiles, D. (2015). *Introduction to magnetism and magnetic materials*. Boca Raton: CRC Press.
- Kandpal, N., Sah, N., Loshali, R., Joshi, R., & Prasad, J. (2014). Co-precipitation method of synthesis and characterization of iron oxide nanoparticles. *Journal of Scientific & Industrial Research*, 87-90.
- Kennedy, R., & Stampe, P. (1999). Films grown by laser ablation on Si (100) and GaAs (100) substrates with and without MgO buffer layers. *Journal of Physics D: Applied Physics*, 32(1), 16.
- Kim, D., Mikhaylova, M., Zhang, Y., & Muhammed, M. (2003). Protective coating of superparamagnetic iron oxide nanoparticles. *Chemistry of Materials*, 15(8), 1617-1627.
- Kim, K., Kim, E., Lee, J., Maeng, S., & Kim, Y. (2008). Synthesis and characterization of magnetite nanopowders. *Current Applied Physics*, 8(6), 758-760.
- Klekotka, U., Satuła, D., Spassov, S., & Kalska-Szostko, B. (2018). Surfactant dependence on physicochemical properties of magnetite nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 537, 452-459.
- Koch, K., Papademetris, X., Rothman, D., & de Graaf, R. (2006). Rapid calculations of susceptibility-induced magnetostatic field perturbations for in vivo magnetic resonance. *Physics in Medicine & Biology*, 51(24), 6381.
- Kodama, R., Berkowitz, A., McNiff Jr, E., & Foner, S. (1996). Surface spin disorder in NiFe₂O₄ nanoparticles. *Physical Review Letters*, 77(2), 394-397.

- Korecki, J., Handke, B., Spiridis, N., Ślęzak, T., Flis-Kabulska, I., & Haber, J. (2002). Size effects in epitaxial films of magnetite. *Thin Solid Films*, 412(1-2), 14-23.
- Kudr, J., Haddad, Y., Richtera, L., Heger, Z., Cernak, M., Adam, V., & Zitka, O. (2017). Magnetic nanoparticles: from design and synthesis to real world applications. *Nanomaterials*, 7(9), 243.
- Langford, J., & Wilson, A. (1978). Scherrer after sixty years: a survey and some new results in the determination of crystallite size. *Journal of Applied Crystallography*, 11(2), 102-113.
- Laurent, S., Forge, D., Port, M., Roch, A., Robic, C., Vander Elst, L., & Muller, R. (2008). Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. *Chemical Reviews*, 108(6), 2064-2110.
- Lee, D., & Condrate, R. (1999). FTIR spectral characterization of thin film coatings of oleic acid on glasses: I. Coatings on glasses from ethyl alcohol. *Journal of Materials Science*, 34(1), 139-146.
- Lee, D., Condrate, R., & Lacourse, W. (2000). FTIR spectral characterization of thin film coatings of oleic acid on glasses Part II Coatings on glass from different media such as water, alcohol, benzene and air. *Journal of Materials Science*, 35(19), 4961-4970.
- Lei, W., Liu, Y., Si, X., Xu, J., Du, W., & Yang, J. (2017). Synthesis and magnetic properties of octahedral Fe₃O₄ via a one-pot hydrothermal route. *Physics Letters A*, 381(4), 314-318.
- Li, C., & Chang, M. (2004). Colloidal stability of CuO nanoparticles in alkanes via oleate modifications. *Materials Letters*, 58(30), 3903-3907.
- Li, F., & Han, X. (2018). One-pot synthesis of monodisperse magnetite in aqueous mixed surfactant solutions. *In AIP Conference Proceedings*, 1944(1), 020053.

