

UNIVERSITY OF BAHRAIN

College of Science

Department of Physics



Characterizations and Heavy Metals Removal by Using Magnetic Nanoparticles (MNPs) from Wastewater

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Degree in Applied Physics**

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DECLARATION

I declare that the thesis entitled ‘ ‘ **Characterization and Heavy Metals Removal by Using Magnetic Nanoparticles (MNPs) from Wastewater** ‘ ‘ submitted by me to the University of Bahrain for the degree of Master of applied physics is the record of research work carried out by me independently during the period 2013-2018 under the guidance of **Dr. Mohamed Salim Akhter** and has not formed the basis for the award of any degree, diploma, associateship, fellowship, titles in this or any other University or other similar institution of higher learning.

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ABSTRACT

Spinel ferrite MFe_2O_4 , ($M=Co, Ni, Cu$ and Zn) nanoparticles are prepared by Microwave Combustion Method (MCM). For as-prepared, Rietveld analysis of X-ray diffraction patterns indicates the formation of single phase for $NiFe_2O_4$ and $ZnFe_2O_4$, while new ($\alpha-Fe_2O_3$ and CuO) phases precipitate for $CoFe_2O_4$ and $CuFe_2O_4$, respectively, meanwhile the crystallite size ranges between 40-51 nm. After annealing, a single phase is obtained for all spinel ferrite system, $CuFe_2O_4$ transforms from tetragonal structure to cubic structure after annealing. Magnetisation-field (M-H) curves reveal ferromagnetic order for $CoFe_2O_4$, $NiFe_2O_4$ and $CuFe_2O_4$, while a superparamagnetic behaviour is observed for $ZnFe_2O_4$, and the magnetic properties (saturation magnetization, remanence and coercivity) are found to slightly change after annealing, except $CuFe_2O_4$, due to phase transformation from tetragonal to cubic and grain growth; both saturation magnetisation and remanence decrease from 25.97 to 1.685 emu/g and 13.93 to 2.635×10^{-3} emu/g, respectively. Interestingly, after annealing $CuFe_2O_4$ shows a superparamagnetic behaviour. SEM observations show particles with undefined shape and broad particle size distribution. It can be concluded that MCM is very suitable to prepare method to obtain single phase of $NiFe_2O_4$ and $ZnFe_2O_4$. The obtained spinel ferrite nanopowders as prepared by MCM and after annealing are used for up take tests toxic metal ions removal from wastewater including Cadmium (Cd^{2+}) and lead (Pb^{2+}) were investigated. The adsorption was carried out in batch mode by adding 10, 20 and 30 mg of MNPs to 25 ppm solutions of Cd^{2+} and Pb^{2+} ions in 50 ml Erlenmeyer flask at pH equal 2. The maximum adsorption capacities are found for 10 mg compared to higher concentrations; i.e. 20 and 30 mg. the highest amount of 30 mg has the lowest adsorption capacities. It is observed that the adsorption capacity is greater for Cd^{2+} than Pb^{2+} ; 69.4 and 47.1 mg/g, respectively. Then lower amount of MNPs is opted to investigate, the value of adsorption capacities almost double for Cd^{2+} (120-1220 mg/g compared to 10 mg (52-60) mg/g, while no considerable effect has been noticed for Pb^{2+} . Moreover, the adsorption capacity is influenced by pH; a basic media is found to be better than acidic for both Cd^{2+} and Pb^{2+} , but Pb^{2+} shows a much higher capacity (almost double).

ORGANISATION OF THE THESIS

The Thesis contains 7 chapters:

- 1. Introduction:** a brief introduction of Nanotechnology and its applications.
- 2. History and Background:** covers different synthesis methods of MNPs, properties and applications, as well as literature review.
- 3. Experimental Procedure:** includes synthesis of MNPs and their characterizations using various techniques such as XRD, VSM and SEM/EDS.
- 4. Removal of Heavy Metals:** investigation of the adsorption properties of MNPs.
- 5. Analysis:** covers and describes some empirical models used to determine thermodynamic/kinetics parameters of heavy metal ions adsorption.
- 6. Results and Discussion:** analysis and discussion of the obtained results.
- 7. Summary and Conclusion:** presents a summary and concluding remarks of the obtained results, as well as giving some future recommendations

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LIST OF ABBREVIATIONS

a.u.	-	Arbitrary units
AAS	-	Atomic absorption spectrophotometer
EDX	-	Electron dispersive x-ray
FESEM	-	FEI Sirion gun Scanning Microscope
MCM	-	Microwave combustion method
MNPs	-	Magnetic nanoparticles
MRI	-	Magnetic resonance imaging
NPs	-	Nanoparticles
ppm	-	parts per million
SEM	-	Scanning electronic microscopy
XRD	-	X-ray diffractometer
VSM	-	Vibrating scanning microscope

Chapter 1

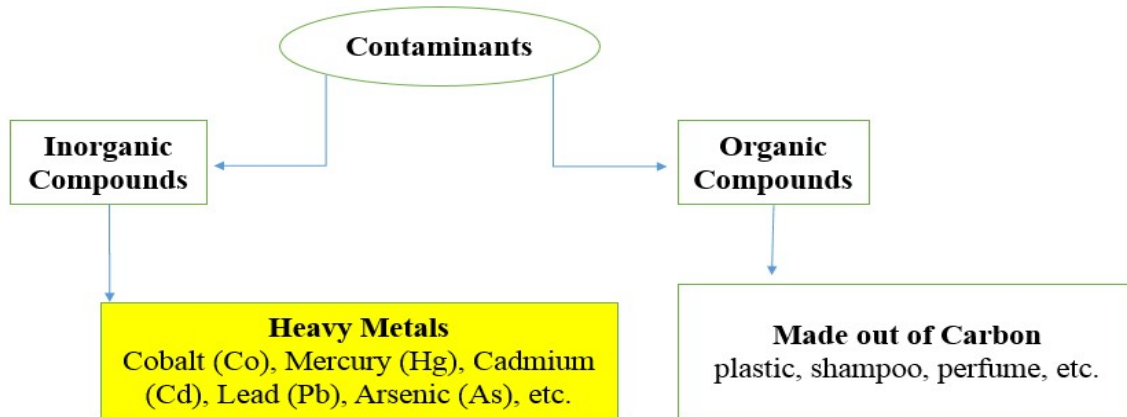
INTRODUCTION

1.1 Nanotechnology and Spinel Ferrite

Nanotechnology is one of the greatest interest nowadays; it has contributed to immense improvement in many fields including manufacturing, electronics, telecommunications and medical (Qu et al., 2013). Nanotechnology includes the discovery of new materials and fabrication of devices in the range of 1 to 100 nm. The materials at the nanoscale show unique and enhanced properties compared to their bulk-sized counterparts (Xu et al., 2012). This can be attributed to size and shape effect, structural defects, quantum confinement and Surface Plasmonic Resonance (SPR) effect. Nanotechnology offers numerous methods classified as top-down or bottom-up to fabricate nanostructures with various morphologies and size (Pitaksuteepong et al., 2015). Therefore, nanotechnology is an eco-friendly and cost-effective approach for the development of nanostructured materials with high adsorption capacity for the removal of heavy metal ions from wastewater (Barakat et al., 2015).

Water scarcity and water pollution are considered as two major problems facing the world in the 21st Century. Industrialization, urbanization, expansion of population and environmental changes are reported to be the main causes for wastewater contamination (Wang et al., 2013), which increases day by day. Among contaminants are organic and inorganic compounds as well as heavy metals as shown in Figure 1.1 (Tang et al., 2014).

Types of contaminants in wastewater



***** Heavy metals are the most dangerous contaminants *****

Figure (1.1)

Types of contaminants in wastewater

It has been reported that heavy metals are toxic even at very low concentration, hence may cause different types of cancers to humans, asthma, lung disease, allergy, damage the central nervous system and brain, as shown in Figure 1.2 (Mahmoud et al., 2013; Gautam et al., 2014), etc. Among the heavy metals are Cobalt (Co), Mercury (Hg), Cadmium (Cd), Lead (Pb), Arsenic (As), etc.

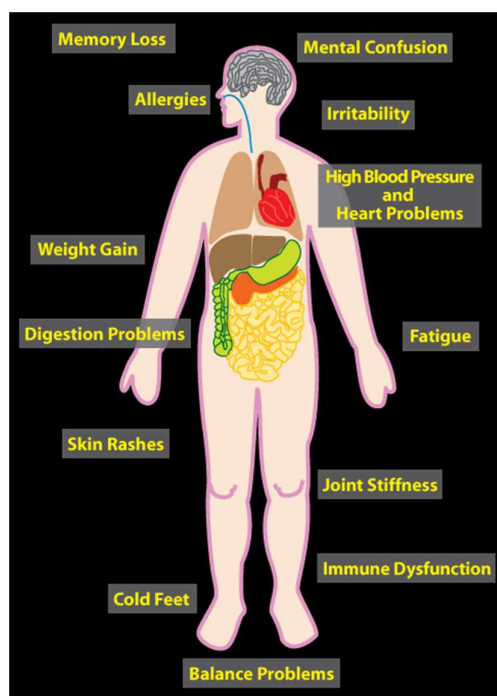


Figure (1.2)
Heavy Metal Poisoning

1.1.1 Spinel Ferrites Phase (SFs) and Properties

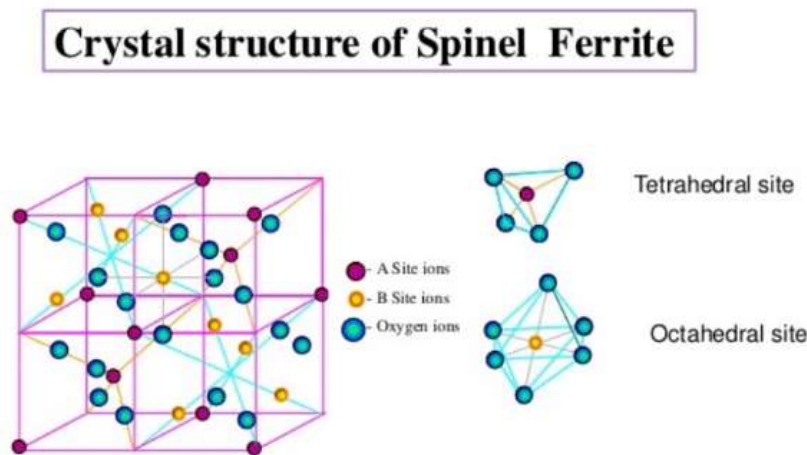


Figure (1.3)
Spinel Ferrites Crystal Structure

Recently, research has been developed to Spinel Ferrites (SFs) due to their potential extensive applications. In particular, magnetic SFs– Nanoparticles

(NPs) exhibit unique properties compared to their bulk counterparts. For example, the magnetic properties are drastically changed at the nanoscale range, because each particle can behave as a single domain. In addition, NPs have a very large surface area when the size is reduced to the nanoscale (Yadav et al., 2015).

SFs represent a special class of oxides group with the general formula unit AB_2O_4 , where A refers to the metal (Zn, Mg, Co, Mn, etc.) and B (Fe, Cu, Al, etc.) (Bhowmik et al., 2015).

In this project, iron-based oxides have been adopted with different transition metal ions, (e.g. Co^{2+} , Cu^{2+} and Mn^{2+}) to get special properties as fine tuning of the catalytic/redox activity, electrical and magnetic (Cunha et al., 2015). SFs have a great potential in adsorption, because they have an excellent redox pair based on Fe^{2+}/Fe^{3+} . Moreover, SFs is used in the adsorption techniques, because they have many advantages such as low-cost, excellent control of the structure, thermal stability (compared to enzyme) and they have important magnetic properties, so they can be used to remove the heavy metal ions from the solution by a simple magnetic process (Cunha et al., 2015).

The properties of SFs have been found to strongly depend on the preparation method. For example, $NiFe_2O_4$ prepared by sol-gel method showed a crystallite size ~ 27 nm with a saturation magnetization of 31 emu/g where as $NiFe_2O_4$ prepared by hydrothermal method showed a smaller crystallite size ~ 9 nm with a relatively higher saturation magnetization of 46 emu/g (Elshahawy et al., 2015).

1.1.2 Crystal Structure of SFs

The crystal structure of SFs is described as a cubic close-packed arrangement of oxygen ions A^{2+} (e.g. Co^{2+}) and B^{3+} (e.g. Fe^{3+}) as two different crystallographic sites: The tetrahedral (A) and octahedral (B) are occupied by metal ions and oxygen (O) ions occupy the Face Central Cube (FCC) positions of the lattice structure (Bhowmik et al., 2015);(Sundararajan et al., 2015), A

tetrahedral site lies in the centre of a 4-atom cluster and an octahedral site is a space at the centre of a cluster of 6- atoms within the crystal as shown in Figure 1.3. A and B sites are occupied by metal cations, depending on their radii, the electrostatic energies of the lattice and the matching of the electronic configuration with the surrounding oxygen (Thi et al., 2015) there play an important role in modifying the physical properties (Elshahawy et al., 2015). As magnetic properties are greatly influenced by grain size, cation distribution and surface of NPs (Yadv et al., 2015).