- Liu, F., Cao, P., Zhang, H., Tian, J., Xiao, C., Shen, C., . . . Gao, H. (2005). Novel nanopyramid arrays of magnetite. *Advanced materials*, 17(15), 1893-1897.
- Liu, Q., & Xu, Z. (1995). Self-assembled monolayer coatings on nanosized magnetic particles using 16-mercaptohexadecanoic acid. *Langmuir*, 11(12), 4617-4622.
- Liu, X., Kaminski, M., Guan, Y., Chen, H., Liu, H., & Rosengart, A. (2006). Preparation and characterization of hydrophobic superparamagnetic magnetite gel. *Journal of Magnetism and Magnetic Materials*, 306(2), 248-253.
- Long, G., Zhang, H., Li, D., Sabirianov, R., Zhang, Z., & Zeng, H. (2011). Magnetic anisotropy and coercivity of Fe₃Se₄ nanostructures. *Applied Physics Letters*, 99(20), 202103.
- Lopez, J., González, F., Bonilla, F., Zambrano, G., & Gomez, M. (2010). Synthesis and characterization of Fe₃O₄ magnetic nanofluid. *Revista Latinoamericana de Metalurgia y Materiales*, 30(1), 60-66.
- López-Quintela, M., & Rivas, J. (1993). Chemical reactions in microemulsions: a powerful method to obtain ultrafine particles. *Journal of Colloid and Interface Science*, 158(2), 446-451.
- Lu, A., Salabas, E., & Schüth, F. (2007). Magnetic nanoparticles: synthesis, protection, functionalization, and application. *Angewandte Chemie International Edition*, 46(8), 1222-1244.
- Lu, J., Jiao, X., Chen, D., & Li, W. (2009). Solvothermal synthesis and characterization of Fe₃O₄ and γ -Fe₂O₃ nanoplates. *The Journal of Physical Chemistry C*, 113(10), 4012-4017.
- Lysenko, S., Astafeva, S., Yakusheva, D., & Balasoiu, M. (2019). Novel parameter predicting stability of magnetic fluids for possible application in nanocomposite preparation. *Applied Surface Science*, 463, 217-226.
- Mahdavi, M., Ahmad, M., Haron, M., Namvar, F., Nadi, B., Rahman, M., & Amin, J. (2013). Synthesis, surface modification and characterisation of biocompatible

- magnetic iron oxide nanoparticles for biomedical applications. *Molecules*, 18(7), 7533-7548.
- Majidi, S., Zeinali Sehrig, F., Farkhani, S., Soleymani Goloujeh, M., & Akbarzadeh, A. (2016). Current methods for synthesis of magnetic nanoparticles. *Artificial cells, Nanomedicine, and Biotechnology*, 44(2), 722-734.
- Measuring magnetic media using a vsm* (n.d.), Retrieved December 5, 2019, from Azo Materials: <https://www.azom.com/article.aspx?ArticleID=4959>.
- Mekki, A., Holland, D., McConville, C., & Salim, M. (1996). An XPS study of iron sodium silicate glass surfaces. *Journal of Non-crystalline Solids*, 208(3), 267-276.
- Mirzaei, A., Janghorban, K., Hashemi, B., Bonyani, M., Leonardi, S., & Neri, G. (2016). Highly stable and selective ethanol sensor based on α -Fe₂O₃ nanoparticles prepared by Pechini sol–gel method. *Ceramics International*, 42(5), 6136-6144.
- Mourdikoudis, S., & Liz-Marzán, L. (2013). Oleylamine in nanoparticle synthesis. *Chemistry of Materials*, 25(9), 1465-1476.
- Muhler, M., Schlögl, R., & Ertl, G. (1992). The nature of the iron oxide-based catalyst for dehydrogenation of ethylbenzene to styrene 2. Surface chemistry of the active phase. *Journal of Catalysis*, 138(2), 413-444.
- Nakamoto, K. (1997). *Infrared and raman spectra of inorganic and coordination compounds (Part A: Theory and applications in inorganic chemistry)(Volume 1A)(Part B: Applications in coordination, organometallic, and bioinorganic chemistry)(Volume 1B)*. New York: John Wiley & Sons, Inc.
- Neri, G., Bonavita, A., Rizzo, G., Galvagno, S., Pinna, N., Neiderberger, M., . . . Siciliano, P. (2007). Towards enhanced performances in gas sensing: SnO₂ based nanocrystalline oxides application. *Sensors and Actuators B: Chemical*, 122(2), 564-571.
- Ozel, F., Kockar, H., & Karaagac, O. (2015). Growth of iron oxide nanoparticles by hydrothermal process: effect of reaction parameters on the nanoparticle size. *Journal of Superconductivity and Novel Magnetism*, 28(3), 823-829.