There are three ideal structures referring to the crystallographic sites: normal, inverse and mixed spinel structures (Sundararajan et al., 2015). In normal spinels, the ions of ferrite A Fe_2O_4 are located only on tetrahedral (8a) sites and Fe ions are located on the octahedral (16d) sites within the $\text{Fd}\bar{3}\text{m}$ space group, where a and d are sites in crystal lattice. In an inverse spinel, half of the Fe ions are located on tetrahedral sites and the rest of Fe ions in addition to A ions occupy the octahedral sites. Mixed spinel is formed when cation distribution is mixed (Yadv et al., 2015). Some examples of spinel ferrite are MgFe_2O_4 (Mahmoud et al., 2013), ZnFe_2O_4 (Qu et al., 2013), NiFe_2O_4 (Xu et al., 2012), etc.

1.1.3 Applications of SFs

SFs are very important group of magnetic materials that offer wide range of application due to their chemical, structural, mechanical, electrical, optical and magnetic properties (Kumar et al., 2015). Therefore, SFs have been used in biotechnology, electromagnetic (Ben Ali et al., 2016), electric, electronic devices such as Mn-Zn ferrite (Ding et al., 2014), magnetic high-density storage, magnetic media and ferrofluids (Gao et al., 2015).

1.2 Problem statement

To remove heavy metal ions from aqueous solution by using Magnetic Nanoparticles (MNPs).

1.3 Objectives

- 1- Understand Nanotechnology to solve one of the most challenging worldwide problems; i.e. wastewater.
- 2- Develop new nanomaterials with specific properties for the removal of heavy metal ions.
- 3- Perform experiments by using some advanced techniques.
- 4- Carry out some measurements on heavy metal ions removal and end up with some recommendations.

1.4 Justification of The problem

Nowadays, water pollution has been identified as a crucial and very challenging problem for all the world. The pollution of water usually occurs through various sources and lead to the accumulation of important amounts of contaminants. Heavy metals are considered among the most dangerous contaminants, as they present some environmental and human health concerns. For example, some typical effects are:

- (i) Co decreases the function of pulmonary tissue and may cause asthma and lung disease;
- (ii) Hg causes cancer and damages the central nervous system and brain (Gautam et al., 2014).

In the last two decades, nanotechnology promises an immense improvement in electronics, telecommunication, health and even environmental applications (Xu et al., 2012). MNPs have been found as excellent adsorbents, because they have high specific surface area, high surface chemistry and numerous associated sorption sites (Gautam et al., 2014). Many researches have been devoted to the removal of heavy metals from wastewater by developing new cheap nanomaterials with enhanced properties (Tang et al., 2014; Qu et al., 2013; Khezami et al., 2015).

1.5 Glossary

Amorphous: lacking in long range atomic order.

Crystal: a solid composed of atom, ions, or molecules arranged in a pattern that is repeated in three dimensions.

Crystal structure: a regular three-dimension pattern of atoms or ions in space.

Diamagnetism: a weak, negative, repulsive reaction of material to an applied magnetic field; a diamagnetic material has a small negative magnetic susceptibility.

Ferromagnetic materials: One that is capable of being highly magnetized. Elemental iron, cobalt, and nickel are ferromagnetic materials.

Grain: a single crystal in a polycrystalline aggregate.

Magnetization field H: the magnetic field produced by an external applied magnetic field or the magnetic field produced by a current passing through a conducting wire or coil of wire.

Magnetization M: a measure of the increase in magnetic flux due to the insertion of a given material into a magnetic field of strength H. In SI units the magnetization is equal to the permeability of a vacuum (μ_0) times the magnetization, or $\mu_0 M$. ($\mu_0 = 4(3.14) \times 10^{-4}$ T. m/A)

Paramagnetism: a weak, positive, attractive reaction of a material to an applied magnetic field; a paramagnetic material has a small positive magnetic susceptibility.

Materials: substance of which something is composed or made.

Nanotechnology: engineering and device fabrication conducted at the nanoscale (1 to 100 nm; nm = nanometer).

Nanoscience: discover and study of extremely small particles (1 to 100 nm)

Nanoparticles: ultra-small objects with dimensions in the range 1-100 nm, having unique/enhanced properties compared to their bulk properties.

Space lattice: a three dimensional array of points each of which has identical surroundings.

Lattice point: one point in an array in which all points have identical surroundings.

Unit cell: a convenient repeating unit of a space lattice. The axial length and axial angles are the lattice constants of the unit cell.

Wastewater: a term applied to any type of water that has been utilized in some capacity that negatively impacts the quality of the water. Common examples of wastewater include water that is discharged from households, office and retail buildings, and manufacturing plants. Wastewater may also refer to any water that is utilized in an agricultural facility and is no longer considered suitable and safe for human consumption.

Spinel Ferrites Phase (SFs): a family of oxides with a general formula MM'_2O_4 ($M=Zn, Mg, Co, Mn, \text{ etc.}$) and ($M'=Fe, Cu, Al, \text{ etc.}$) having a cubic crystal structure.

Chapter 2

Background and History

2.1 Theoretical Framework

2.1.1 Application and Magnetic Properties of MFe_2O_4

MNPs show unique enhanced properties, including high surface-to-volume ratio (surface area), numerous associated sorption sites, low modification temperature, low toxicity and superparamagnetic behaviour in some cases. Therefore, MNPs are considered as potential candidates for many applications including biological, environmental and medical fields; drug delivery; contrast agent for Magnetic Resonance Imaging (MRI) and separation, etc. (Gautam et al., 2014; Lemine et al., 2014).

MNPs are used for the adsorption of heavy metal ions from aqueous solution, because they offer various advantages such as high adsorption capacity, fast kinetics and selective sorption toward heavy metals in aqueous solution (Lemine et al., 2014). MNPs enable the separation of contaminate from a solution by using an external magnetic field.

MNPs were used for this purpose because the adsorbed heavy metals can be easily recovered by utilizing magnetic separation. However, it has been reported that magnetic (Fe_3O_4) NPs are very much susceptible to air oxidation and are easily aggregated in aqueous systems, leading to an important reduction of the saturation magnetization and adsorption capacity for metals. Hence, reducing particle size from bulk to the nanoscale can improve the adsorption capacity by several orders of magnitude (Andrew et al., 2014).

The most commonly used MNPs include magnetite (Fe_3O_4) (Gautam et al., 2014; Lemine et al., 2014), hematite ($\alpha\text{-Fe}_2\text{O}_3$) (Lemine et al., 2014), goethite ($\alpha\text{-FeO(OH)}$) (Khezami et al., 2015), and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (Gautam et al., 2014; Lemine et al., 2014).

Additionally, among MNPs are pure metals (such as: Fe and Co) and spinel-type ferrites (based on: AB_2O_4 , where A= Zn, Mg, Co, Mn, etc. B = Fe,

Cu, Al, etc.), (Gautam et al., 2014; Khezami et al., 2015), such as MgFe_2O_4 (Mahmoud et al., 2013), ZnFe_2O_4 (Qu et al., 2013), NiFe_2O_4 (Xu et al., 2012), etc.

2.1.2 Adsorption Mechanism

Several techniques have been developed and already reported in the literature for the removal of heavy metals from aqueous solution; including ion exchange, membrane filtration, reduction, activated carbon, precipitation, coagulation and adsorption (Gautam, R. K. et al, 2014).

2.1.2.1 Adsorption Mechanism

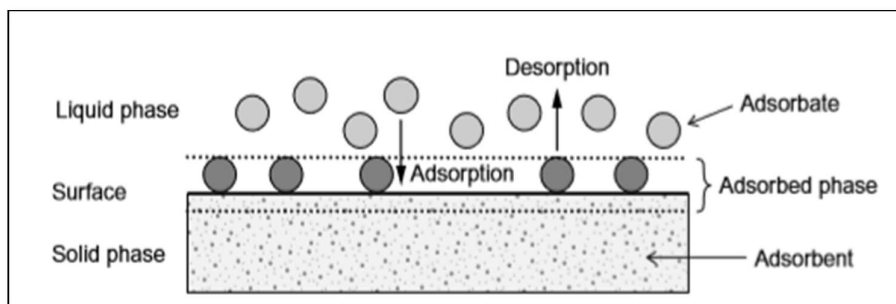


Figure (2.1)

Basic concept of adsorption mechanism

In particular, adsorption has been adopted in this project, because it is used in wastewater treatment. Extensive research efforts have been devoted to adsorption because of the advantages it offers compared to other conventional methods such as simplicity, low cost and effectiveness for the removal of heavy metals from aqueous solution by using MNPs (Mahmoud et al., 2013; Lemine et al., 2014).

Adsorption is defined as an enrichment of chemical species from a fluid phase on the surface of a liquid or a solid as shown in Figure 2.1. Thereby, molecules or ions are removed from the aqueous solution by adsorption onto solid

surfaces. Solid surfaces are active energy-rich sites that are able to interact with solutes in the adjacent aqueous phase.

By changing the properties of the liquid phase (e.g. concentration of heavy metal ions, temperature, pH), the adsorbed species can be released from the surface and transferred back into the liquid phase. This operation is called desorption. The adsorption process depends strongly on the above parameters on solution uptake and its kinetics (Khezami et al., 2015). The removal of heavy metal ions depend on the nature of useful nanomaterials, so the amount of heavy metal ions removed from aqueous solutions are found to vary considerably in the literature as shown in Table (2.1).

Table (2.1)**Literature survey about NMs used for aqueous solutions**

Nanomaterials	Heavy metal ions (mg/g)	Reference
Ni doped α - Fe_2O_3	Cd^{2+} (65.46mg/g), Co^{2+} (43.29mg/g) and Ni^{2+} (42mg/g).	(Lemine et al.,2014)
Cu doped Fe_3O_4	As^{3+} (36.4 mg/g).	(Thi et al.,2015)
Goethite (α - $FeO(OH)$)	Cd^{2+} (167mg/g).	(Khezami et al., 2015)
Maghemite (γ - Fe_2O_3)	Pb^{2+} (10.55mg/g) and Zn^{2+} (4.79 mg/g).	(Ahmadi et al.,2014)
Porous magntic Silica ($Fe_3O_4@nSiO_2@mSiO_2$)	Pb^{2+} (47.61 mg/g) and Cd^{2+} (32.25 mg/g).	(Barakat et al.,2015)
Amino–modified Fe_2O_3	Cu^{2+} (12.43mg/g) and Cr^{6+} (11.24 mg/g).	(Xu et al., 2012)
Montmorillonite supported MNPs $Al_2O_3;SiO_2$	Cr^{6+} (15.3 mg/g).	(Xu et al., 2012)
γ -PGA/ Fe_3O_4	Cr^{3+} (24.60 mg/g).	(Jing et al., 2013)
Aminated polyacrylonitrile (APAN) nanofiber mat	Ag^{1+} (53.48mg/g) and Cu^{2+} (30.40 mg/g).	(Kampalanonwat et al., 2014)

2.1.2.2 Adsorption Mechanism Process

The different mechanisms involved during adsorption of heavy metal ions are namely as shown in Figure (2.2):

- (i) The specific salt or nitrate (source of heavy metal ions) is dissolved in distilled water resulting in a solution where ions are found.
- (ii) MNPs are added to the solution.

- (iii) The obtained solution will be subjected to stirring for a certain period of time.
- (iv) MNPS are separated from solution by using an external magnet.
- (v) The solution is now cleaned from heavy metal ions that are adsorbed onto the surface of MNPs.