- Pan, B., Gao, F., & Gu, H. (2005). Dendrimer modified magnetite nanoparticles for protein immobilization. *Journal of Colloid and Interface Science*, 284(1), 1-6.
- Patterson, A. (1939). The Scherrer formula for X-ray particle size determination. *Physical Review*, 56(10), 978-982.
- Pena-Alonso, R., Rubio, F., Rubio, J., & Oteo, J. (2007). Study of the hydrolysis and condensation of γ -Aminopropyltriethoxysilane by FT-IR spectroscopy. *Journal of Materials Science*, 42(2), 595-603.
- Petcharoen, K., & Sirivat, A. (2012). Synthesis and characterization of magnetite nanoparticles via the chemical co-precipitation method. *Materials Science and Engineering: B*, 177(5), 421-427.
- Phan, C., & Nguyen, H. (2017). Role of capping agent in wet synthesis of nanoparticles. *The Journal of Physical Chemistry A*, 121(17), 3213-3219.
- Pollard, J., Shi, A., & Göklen, K. (2006). Solubility and partitioning behavior of surfactants and additives used in bioprocesses. *Journal of Chemical & Engineering Data*, 51(1), 230-236.
- Professional printers, (n.d.). Retrieved April 10,2020, from <https://images.app.goo.gl/TXeh4kQgeoaAne1C9>.
- Qu, J., Liu, G., Wang, Y., & Hong, R. (2010). Preparation of Fe₃O₄-chitosan nanoparticles used for hyperthermia. *Advanced Powder Technology*, 21(4), 461-467.
- Rajendran, M., Pullar, R., Bhattacharya, A., Das, D., Chintalapudi, S., & Majumdar, C. (2011). Magnetic properties of nanocrystalline CoFe₂O₄ powders prepared at room temperature: variation with crystallite size. *Journal of Magnetism and Magnetic Materials*, 232(1-2), 71-83.
- Ramimoghadam, D., Hussein, M., & Taufiq-Yap, Y. (2012). The effect of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) on the properties of ZnO synthesized by hydrothermal method. *International Journal of Molecular Sciences*, 13(10), 13275-13293.

- Rani, S., & Varma, G. (2015). Superparamagnetism and metamagnetic transition in Fe_3O_4 nanoparticles synthesized via co-precipitation method at different pH. *Physica B: Condensed Matter*, 472, 66-77.
- Rego, G., Mamani, J., Souza, T., Nucci, M., Silva, H., & Gamarra, L. (2019). Therapeutic evaluation of magnetic hyperthermia using Fe_3O_4 -aminosilane-coated iron oxide nanoparticles in glioblastoma animal model. *Einstein (São Paulo)*, 17(4):1-9.
- Roosendaal, S., Van Asselen, B., Elsenaar, J., Vredenberg, A., & Habraken, F. (1999). The oxidation state of Fe (100) after initial oxidation in O_2 . *Surface Science*, 442(3), 329-337.
- Roy, S., Dubenko, I., Edoorh, D., & Ali, N. (2004). Size induced variations in structural and magnetic properties of double exchange $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3-\delta$ nano-ferromagnet. *Journal of Applied Physics*, 96(2), 1202-1208.
- Ruby, C., Humbert, B., & Fusy, J. (2000). Surface and interface properties of epitaxial iron oxidethin films deposited on MgO (001) studied by XPS and Raman spectroscopy. *Surface and interface analysis: An international journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films*, 29(6), 377-380. London: John Wiley & Sons, Ltd.
- Saif, B., Wang, C., Chuan, D., & Shuang, S. (2015). Synthesis and characterization of Fe_3O_4 coated on APTES as carriers for morin-anticancer drug. *Journal of Biomaterials and Nanobiotechnology*, 6(4), 267-275.
- Saksornchai, E., Kavinchan, J., Thongtem, S., & Thongtem, T. (2018). Simple wet-chemical synthesis of superparamagnetic CTAB-modified magnetite nanoparticles using as adsorbents for anionic dye Congo red removal. *Materials Letters*, 213, 138-142.
- Salazar-Alvarez, G., Muhammed, M., & Zagorodni, A. (2006). Novel flow injection synthesis of iron oxide nanoparticles with narrow size distribution. *Chemical Engineering Science*, 61(14), 4625-4633.