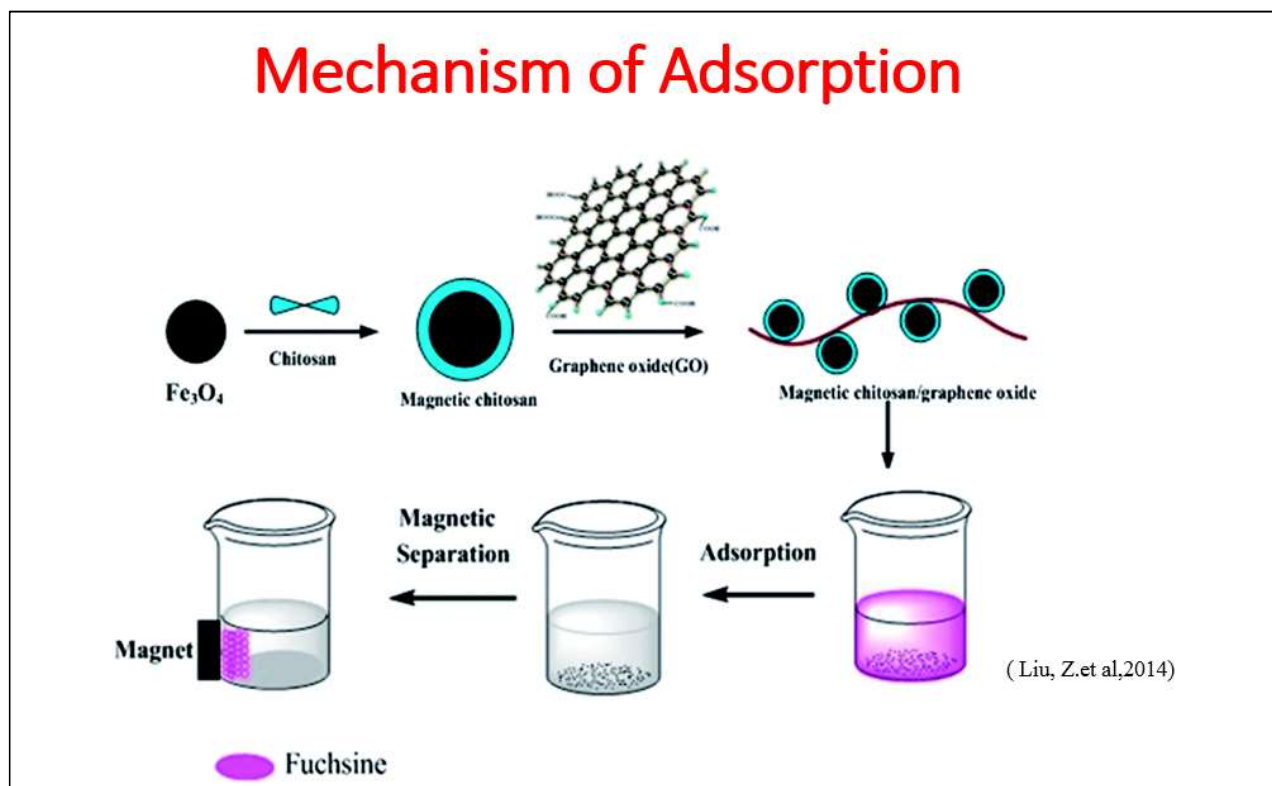


Figure (2.2)

The mechanism of adsorption from aqueous solutions

2.1.3 Kinetics of Adsorption

The sorption of heavy metal ions have been correlated by various isothermal models. So far, Langmuir and Freundlich isotherms are the best models used to better describe the equilibrium isotherm data. The Langmuir mode was derived to describe monolayer adsorption of an adsorbate on a homogenous flat surface of an adsorbent and each adsorptive site can be only occupied once in a one on–

one manner and expressed by the following mathematical equation (Kampalanonwat et al., 2014 ; Khezami et al., 2015):

$$\frac{C_e}{q_e} = \frac{1}{Q_o} C_e + \frac{1}{Q_o \cdot b} \quad (1)$$

where C_e is the equilibrium concentration of metal ions in the testing solution (mg/L), q_e is the amount of metal ions adsorbed per unit mass of (mg/g), and Q_o is the solid phase concentration corresponding to the complete monolayer coverage of adsorption site and b is the constant related to the free energy of adsorption, where $1/b$ equal k_L represents the Langmuir constant related to the affinity of binding sites (mg/L), (Kampalanonwat et al., 2014).

The Freundlich model is used to describe the adsorption of an adsorbate on a heterogeneous surface of an adsorbent and expressed by the following mathematical equation (Kampalanonwat et al., 2014);

$$\ln(q_e) = \frac{1}{n} \ln(C_e) + \ln(k) \quad (2)$$

Where k and n are constant that can be related to the strength of adsorptive bond and the bond distribution, respectively (El Boujaady et al., 2014; Khezami et al., 2015). The values of k and n can be obtained from the intercept and the slope of the linear plot of $\ln(q_e)$ vs. $\ln(C_e)$. The constant k can be defined as a sorption coefficient which represents the quantity of adsorbed metal ions for a unit equilibrium concentration (i.e. $C_e=1$). The slope $1/n$ is a measure of the sorption intensity or surface heterogeneity (El Boujaady et al., 2014).

2.2 Previous Studies (Literature review)

In this section, we will present the results reported in the literature.

(Lemine et al., 2014) studied the effect of Ni-doping on heavy metal ions (Cd^{2+} , Co^{2+} , Ni^{2+} and Cr^{6+}) up take by using hematite $\alpha\text{-Fe}_2\text{O}_3$ prepared by mechanical milling. After milling of $\alpha\text{-Fe}_2\text{O}_3$ with different concentration of Ni

for 5 h, a new phase NiFe_2O_4 was formed. The crystallite size of phase composition would increase for the new phase and decrease for powder mixtures by increasing concentration % of Ni. The diffraction peaks of $\alpha\text{-Fe}_2\text{O}_3$ became border and their relative intensity decreased with increasing % of Ni, due to particle size reduction and accumulation of microstrain during mechanical milling. The main peak position of $\alpha\text{-Fe}_2\text{O}_3$ shifted to lower angles, indicating a volume expansion of the lattice. The lattice parameters (a and c) of hematite phase increased with increasing Ni concentration, because microstrain induced by solid state reaction due to mechanical milling and formation of nickel ferrite phase. Hysteresis M-H curves indicated a ferromagnetic behaviour. While, the magnetic parameters varied with Ni content; remanence and saturation magnetization increased by increasing % of Ni, so Ni induced strong magnetic contribution to the $\alpha\text{-Fe}_2\text{O}_3$. The adsorption of heavy metal ions showed high efficiency sorbent for Cd^{2+} , Co^{2+} , Ni^{2+} and Cr^{6+} at pH 6.5 at 15% of Ni: 65.462, 43.296, 42.011 and 4.666 mg/g, respectively. It was noticed that Cr^{6+} showed low sorbent and this indicated was at pH 6.5, while it gave better adsorption at much lower pH in the range 2-3.

(Jing et al., 2013) studied the effect of poly (γ -glutamic acid)-coated Fe_3O_4 MNPs ($\gamma\text{-PGA/Fe}_3\text{O}_4$ NPs) fabricated by using the co-precipitation method. SEM observation indicated that Fe_3O_4 and $\gamma\text{-PGA/Fe}_3\text{O}_4$ NPs are roughly spherical, with an average particle size 62.0 nm for Fe_3O_4 with a surface area around $76.83 \text{ m}^2\cdot\text{g}^{-1}$, where $\gamma\text{-PGA/Fe}_3\text{O}_4$ has lower particle size of 52.4 nm and higher surface area around $88.41 \text{ m}^2\cdot\text{g}^{-1}$. $\gamma\text{-PGA}$, Fe_3O_4 and ($\gamma\text{-PGA/Fe}_3\text{O}_4$ MNPs), showed effective removal [Cr^{3+} , Cu^{2+} , Pb^{2+} and Ni^{2+}] from aqueous solutions with highest adsorption efficiency obtained for Fe_3O_4 coated by poly (γ -glutamic acid): removal efficiency increased from 33.79 to 77.17%, 46.31 to 99.63%, 59.54 to 99.24% and 99.57 to 99.63 % for Ni^{2+} , Cu^{2+} , Cr^{3+} and Pb^{2+} , respectively. Also, this study showed a good correlation between the amounts of $\gamma\text{-PGA/Fe}_3\text{O}_4$ NPs

with the removal efficiency of heavy metal ions. Reaction time, initial concentration of NPs and pH were found to have a great influence on adsorption rate and this was verified by the increase of the removal rate from 7.19 to 99.66% for Cr^{3+} when pH increased from 2 to 6.

(Thi et al., 2015) studied Mn and Cu doped Fe_3O_4 as potential candidate for the adsorption of As^{3+} by changing concentration of doping and pH in aqueous solutions. Mn and Cu doped Fe_3O_4 NPs were prepared by a chemical method. XRD analysis indicated the formation of single cubic spinel phase where the particle size was formed to vary slightly; 14.49 to 11.78 nm due to doping for $\text{Fe}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ and $\text{Fe}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x=0, 0.10, 0.15$). SEM and TEM observation was an important tendency for agglomeration, while the particle size varied in the range 9.4 to 18.1 nm. M-H curves revealed a superparamagnetic behaviour. Increasing Cu or Mn concentrations from $x=0.0$ to 0.15, the saturation magnetic moments decreased from 65.9 to 53.2 emu/g for $\text{Fe}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ system and from 65.9 to 61.5 emu/g for $\text{Fe}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ system. The adsorption capacity toward As^{3+} of Mn-doped Fe_3O_4 NPs were found lower than Cu-doped Fe_3O_4 . The effect of pH (1, 3, 5, 7, 11 and 14) gave better adsorption in the range 5- 9, then after pH 12 the adsorption capacity decreased; at pH 14 no adsorption occurred. This study showed that pH is an important factor affecting the adsorption. Table (2.2) illustrate the effect of pH in adsorption capacity for different composition.

Table (2.2)**Ions are selectivity adsorption at certain pH**

Composition	Select adsorption ions	pH
Ni doped Fe ₂ O ₃	Cd^{2+} Co^{2+} Ni^{2+}	5-8
	Cr^{3+}	2-3
γ -PGA/Fe ₃ O ₄ MNPs	Cr^{3+} Cu^{2+} Pb^{2+} Ni^{2+}	>6
Fe ₃ O ₄ @nSiO ₂ @mSiO ₂	Pb^{2+} Cd^{2+}	>5.5
Goethite	As^{3+}	7

(Barakat et al., 2015) synthesized magnetic core and porous silica shell ($Fe_3O_4@nSiO_2@mSiO_2$) composite by using surfactant assisted template approach, for removal of heavy metal ions. XRD patterns indicated an amorphous phase. SEM and TEM showed spherical particle agglomerates with dimension in the range 174–202 nm. This study investigated the effects of pH of solution, time, intra-particle- diffusion, initial and binary concentration. The adsorption capacity for Pb^{2+} increased with pH from 2 to 5.5 and reached maximum at 5.5 around 32 mg g⁻¹ for Cd^{2+} , the capacity increased with pH from 2 to 6.5 to reach the maximum at 6.5 around 48.4 mg g⁻¹. Moreover, adsorption increased with time for both Pb^{2+} and Cd^{2+} reaching equilibrium within 4 h.

(Khezami et al., 2015) studied the uptake of Cd^{2+} from aqueous solution by milled nanocrystalline goethite prepared by high-energy ball milling (ball - powers mass ratio of 10:1 and 40 h of milling. XRD pattern of initial goethite powder revealed crystalline peaks that were narrow and strong. After milling, the peaks became very broader and their intensity decreased, due to the reduction of crystallite size and accumulation of microstrain. After 40 h, the major peaks disappeared and new phase ($\alpha\text{-Fe}_2\text{O}_3$) appeared. TEM showed an average particles size of milled powder around 15 nm after milling for 40 h. Hysteresis M–H loop curves revealed superparamagnetic behaviour for goethite powder, then transformed totally to ferromagnetic for the powder milled for 40 h, the magnetization was around 8.509 emu/g. The adsorption capacity was investigated for four toxic heavy metal ions (Cd^{2+} , Ni^{2+} , Co^{2+} and Cr^{6+}) at room temperature with a fixed pH then changed and tested only for Cd^{2+} . The results revealed the highest adsorption at pH =7 for Cd^{2+} with an amount of 66.11 mg L⁻¹ followed by Co^{2+} , Ni^{2+} and Cr^{6+} with 53.91, 53.11 and 45.38 mg L⁻¹. By changing pH, the capacity was found to be sensitive to value of pH, (7, 6, 7 and 8); 7.85 mg/g for 8; 30.21 mg/g for 4 then 33.02 mg/g for 6.

2.3 MFe_2O_4 (M= Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) properties and applications

In this research project, four MNPs are selected, CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 and ZnFe_2O_4 . The elements are chosen specifically as shown in periodic Table. Figure (2.3) and Table (2.3) shows some common properties of these elements.

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

Figure (2.3)

The Periodic Table of elements

(<http://www.lenntech.com/periodic/elements/co.htm>.)

Table (2.3)

Properties of elements

	Co	Ni	Cu	Zn
Atomic No.	27	28	29	30
Atomic mass	58.9332 g. mol ⁻¹	58.71 g.mol ⁻¹	63.546 g.mol ⁻¹	65.37 g.mol ⁻¹
Density	8.9 g.cm ⁻³ at 20°C	8.9 g.cm ⁻³ at 20°C	8.9 g.cm ⁻³ at 20°C	7.11 g.cm ⁻³ at 20°C
Melting point	1495 °C	1453 °C	1083 °C	420 °C
Configuration	[Ar]3d ⁷ 4s ²	[Ar]3d ⁸ 4s ²	[Ar]3d ¹⁰ 4s ¹	[Ar]3d ¹⁰ 4s ²
Kind of materials	Ferromagnetic	Ferromagnetic	Ferromagnetic	Paramagnetic
Discovered by	George Brandt in 1737	Alex Constedt in 1751	The ancients	Andreas Marggraf in 1746

(<http://math.nist.gov/DFTdata/atomdata/configuration.html> (configuration).Lenntech.com.

2.3.1 Cobalt ferrite (CoFe₂O₄) properties and applications

CoFe₂O₄ has an inverse spinel structure. It has high coercivity, moderate saturation magnetization, large magneto crystalline anisotropy and large magnetostrictive coefficient at room temperature (Ali et al., 2016). In recent years, CoFe₂O₄ is largely studied in the search to improve its properties such as magnetic properties (Ali et al., 2016). It was found that the substitution of Co by Zn results in an increase of its saturation of magnetization. The remarkable properties of cobalt ferrite makes it a very important magnetic material for many applications in new areas, such as drug delivery, hyperthermia treatment and microwave device (Ali et al., 2016).

In addition, inverse spinel structure also has special properties such as mechanical hardness, chemical stability, tunable magnetic properties, there by offering new range of applications such as magneto-optical recording devices, photo-magnetic devices, supercapacitors and photocatalysis (Sundararajan et al., 2015). Shape and particle size and hence magnetic properties of CoFe₂O₄ are found to depend on the method of preparation as shown in Table 2.4.

Table (2.4)

Comparison between CoFe₂O₄ synthesized in the proposed work and those obtained from the literature

	Method	T(k)	D(nm)	a(Å)	Magnetic behaviour	H _C (Oe)	M _r (emu/g)	M _s (emu/g)
This Study	MCM	AP	45.2	8.3911(9)	Ferro	557.0	28.71	67.97
		A	41.4	8.3893(12)	Ferro	584.2	27.84	66.05
Hosni.,2017	Co-pre	733-1223	30-178	8.3789(4)-8.3890(2)	Ferro	610	14.83	59.32
Kovalenko, 2016	Co-pre	AP	8.73	8.36	Ferro	-	-	-
Sundarajan, 2015	MCM	AP	46.22	8.380		-	-	-
Yadav,2016	Sol-gel*	AP	41.5	8.737	-	51.97	0.56	14.04

2.3.2 Nickel ferrite (NiFe₂O₄) properties and applications

NiFe₂O₄ has also an inverse spinel structure (Gao et al., 2015). It has a low power loss, high resistivity, large permeability at high frequency with particular magnetic properties such as high saturation magnetization (e.g. Mn-Zn ferrite) has excellent soft magnetic properties. This makes Ni ferrite useful in the radio frequency range (Elshahawy et al., 2015). Moreover, it has been widely used in electronic devices and in (MRI) contrast agent, as well as anode material for lithium ion rechargeable batteries (Yadav et al., 2015; Ding et al., 2014). Similarly the method of preparation, has a great influence on particles shape and size, hence its magnetic properties, see Table 2.5.

Table (2.5)

Comparison between NiFe₂O₄ synthesized in the proposed work and those obtained from the literature

	Method	T(k)	D(nm)	a(Å)	Magnetic behaviour	H _C (Oe)	M _r (emu/g)	M _s (emu/g)
This Study	MCM	AP	43.3(4)	8.3399(12)	Ferro	112.2	10.16	38.56
		A	47.7(2)	8.3409(8)	Ferro	107.8	10.92	41.49
Springer .,2016	Co-pre	873	16.6-20	-	Ferro	95	2.7	28
Kovalenko, 2016	Co-pre	AP	2.51	8.71	Super para	0	0	-
Wang, 2012	Hydro	473	10-20	-		166.7	13.6	56
Vingswari, 2016	Co-pre	AP	-	8.23	-	65.53	5.98	38.23

2.3.3 Cupper ferrite (CuFe₂O₄) properties and applications

CuFe₂O₄ has also an inverse spinel structure. Due to their interesting characteristics, it is used as sensor, anode for Li-ion rechargeable batteries, semiconductors, catalyst and magnetic material (Phuruangrante et al., 2015). It is very important to highlight that very few if not limited papers are reported on CuFe₂O₄ phase.

2.3.4 Zinc ferrite (ZnFe₂O₄) properties and application

ZnFe₂O₄ has a normal spinel structure. It offers various technological applications such as (MRI) contrast agent, magnetic carrier for drug targeting and gas sensing. This is due to its large resistivity, high magnetization, high permeability and low coercivity (Heiba et al., 2016; Joseph et al, 2015). Manganese Zinc ferrite (Mn- Zn ferrite) particularly was used in magnetic sensors, deflection Yoke rings, reading heads for magnetic recording media and spintronic devices (Joseph et al., 2015). The dependence of magnetic properties with particle shape/ size is shown in Table 2.6.

Table (2.6)

Comparison between ZnFe₂O₄ synthesized in the proposed work and those obtained from the literature

	Method	T(k)	D(nm)	a(Å)	Magnetic behaviour	H _c (Oe)	Mr(emu/g)	Ms(emu/g)
This Study	MCM	AP	51.4(3)	8.4939(7)	Para	16.06	3.859*10 ⁻³	1.812*
		A	51.0(4)	8.4397(10)	Para	10.11	3.032*10 ⁻³	1.745*
Kovalenko, 2016	Co-pre	AP	4.12	8.45	Super para	0	0	0
Shoushtari, 2016	Co-pre	AP	-	8.374	Super para	40.05	7.77	33.85
Heiba, 2016	Citrate	-	30.9	8.4476	para	5.48	784	-

Co-pre: co precipitation, MCM, hydro: hydrothermal, AP: as-prepared, A: annealed.

*Starch assisted sol gel auto combustion method.

Chapter 3

Experimental Procedure

3.1 Microwave Combustion Method (MCM)

Spinel ferrites (SFs) materials are based on: $\text{MeO} + \text{Fe}_2\text{O}_3 = \text{MFe}_2\text{O}_4$ where $\text{M} = \text{Ni}, \text{Co}, \text{Cu}$ and Zn . SFs can be synthesised via various preparation methods including microemulsions, solvo-thermal, hydrothermal, sol-gel (Elshahawy et al., 2015), chemical co-precipitation technique, laser deposition, thermal decomposition method (Sundararajan et al., 2015), etc.

3.1.1 Significance of MCM

In this project, we adopted MCM, because it offers several advantages:

- 1- High purity: single phase (Sundararajan et al., 2015),
- 2- During the preparation; heat is generated from the inside that propagates uniform heating (Elshahawy et al., 2015; Sun, H et al., 2015),
- 3- Short reaction time with high reaction kinetics (Elshahawy et al., 2015); (Sun et al., 2015),
- 4- Improved characteristics of the as prepared materials (Sundararajan, M et al., 2015),
- 5- Finer particle size in the nanoscale (Sun et al., 2015), etc.

3.2 Synthesis of MFe_2O_4 ($\text{M} = \text{Zn}, \text{Cu}, \text{Ni}, \text{Co}$) NPs by MCM

All the reagents used were analar grade obtained from Merck, India and were used as received without further purification. MCM method relies on the advantage of the propellant chemistry in constructing the redox mixtures, in which metal oxide $\text{MO} + \text{Fe}_2\text{O}_3 = \text{MFe}_2\text{O}_4$ where $\text{M} = \text{Ni}, \text{Co}, \text{Cu}$ and Zn , and ferric oxide acts as an oxidizing reactant and fuel urea ($\text{CO}(\text{NH}_2)_2$) as a reducing reactant. Stoichiometric amounts of metal oxide, ferric oxide and urea were dissolved separately in 10 ml of de-ionized water and poured into a silica crucible and stirred for 15 min to obtain clear solutions. The obtained

solutions were placed in a household microwave-oven (2.45 GHz, 850 W) for 10 min. Initially, the solutions boiled and underwent dehydration followed by decomposition with the evolution of gases. When the solutions reached the point of spontaneous combustion, they were vaporized and instantly became a solid. The obtained samples are shown in Figure 3.1.

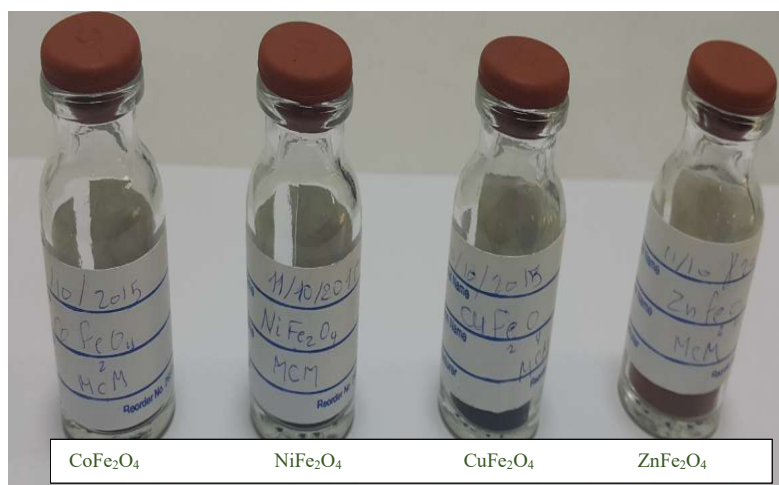


Figure (3.1)

The as-prepared MNPs

3.3 Annealing

The as prepared samples by MCM have been subjected to annealing at 800 C° for 16 h. The aim of annealing is to obtain crystallinity and to obtain large particles (grain growth) which will have a direct influence on magnetic properties and adsorption performance (Kumar et al., 2015). A CARBOLITE oven was used to anneal samples as shown in Figure 3.2. The as prepared and annealed samples shown in Figure 3.3 clearly reveal the change of powders color after annealing indicating that some changes occurred.



Figure (3.2)
CARBOLITE oven opened and closed

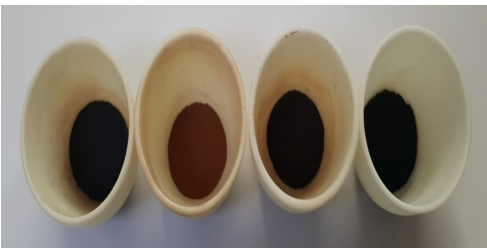
As prepared	Annealed (16 h at 800 C°)
	

Figure (3.3)
MNPs samples as-prepared and annealed

3.4 Characterization

3.4.1 X-Ray Diffraction Technique (XRD)

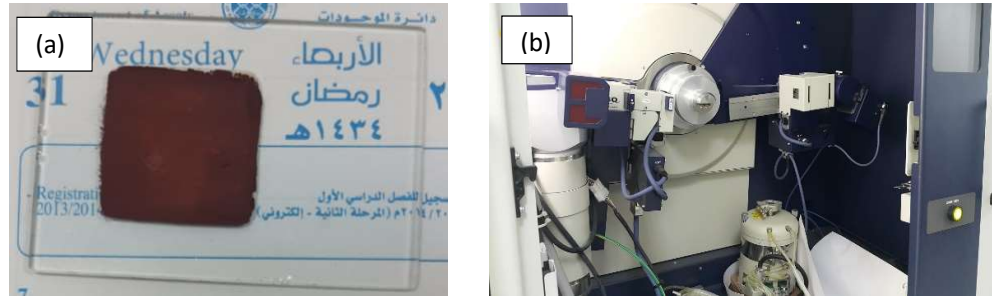


Figure (3.4)

(a) MNPs on sample holder, (b) XRD Device

XRD is very important method for qualitative and quantitative analyses in order to study the crystal structure of solids. Materials are classified as amorphous, crystalline and nanocrystalline refer to range order of atoms.

XRD is obtained by producing x-rays whose wavelength are the same as the distance between crystal lattice planes. Space lattice are three –dimensional array, which has identical surrounding and described atomic arrangement in crystalline solids. Each space lattice is described by specifying the atom positions in repeating unit cell in which the axial lengths and axial angles are the lattice constants of the unit cells.

Bragg's law describes simple equation which refers to explain why the faces of crystals appear to reflect (diffraction) X-ray beams at certain angles of incidence θ as shown in Figure (3.5).

$$n \lambda = 2d \sin \theta \quad (3)$$

Where n is an integer number, d is a lattice inter planar spacing of the crystal, θ : x-ray incidence angle (Bragg's angle) and λ wavelength of the characteristic x-rays.

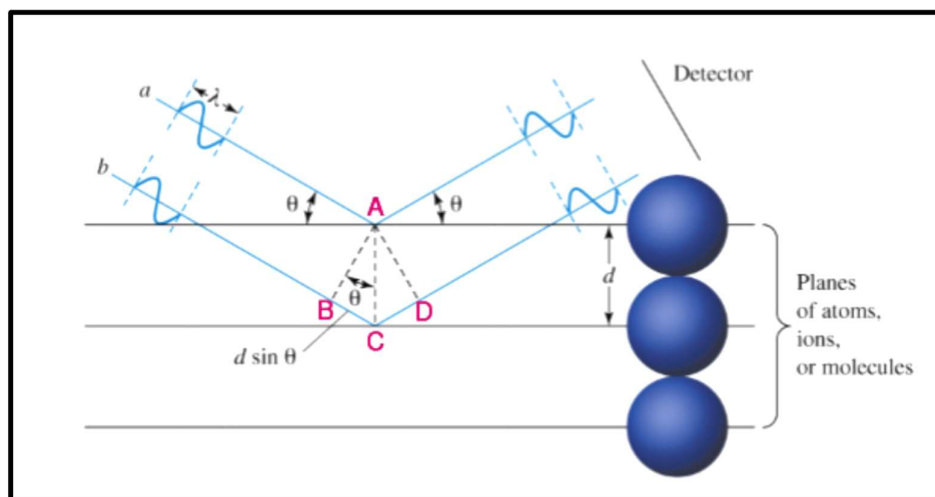


Figure (3.5)

Bragg's Law of diffraction

(https://materialsection.files.wordpress.com/2011/09/1-1-xray_diffraction-bragg-law.pdf)

XRD technique is a powerful technique for:

- Phase identification,
- Phase composition of multiple- phase materials (amount in % of each phase),
- Crystallinity and preferred orientation (for thin films),
- Microstructural parameters (crystallite size; microstrain),
- Structure parameter (lattice constant), etc.