- Sarkar, Z., & Sarka, F. (2011). Synthesis and magnetic properties investigations of Fe_3O_4 nanoparticles. *International Journal of Nanoscience and Nanotechnology*, 7(4), 197-200.
- Scherrer, P. (1918). Determination of the size and internal structure of colloidal particles using X-rays. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen*, 2, 98-100.
- Shah, S., Khan, U., Riaz, S., & Naseem, S. (2015). Effect of pH on iron oxide nanoparticles. *Materials Today: Proceedings*, 2(10), 5214-5219.
- Shen, L., Qiao, Y., Guo, Y., Meng, S., Yang, G., Wu, M., & Zhao, J. (2014). Facile co-precipitation synthesis of shape-controlled magnetite nanoparticles. *Ceramics International*, 40(1), 1519-1524.
- Shen, X., Fang, X., Zhou, Y., & Liang, H. (2004). Synthesis and characterization of 3-aminopropyltriethoxysilane-modified superparamagnetic magnetite nanoparticles. *Chemistry Letters*, 33(11), 1468-1469.
- Shi, D., Cho, H., Chen, Y., Xu, H., Gu, H., Lian, J., . . . Ewing, R. (2009). Fluorescent polystyrene- Fe_3O_4 composite nanospheres for in vivo imaging and hyperthermia. *Advanced Materials*, 21(21), 2170-2173.
- Shukla, N., Liu, C., Jones, P., & Weller, D. (2003). FTIR study of surfactant bonding to FePt nanoparticles. *Journal of Magnetism and Magnetic Materials*, 266(1-2), 178-184.
- Si, S., Li, C., Wang, X., Yu, D., Peng, Q., & Li, Y. (2005). Magnetic monodisperse Fe_3O_4 nanoparticles. *Crystal Growth & Design*, 5(2), 391-393.
- Silva, V., Andrade, P., Silva, M., Valladares, L., & Aguiar, J. (2013). Synthesis and characterization of Fe_3O_4 nanoparticles coated with fucan polysaccharides. *Journal of Magnetism and Magnetic Materials*, 343, 138-143.
- Sinclair, R., McKay, A., Myers, G., & Jones, R. (1952). The infrared absorption spectra of unsaturated fatty acids and esters. *Journal of the American Chemical Society*, 74(10), 2578-2585.

- Storozhuk, L., & Iukhymenko, N. (2018). Synthesis of iron oxide nanoparticles modified with silanes and their heating ability in alternating magnetic fields. *In Advanced Nanotechnologies for Detection and Defence against CBRN Agents*, 299-306. Berlin: Springer.
- Storozhuk, L., & Iukhymenko, N. (2019). Iron oxide nanoparticles modified with silanes for hyperthermia applications. *Applied Nanoscience*, 9(5), 889-898.
- Sundar, S., Mariappan, R., & Piraman, S. (2014). Synthesis and characterization of amine modified magnetite nanoparticles as carriers of curcumin-anticancer drug. *Powder Technology*, 266, 321-328.
- Taniguchi, T., Nakagawa, K., Watanabe, T., Matsushita, N., & Yoshimura, M. (2009). Hydrothermal growth of fatty acid stabilized iron oxide nanocrystals. *The Journal of Physical Chemistry C*, 113(3), 839-843.
- Tao, K., Dou, H., & Sun, K. (2008). Interfacial coprecipitation to prepare magnetite nanoparticles: Concentration and temperature dependence. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 320(1-3), 115-122.
- Thistlethwaite, P., & Hook, M. (2000). Diffuse reflectance Fourier transform infrared study of the adsorption of oleate/oleic acid onto titania. *Langmuir*, 16(11), 4993-4998.
- Toner, (n.d.). Retrieved April 10,2020 from <https://images.app.goo.gl/xgQDL4ACqmCEXpxq5>.
- Toner cartridge, (n.d.). Retrieved April 10,2020, from <https://images.app.goo.gl/ZREiEBesGrY9NZdo7>.
- Van de Waterbeemd, M., Sen, T., Biagini, S., & Bruce, I. (2010). Surface functionalisation of magnetic nanoparticles: quantification of surface to bulk amine density. *Micro & Nano Letters*, 5(5), 282-285.
- Vega-Chacón, J., Picasso, G., Avilés-Félix, L., & Jafelicci Jr, M. (2016). Influence of synthesis experimental parameters on the formation of magnetite nanoparticles