Rigaku Ultima IV high resolution x-ray diffraction, equipped with Cu-K α radiation source (0.154 nm) with 2θ angle ranging from 20° to 80° with 0.04° step size and 1 second counting time as shown in Figure (3.4b). The experimental condition are:

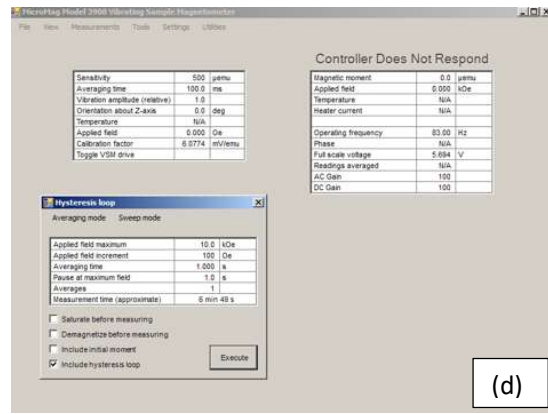
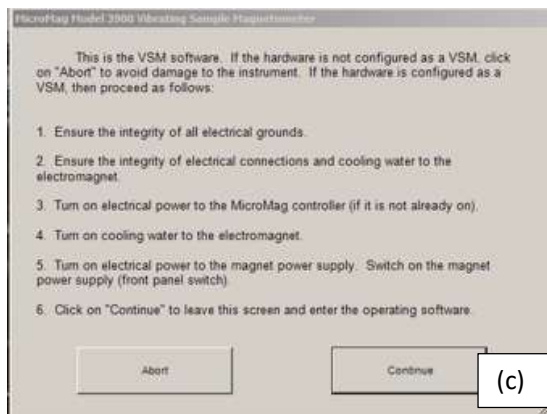
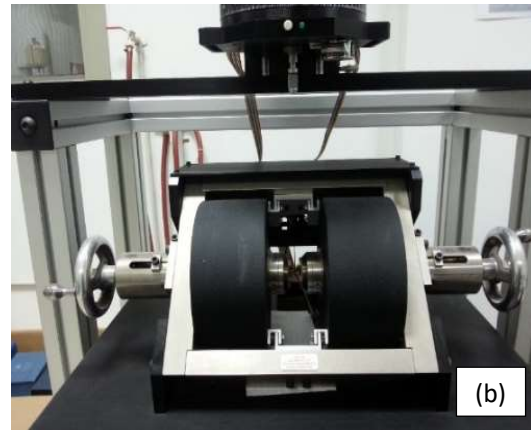
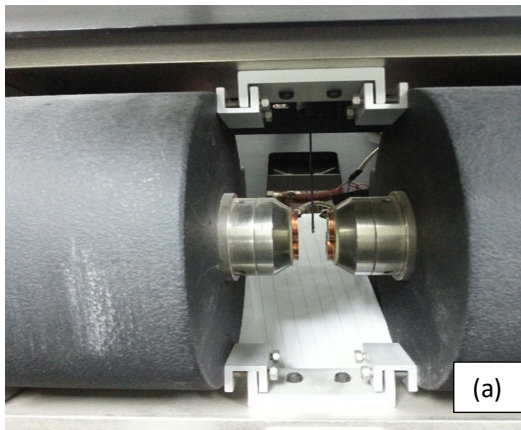
- Current: 40 mA
- Voltage: 40 KV
- Output power: 1.6 kWatt.

The powder samples were fixed in glass substrate (see Figure (3.4a)) which is placed in XRD device.

3.4.2 Vibrating Sample Magnetometer (VSM)

The magnetic properties are determined by measuring magnetisation field (M-H) hysteresis loops using MicroMag 3900 VSM equipped with 1 Tesla magnet as shown in Figure 3.6. VSM is a high sensitive of 0.5 μemu , computer-controlled susceptibility measured system. (Vibrating Sample Magnetometers | Lake Shore Cryotronics, Inc.", 2017).

Magnetization – field (M-H) curves were recorded at room temperature. The measurement were carried out using the following procedures as shown in (Figures 3.6(c) and 3.6(d)). The powdered samples are placed in Al foil, then fixed onto non-magnetic rod with a specific grease. The rod is then fixed in the VSM and the experiment was run at room temperature under the following condition: maximum field 10,000 Oe, step field 100 Oe and step time 1 sec.



Figures (3.6)

VSM Device and instructions

3.4.2.1 Types of magnetic materials

Materials are grouped according to their behaviour subjected to an external magnet field. All behaviours are shown in schematic in Figure (3.7).

a- Paramagnetic Materials (PM)

Magnetize positively parallel with the field. One example of paramagnetic material is Aluminium (Al).

b- Ferromagnetic Materials (FM)

When it is placed in external magnetic field or after its removal. The magnetic moment align parallel to each other except in a weak external magnetic field, transition metal are ferromagnetic.

c- Diamagnetic Materials (DM)

When an external magnetic field is applied, a weak magnetic moment is induced in the opposite direction of the external applied field (negative external magnetic field with an angle 180°).

d- Antiferromagnetic Materials (AFM)

When it is placed in an external magnetic field, atoms or molecules are induced magnetic moment opposite to the external field; the net magnetic moment is equal zero. This behavior is related to the spin of electrons.

e- Super paramagnetic Materials (SPM)

It is a special case for paramagnetic NPs material. Super ParaMagnetism (SPM) occurs in NPs with diameter (3-50 nm) and not in all materials, which are single-domain such as Fe_3O_4 . The magnetization of NPs, can randomly flip its direction under the change in temperature. An external magnetic field is able to magnetize the NPs, similar to a paramagnet. In SPM, there is no hysteresis loop but it appears when particle size is cooled at certain temperature or if diameter is increased in size. When an external magnetic field is applied to an assembly SPM of NPs, their magnetic moments tend to align along the applied field, leading to a net magnetization. The magnetization curve of the assembly is S-shaped (Sodipo, et al. 2016).

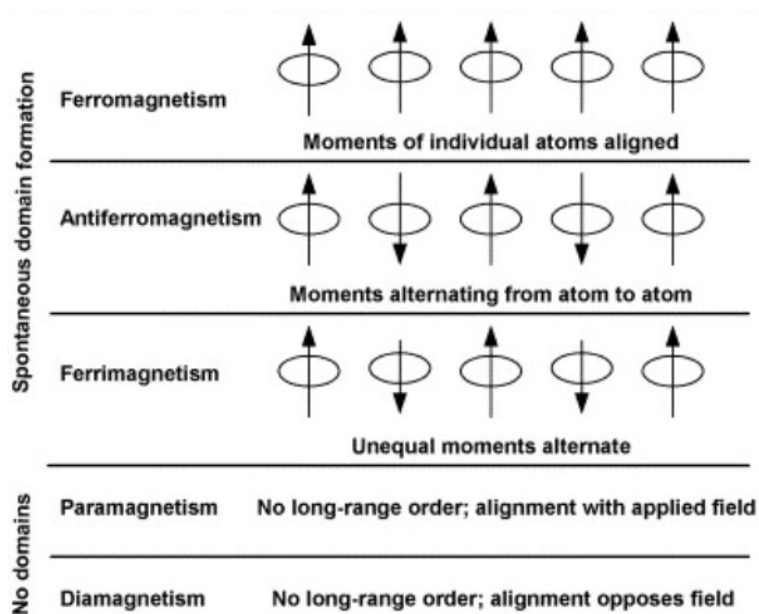
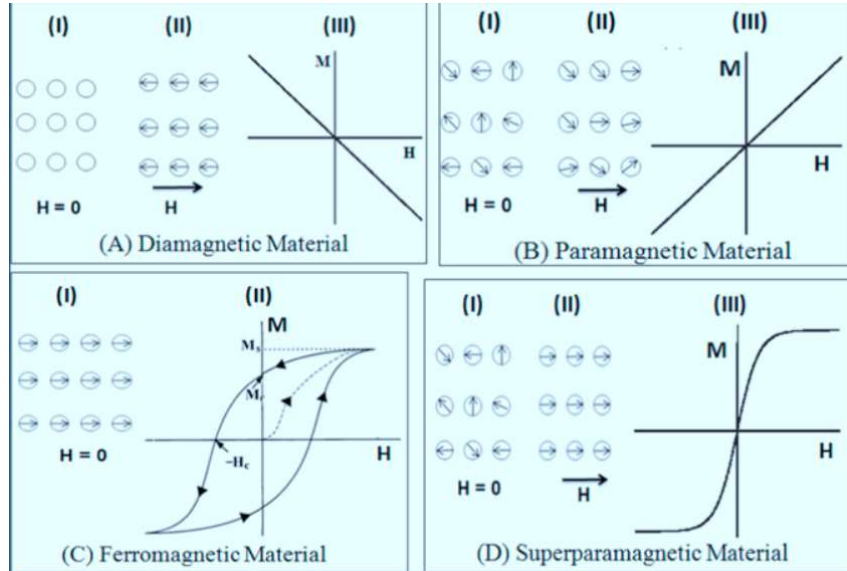


Figure (3.7)

Types of magnetic materials

(<http://www.sciencedirect.com/science/article/pii/S0304885316305704>)

3.4.3 Scanning Electronic Microscopy (SEM)

SEM is an important characterization technique in materials, which is used for imaging of surface topography by focusing an electron beam Figure (3.8). Also, it is used for microstructural study failure analysis, surface contamination examination and fracture characterization, etc.

SEM works basically by the interaction of electrons with the atoms of the analysed sample, then produce signals that can be detected of the beam, then converted into images to get information about the sample. The resolution of SEM is around 1 nm with magnification between 15 to 100,000 $\times$ (Smith & Hashemi et al., 2006).

Morphological observation were performed using FEI Sirion gun Scanning Microscope (FESEM) equipped with Electron Dispersive X-ray (EDX) spectrometer for chemical analysis.



Figure (3.8)
Scanning Electronic Microscopy (SEM)

3.5 Batch adsorption of heavy metal ions from aqueous solutions

The adsorption of heavy metal ions by MNPs was studied by a batch technique and the schematic diagram is shown in Figure (3.5a). Standard solutions of heavy metal ions of Cadmium (Cd^{2+}) and Lead (Pb^{2+}) were prepared by standard solution of 1000 ppm as shown in Figure (3.5b) and the information of these heavy metal ions are listed in Table (3.5a)

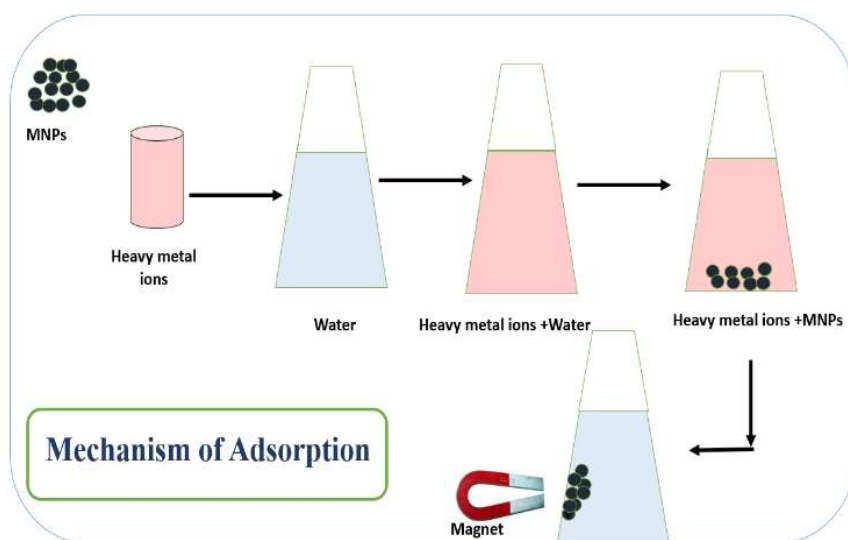


Figure (3.9(a))

Schematic diagram of the removal of heavy metal ions using MNPs



Figure (3.9(b))

Standard solutions (Cd^{2+} and Pb^{2+}) with 1000 ppm



Figure (3.9(c))

Standard solutions with different concentrations

Table (3.1)

Information of used heavy metal ions solution

Heavy metal ion	Cd^{2+}	Pb^{2+}
Name of the solution	Cadmium standard solution	Lead Atomic Spectroscopy standard solution
Company	Spectrosol, England	Fluka- Chemika, Switzerland
Prepared	Cadimium nitrate $[\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}]$ Matrixacid, $c(\text{HNO}_3)=0.5\text{mol/l}$	$\text{Pb}(\text{NO}_3)_2$ and HNO_3
Concentration (mg/L)	$1000 \pm 5 \text{ mg/L}$	$1000 \pm 5 \text{ mg/L}$

3.5.1 Adsorption experimental procedure

Experiments were Adsorption carried out as follows:

- 1- 12.5 ml stock solution (1000 ppm) of Cd^{2+} and Pb^{2+} was diluted with deionized water to prepare 50 ppm solutions in 250 ml volumetric flask as shown in Figure (3.9b).

- 2- Standard solutions of Cd^{2+} was prepared of 2,4,6 and 8 ppm and Pb^{2+} was prepared 5,10,15 and 20 ppm in 50 ml volumetric flask from their stock solutions as shown in Figure (3.9c).
- 3- Cd^{2+} and Pb^{2+} stock solutions of 25 ppm were prepared by mixing 12.5 ml of prepared solutions 50 ppm of Cd^{2+} and Pb^{2+} with 12.5 ml of deionized water in 50 ml Erlenmeyer flask as shown in Figure (3.9d).
- 4-The experiment was carried out in batch mode by adding 10, 20 and 30 mg of MNPs to 25 ppm solutions of Cd^{2+} and Pb^{2+} ions in 50 ml Erlenmeyer flask. The amount of mass was measured by using Balance Sartorius made in Germany as shown in Figure (3.9g).
- 5- The following parameters were fixed as:
 - Initial concentrations of heavy metal ions in solution was 25 ppm,
 - Temperature was at RT,
 - Time for the mixtures stirred for 12 h by magnetic stirrer as shown in Figure (3.9d),
 - A pH at 2 was calibrated by a digital pH meter as shown in Figure (3.9h).
- 6- The solutions were filtered using vacuum as shown in Figure (3.9e).
- 7- The residual Cd^{2+} and Pb^{2+} ions concentrations are measured by Atomic Absorption Spectrophotometer (AAS) as shown in Figure (3.9f). pH of the solution was maintained at 2 using a calibrated pH-meter.

The results are given as a unit of adsorbed and un-adsorbed metal ions concentrations per gram of adsorbent in solution at equilibrium and calculated by using the following equation:

$$q_e = \frac{(C_o - C_e)}{m}$$

Where m is the mass of adsorbent (g), q_e the adsorbed metal ion quantity per gram of adsorbent at equilibrium (mg/g), C_o the initial metal concentration (ppm), C_e

the metal concentration at equilibrium (ppm) and V is the working solution volume (L).



Figure (3.9d)
Magnetic Stirrer



Figure (3.9e)
Filter appraise



Figure (3.9f)
AAS Device



Figure (3.9.g)
Balance



Figure (3.9.h)
A digital pH

Chapter 4

Results and Discussions

Chapter 4 - Section 1

XRD Analysis

4.1 X-ray Diffraction Analysis

4.1.1 XRD as-prepared

Figure 4.1.1 shows the evolution of XRD patterns of as Prepared MFe_2O_4 nanopowders (M=Co, Ni, Cu and Zn) by MCM. It can be observed that all XRD patterns show well defined peaks, which means that as prepared powders are crystalline in nature. Meanwhile, the peaks are relatively broad with low intensity, indicating the presence of nanocrystals in the analysed powders.

By using database provided with the X-ray diffractometer, all peaks were identified (see Figure (4.1.2)) and after that used for the refinements by the Rietveld method.

Table (4.1.1)

Crystal Structure parameters as obtained from database.

Samples	Crystal Structure	Space group	Lattice parameter (Å)	JCPDs Card No.
CoFe_2O_4	Cubic	$\text{Fd}\bar{3}\text{m}(227)$	$a=b=c=8.3874$	01-086-1338
NiFe_2O_4	Cubic	$\text{Fd}\bar{3}\text{m}(227)$	$a=b=c=8.3367$	01-074-2081
CuFe_2O_4	Tetragonal	$I41 \text{ amd}(141)$	$a=b=5.800, c=8.7300$	01-072-1174
ZnFe_2O_4	Cubic	$\text{Fd}\bar{3}\text{m}(227)$	$a=b=c=8.4411$	01-075-9714
$\alpha\text{-Fe}_2\text{O}_3$	Trigonal	$\text{R}\bar{3}\text{c}(167)$	$a=b=5.0385, c=13.7400$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	01-071-5088
CuO	Monoclinic	$\text{C}2/\text{c}(15)$	$a=4.6620, b=3.4160, c=5.1180$ $\beta=99.490^\circ$	03-065-2309

Table (4.1.2) contains the different phases and crystallographic information.

Table (4.1.2)

Structural and microstructural parameters of as-prepared MFe₂O₄ nanopowders obtained from Rietveld refinements.

As-prepared				
Samples	Phase Composition	Crystal Size (nm)	Micro Strain (%)	Lattice parameter(Å)
CoFe ₂ O ₄	CoFe ₂ O ₄ 93%	45.2(1)	0.02(3)	a=b=c=8.3911(9)
	(α -Fe ₂ O ₃) 7%	59.5(2)	0.07(4)	a=b=5.0395(6) c=13.7560(20)
NiFe ₂ O ₄	NiFe ₂ O ₄ 100%	43.3(4)	0.08(7)	a=b=c=8.3399(12)
CuFe ₂ O ₄	CuFe ₂ O ₄ 88.1%	40.6(3)	0.24(2)	a=b=5.8209(13),c=8.6976(30)
	CuO 11.9%	6.1(3)	0.81(2)	a=4.672(5),b=3.431(3),c=5.183(4) $\alpha = \gamma = 90^\circ$, $\beta = 99.47(6)$
ZnFe ₂ O ₄	ZnFe ₂ O ₄ 100%	51.4(3)	0.06(4)	a=b=c=8.4439(7)

Samples	$R_{wp}(\%)$	$R_p(\%)$	$R_e(\%)$	S	$\chi^2 = S^2$
CoFe ₂ O ₄	28.23	17.00	23.00	1.2192	1.4866
NiFe ₂ O ₄	21.36	13.61	12.27	1.2348	1.5249
CuFe ₂ O ₄	11.23	8.93	9.81	1.1424	1.3050
ZnFe ₂ O ₄	22.08	12.66	17.81	1.2378	1.5322

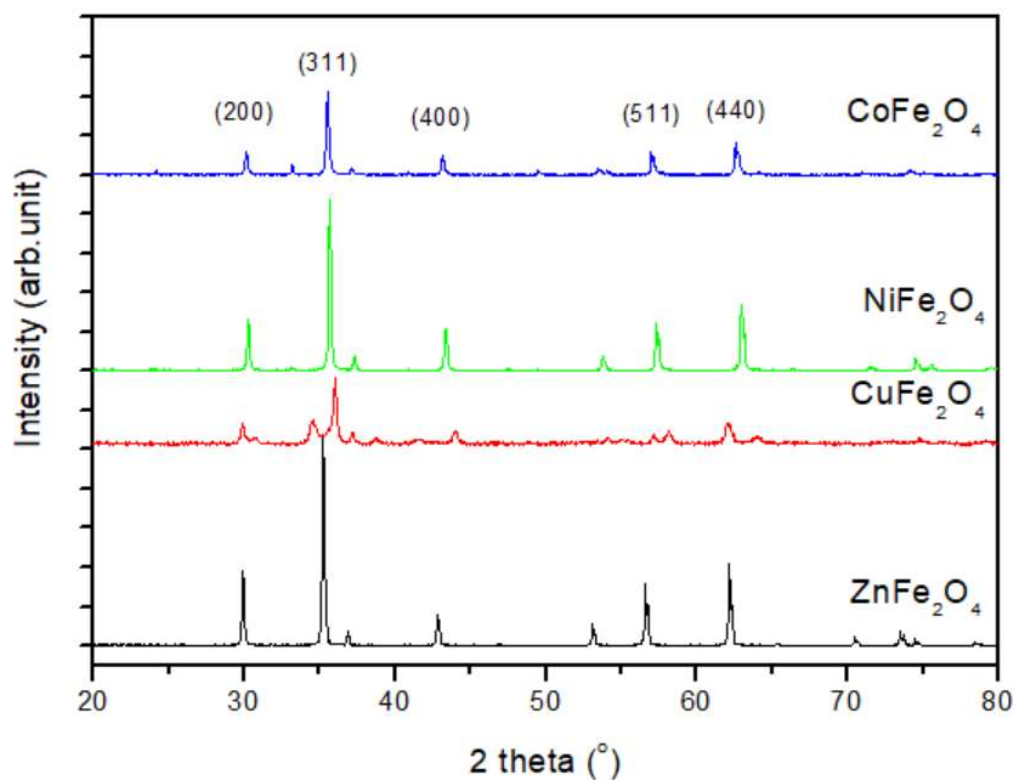


Figure (4.1.1)

XRD patterns of as- prepared MFe_2O_4 nanopowders

Table (4.1.3)

The volume per unit cell of as-prepared MFe_2O_4 (M= Co, Ni, Cu and Zn) nanopowders.

Samples	Volume ($\text{\AA}^3$)	Volume/unit cell ($\text{\AA}^3$)	Ionic radius (nm)
CoFe ₂ O ₄	590.8	73.9	0.070
NiFe ₂ O ₄	580.3	72.4	0.070
CuFe ₂ O ₄	293.7	73.4	0.073
ZnFe ₂ O ₄	601.4	75.2	0.074

4.1.2 XRD Analysis of Annealed nanopowders

Table (4.1.4)

Structural and microstructural parameters of annealed MFe_2O_4 nanopowders obtained from Rietveld refinements.

Annealed (16 h at 800°C)				
Samples	Phase Composition	Crystal Size (nm)	Micro Strain (%)	Lattice parameter(Å)
CoFe ₂ O ₄	CoFe ₂ O ₄ 93.2%	41.4(1)	0.04(1)	a =b=c =8.3893(12)
	α -Fe ₂ O ₃ 6.8%	27.1(1)	0.02(4)	a=b=5.0353(9) c=13.751(2)
NiFe ₂ O ₄	NiFe ₂ O ₄ 100%	47.7(2)	0.06(1)	a=b=c=8.3409(8)
CuFe ₂ O ₄	CuFe ₂ O ₄ 100 %	52.8(1)	0.05(1)	a=b=c=8.4428(6)
ZnFe ₂ O ₄	ZnFe ₂ O ₄ 100%	51.0(4)	0.07(1)	a=b=c=8.4397(10)

Samples	R_{wp} (%)	R_p (%)	R_e (%)	S	$\chi^2 = S^2$
CoFe ₂ O ₄	28.55	17.95	23.53	1.2111	1.4667
NiFe ₂ O ₄	22.83	14.73	18.03	1.2644	1.5988
CuFe ₂ O ₄	24.67	16.39	18.19	1.3546	1.8349
ZnFe ₂ O ₄	22.77	13.07	18.11	1.2541	1.5728

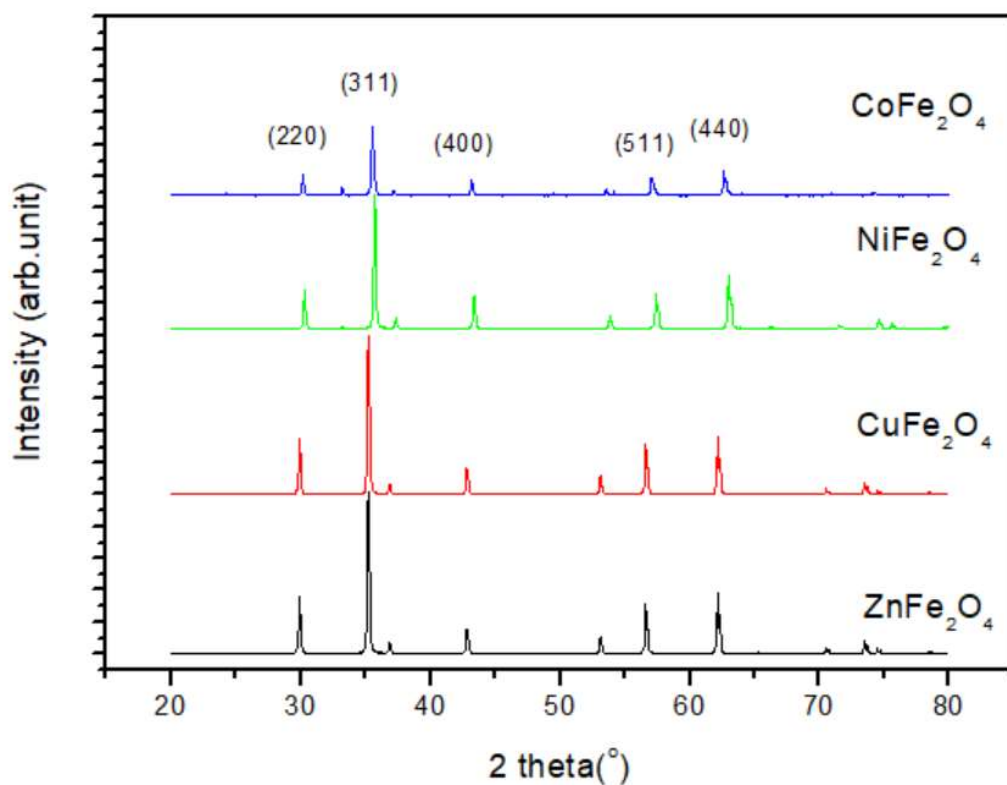


Figure (4.1.2)

XRD patterns of annealed MFe_2O_4 nanopowders

Table (4.1.5)

The volume per unit cell of annealed MFe_2O_4 (M= Co, Ni, Cu and Zn) nanopowders.