- prepared by polyol method. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 7(1), 015014.
- Vogel-Weill, C., & Gruger, A. (n.d.). Etude de la conformation des acides n-nonanoïque, Z et E-9 octadécénoïques à 90 K par spectrométries infrarouge et Raman II. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 52(13), 1737-1755.
- Waldron, R. (1955). Infrared spectra of ferrites. *Physical Review*, 99(6), 1727-1735.
- Wang, J., Chen, Q., Zeng, C., & Hou, B. (2004). Magnetic-field-induced growth of single-crystalline Fe₃O₄ nanowires. *Advanced Materials*, 16(2), 137-140.
- Wang, J., Sun, J., Sun, Q., & Chen, Q. (2003). One-step hydrothermal process to prepare highly crystalline Fe₃O₄ nanoparticles with improved magnetic properties. *Materials Research Bulletin*, 38(7), 1113-1118.
- Wang, Y., Cheng, R., Wen, Z., & Zhao, L. (2012). Facile preparation of Fe₃O₄ nanoparticles with cetyltrimethylammonium bromide (CTAB) assistant and a study of its adsorption capacity. *Chemical Engineering Journal*, 181, 823-827.
- Wei, Y. (2020). Synthesis of Fe₃O₄ nanoparticles and their magnetic properties. *arXiv preprint arXiv*, 2001.06583.
- Wei, Y., Han, B., Hu, X., Lin, Y., Wang, X., & Deng, X. (2012). Synthesis of Fe₃O₄ nanoparticles and their magnetic properties. *Procedia Engineering*, 27, 632-637.
- Willis, A., Turro, N., & O'Brien, S. (2005). Spectroscopic characterization of the surface of iron oxide nanocrystals. *Chemistry of Materials*, 17(24), 5970-5975.
- Xu, J., Yang, H., Fu, W., Du, K., Sui, Y., Chen, J., . . . Zou, G. (2007). Preparation and magnetic properties of magnetite nanoparticles by sol-gel method. *Journal of Magnetism and magnetic Materials*, 309(2), 307-311.
- Xu, L., Wang, L., Shen, Y., Ding, Y., & Cai, Z. (2015). Preparation of hexadecyltrimethoxysilane-modified silica nanocomposite hydrosol and superhydrophobic cotton coating. *Fibers and Polymers*, 16(5), 1082-1091.

- Xu, Z., Shen, C., Tian, Y., Shi, X., & Gao, H. (2010). Organic phase synthesis of monodisperse iron oxide nanocrystals using iron chloride as precursor. *Nanoscale*, 2(6), 1027-1032.
- Yamashita, T., & Hayes, P. (2006). Effect of curve fitting parameters on quantitative analysis of Fe_{0.94}O and Fe₂O₃ using XPS. *Journal of Electron Spectroscopy and Related Phenomena*, 152(1-2), 6-11.
- Yamashita, T., & Hayes, P. (2008). Analysis of XPS spectra of Fe²⁺ and Fe³⁺ ions in oxide materials. *Applied Surface Science*, 254(8), 2441-2449.
- Yang, J., Zhang, Z., Men, X., Xu, X., & Zhu, X. (2011). A simple approach to fabricate superoleophobic coatings. *New Journal of Chemistry*, 35(3), 576-580.
- Yoon, K., Kotsmar, C., Ingram, D., Huh, C., Bryant, S., Milner, T., & Johnston, K. (2011). Stabilization of superparamagnetic iron oxide nanoclusters in concentrated brine with cross-linked polymer shells. *Langmuir*, 27(17), 10962-10969.
- Yoshida, W., Castro, R., Jou, J., & Cohen, Y. (2001). Multilayer alkoxy silane silylation of oxide surfaces. *Langmuir*, 17(19), 5882-5888.
- Zhang, D., Zhang, X., Ni, X., Song, J., & Zheng, H. (2007). Fabrication and characterization of Fe₃O₄ octahedrons via an EDTA-assisted route. *Crystal Growth & Design*, 7(10), 2117-2119.
- Zhang, J., & Misra, R. (2007). Magnetic drug-targeting carrier encapsulated with thermosensitive smart polymer: core-shell nanoparticle carrier and drug release response. *Acta Biomaterialia*, 3(6), 838-850.
- Zhang, W., Jia, S., Wu, S., Zhang, S., & Liu, Y. (2013). Effects of alkaline precipitating agents on synthesis of magnetite nanomaterials by hydrothermal D-glucose method. *Journal of Nanoparticle Research*, 15(6), 1701-1707.
- Zhang, X., Niu, H., Pan, Y., Shi, Y., & Cai, Y. (2010). Chitosan-coated octadecyl-functionalized magnetite nanoparticles: preparation and application in extraction

of trace pollutants from environmental water samples. *Analytical Chemistry*, 82(6), 2363-2371.

Zhen, G., Muir, B., Moffat, B., Harbour, P., Murray, K., Moubaraki, B., ... (2011). Comparative study of the magnetic behavior of spherical and cubic superparamagnetic iron oxide nanoparticles. *The Journal of Physical Chemistry C*, 115(2), 327-334.

Zhu, J., Liu, B., Li, L., Zeng, Z., Zhao, W., Wang, G., & Guan, X. (2016). Simple and green fabrication of a superhydrophobic surface by one-step immersion for continuous oil/water separation. *The Journal of Physical Chemistry A*, 120(28), 5617-5623.