Samples	Volume ($\text{\AA}^3$)	Volume/unit cell ($\text{\AA}^3$)	Ionic radius (nm)
CoFe_2O_4	590.4	73.8	0.070
NiFe_2O_4	580.3	72.5	0.070
CuFe_2O_4	601.8	75.2	0.073
ZnFe_2O_4	601.1	75.1	0.074

4.1.3 Phase Identification

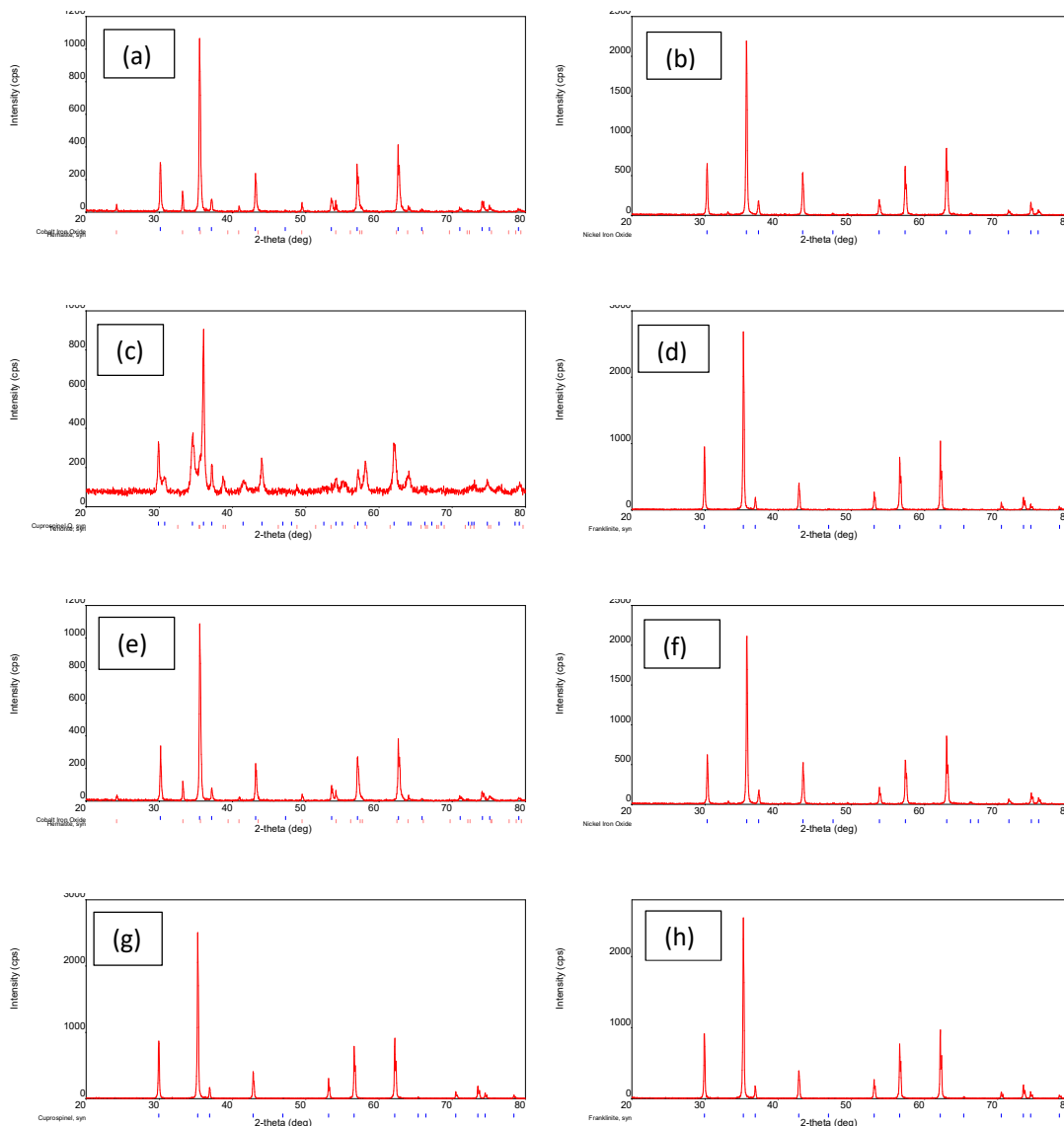


Figure (4.1.3)

Phase identification patterns using the Rietveld method of MNPs nanpowders

**As-prepared: (a) CoFe_2O_4 , (b) NiFe_2O_4 , (c) CuFe_2O_4 and (d) ZnFe_2O_4
Annealed: (e) CoFe_2O_4 , (f) NiFe_2O_4 , (g) CuFe_2O_4 and (h) ZnFe_2O_4**

Qualitative and quantitative phase analyses using the Rietveld method have been carried out. The refinements of XRD patterns allow distinguishing MFe_2O_4 ($\text{M}=\text{Ni, Co, Cu and Zn}$) nanopowders by MCM and after annealing for 16 h at

800°C. Phase identification confirmed the formation of nanocrystalline phase; it is found that for M= Ni and Zn a single phase is obtained, while for M=Co and Cu a secondary phase appears: α -Fe₂O₃ around 7 % for CoFe₂O₄ and CuO around 12% for CuFe₂O₄.

4.1.4 Evaluation of Crystalline Size and Microstrain

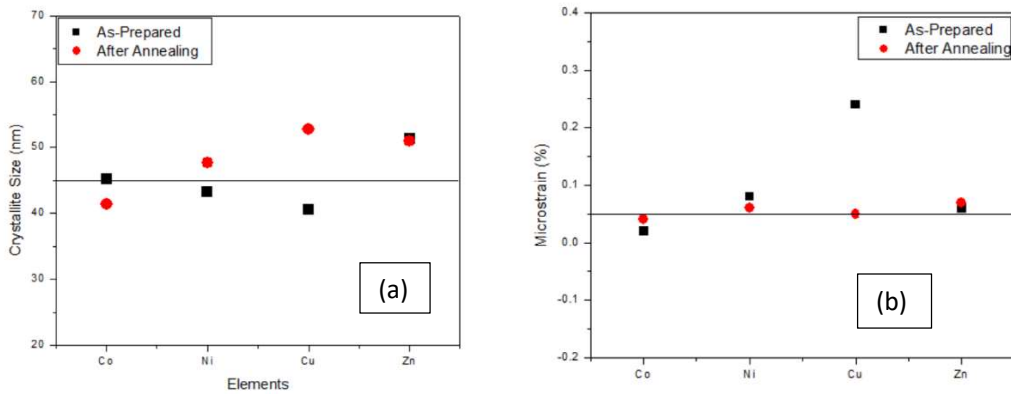


Figure (4.1.4)

Evolution of: (a) crystalline size and (b) microstrain as-prepared and annealed MFe₂O₄ nanopowders

Figure (4.1.4) shows the evolution of crystalline size and microstrain. It can be noticed that both the crystalline size and microstrain seem not very much influenced by the nature of elements M; the crystallite size slightly varies in the range 40.6-51.4 nm while 41.4-52.8 nm before and after annealing respectively, while the microstrain varies in the range 0.02-0.24 % and 0.04-0.07 % before and after annealing receptivity. It is interesting to note that CuFe₂O₄ transforms from tetragonal for as-prepared into cubic form after annealing.

4.1.5 Evolution of the unit cell volume

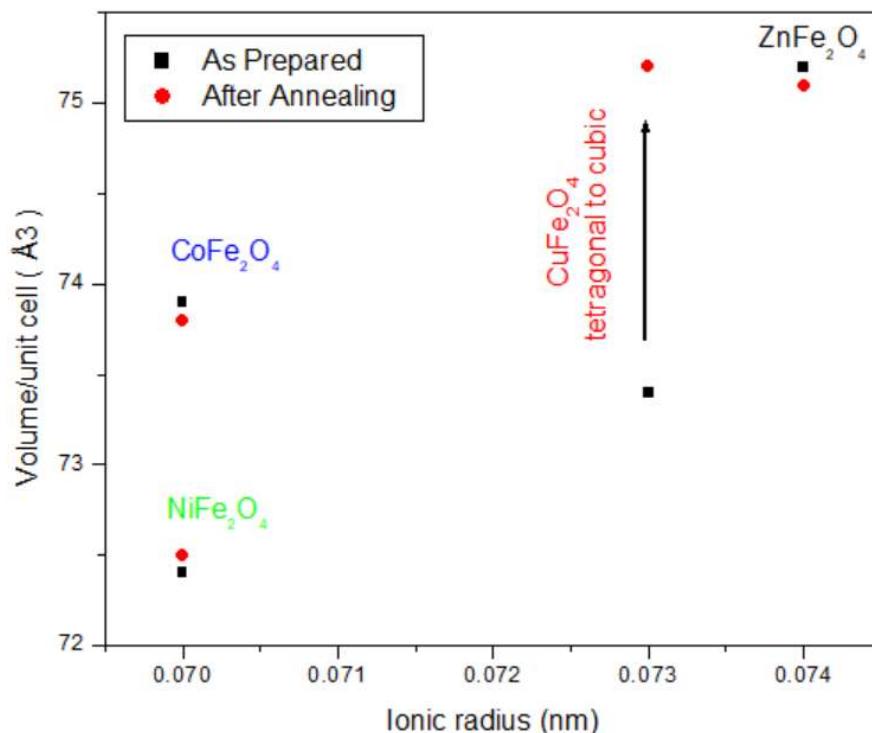


Figure (4.1.5)

Evolution of volume per unit cell vs. ionic radius of elements as-prepared and annealed MFe₂O₄ nanopowders prepared by MCM

Figure (4.1.5) shows the variation of the unit cell volume calculated for each element M. It can be noticed that the unit cell volume before and after annealing are very similar, except for CuFe₂O₄. This can be associated with the observed phase transformation:

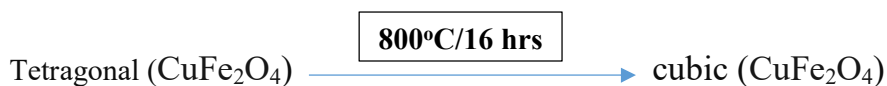


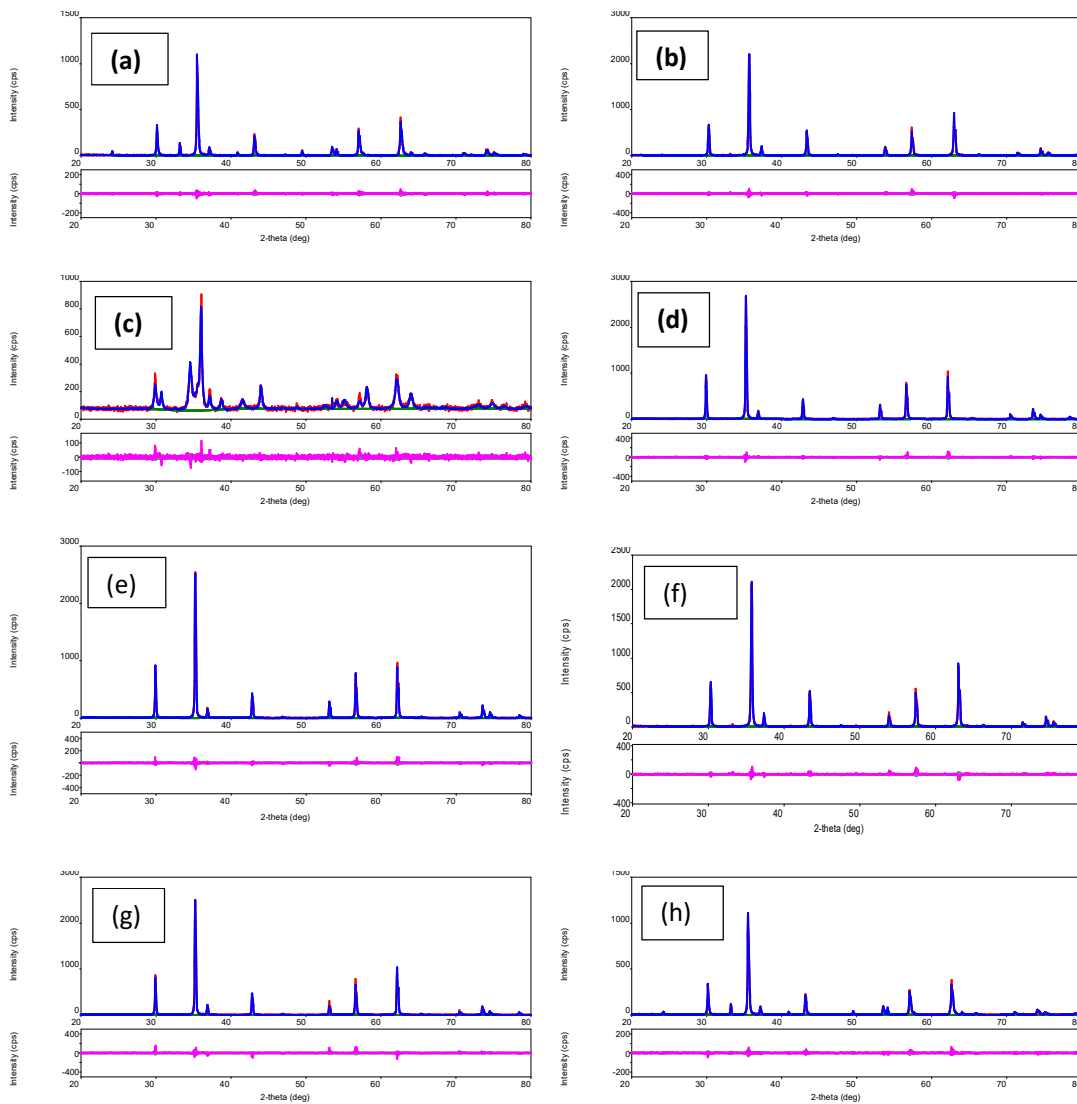
Table (4.1.6)
Ionic radius of elements.

Ionic Radius	
Ions	r (nm)
O^{2-}	0.140
Fe^{3+}	0.060
Co^{2+}	0.070
Ni^{2+}	0.070
Cu^{2+}	0.073
Zn^{2+}	0.074

(<http://www.wiredchemist.com/chemistry/data/metallic-radii>)

4.1.6 Rietveld analysis as prepared and after annealing

Rietveld refinements were performed and XRD patterns and the obtained results are reported in Tables (4.1.2) and (4.1.4) and Figure (4.1.6). It can be noticed that the goodness-of-fit (GOF) is close to the unity (around 1), which dictates that the refinements are of good quality.



Figures (4.1.6)

Refined patterns using the Rietveld method of MFe_2O_4 nanopowders

As-prepared of (a) ZnFe_2O_4 , (b) NiFe_2O_4 , (c) CuFe_2O_4 and (d) CoFe_2O_4 ,
Annealed: (e) ZnFe_2O_4 , (f) NiFe_2O_4 , (g) CuFe_2O_4 and (h) CoFe_2O_4

Chapter 4 - Section 2

VSM Analysis

Chapter 4 - Section 2

4.2 VSM Analysis

Hysteresis (M-H) loop curves of MFe_2O_4 nanopowders prepared by MCM and with subsequent annealing at room temperature are shown in Figures (4.2.1) and the magnetic properties are reported in Table (4.2.2).

4.2.1 Magnetic Properties

Table (4.2.1)

The amounts of as-prepared and annealed MFe_2O_4 nanopowders.

As Prepared				
	CoFe_2O_4	NiFe_2O_4	CuFe_2O_4	ZnFe_2O_4
Mass (g)	0.0063	0.0067	0.0072	0.0061

Annealed (16 h at 800°C)				
	CoFe_2O_4	NiFe_2O_4	CuFe_2O_4	ZnFe_2O_4
Mass (g)	0.0123	0.0117	0.0123	0.0117

Table (4.2.2)

Magnetic parameters obtained from VSM measurements of as-prepared and annealed MFe_2O_4 nanopowders.

As-Prepared				
Samples	Behaviour	$H_C(O_e)$	$M_r(\text{emu/g})$	$M_s(\text{emu/g})$
CoFe_2O_4	Ferromagnetic	557.0	28.71	67.97
NiFe_2O_4	Ferromagnetic	111.2	10.16	38.58
CuFe_2O_4	Ferromagnetic	698.5	13.93	25.97
ZnFe_2O_4	Superparamagnetic	16.06	3.859×10^{-3}	1.812 *

Annealed (16 h at 800°C)				
Samples	Behaviour	$H_c(O_e)$	$M_r(\text{emu/g})$	$M_s(\text{emu/g})$
CoFe ₂ O ₄	Ferromagnetic	584.2	27.84	66.05
NiFe ₂ O ₄	Ferromagnetic	107.8	10.92	41.49
CuFe ₂ O ₄	Superparamagnetic	11.44	2.635 $\times 10^{-3}$	1.685 *
ZnFe ₂ O ₄	Superparamagnetic	10.11	3.032 $\times 10^{-3}$	1.745 *

*Magnetization at maximum field.

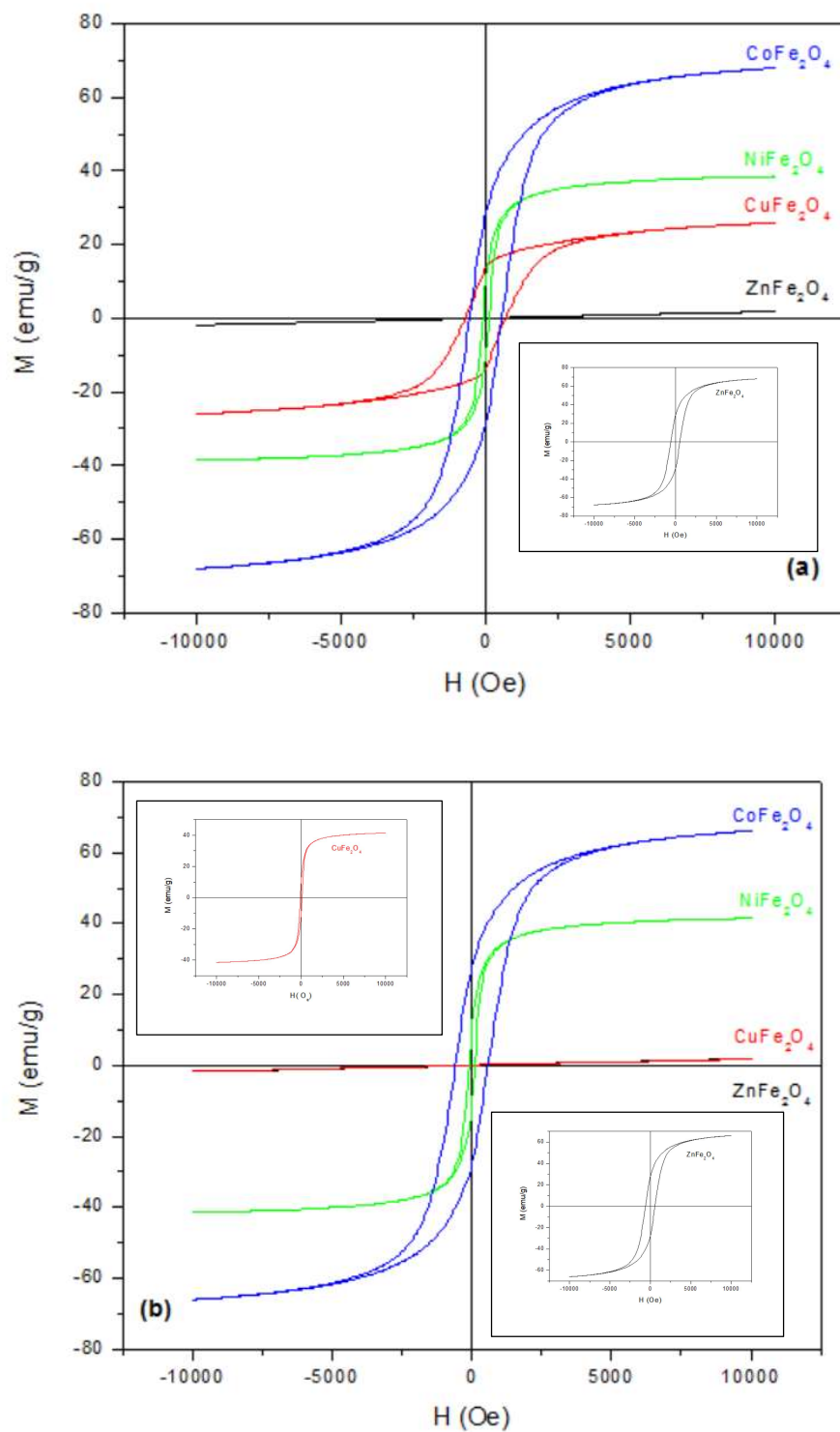


Figure (4.2.1)

M-H curve of MFe_2O_4 (a) As Prepared and (b) Annealed. The insets show M-H curves of CuFe_2O_4 and ZnFe_2O_4 separately at room temperature

M-H curves allow to determine the magnetic properties of materials; as shown in Figure (4.2.2):

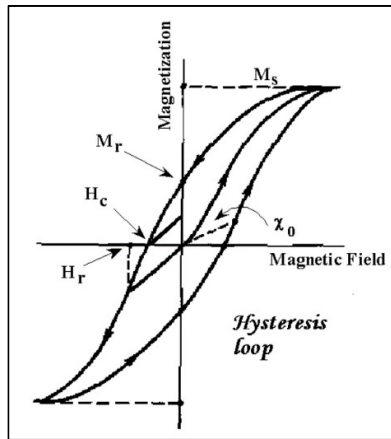


Figure (4.2.2)

The ferromagnetic hysteresis loop

- 1- Saturation Magnetisation (M_s): represents the state reached when an increase in applied external magnetic field cannot increase the magnetization of the material.
- 2- Remanence (M_r): represents is the reverse field, when an external field applied is removed, then reduced the saturation remanence to zero. It is always larger than the coercive force.
- 3- Coercivity (H_c): The ability of a ferromagnetic material to become demagnetized without an external magnetic field, which means the reverse field needed to reduce the magnetization to zero.
- 4- Energy product ($H_c M_r$): The new energy source and it is enhanced in increasing energy efficiency in the total energy life cycle. This energy is presented in many devices as: electric power generation and transportation.

5- Hysteresis loop: Ferromagnetism can retain a memory of an applied field when it is removed. This behaviour is called hysteresis and a plot of the variation of magnetization with magnetic field is called a hysteresis loop as shown in Figure (4.2.2).

From M-H curves shown in Figures (4.2.1.a and 4.2.1.b), it can be noticed that the as-prepared MFe_2O_4 (with $M=Co, Ni$ and Cu) show a ferromagnetic behaviour, while $ZnFe_2O_4$ reveals a superparamagnetic behaviour. After annealing at $800^\circ C$ for 16 hours, both $CoFe_2O_4$ and $NiFe_2O_4$ remain ferromagnetic, $ZnFe_2O_4$ remains also superparamagnetic. Meanwhile, $CuFe_2O_4$ becomes superparamagnetic due to the phase transformation tetragonal to cubic.

The magnetic properties (saturation magnetisation, remanence and coercivity) are slightly affected by annealing except for $CuFe_2O_4$. From Table (4.2.1) a large coercivity is recorded for both $CuFe_2O_4$ and $CoFe_2O_4$ with 698.5 and 557.0 Oe, then drops by 7-5 times for $NiFe_2O_4$ 111.2 Oe to reach a very low value of ~ 16.06 Oe for the superparamagnetic $ZnFe_2O_4$. After annealing for both $CoFe_2O_4$, $NiFe_2O_4$ and $ZnFe_2O_4$ the coercivity is not really affected by annealing, while drops drastically for $CuFe_2O_4$ reaching a very low value of 11.4 Oe due to magnetic transformation ferro-para accompanying the crystallographic transformation tetragonal $\longrightarrow$ cubic.

Also, it can be noticed that as prepared $CoFe_2O_4$ has the largest saturation magnetisation and remanence among other MFe_2O_4 nanopowders with 67.97 and 28.71 emu/g, respectively. After annealing all MFe_2O_4 nanopowders show some slight changes except $CuFe_2O_4$, both its saturation magnetisation and remanence decrease from 25.97 to 1.685 emu/g and 13.93 to 2.635×10^{-3} emu/g,

respectively. These changes are due to the phase transformation, from tetragonal to cubic as Tran firmed by XRD analysis.

4.2.2 Calibration of Magnetic moment with Remanence

The magnetic moment of elements are listed in Table (4.2.3) whereas Figure (4.2.3) shows the evaluation of saturation magnetisation versus the magnetic moment of M ions. It can be noticed the existence of good correlation (linear relationship) between M_s and magnetic moment of (Co^{2+} , Ni^{2+} and Cu^{2+}) excepted for ZnFe_2O_4 because both as prepared and annealed are superparamagnetic with very low magnetization (25.97 emu/g) while CuFe_2O_4 is subjected to phase transformation (tetragonal $\longrightarrow$ cubic) resulting in magnetic transition (Ferro- to -Para) reaching a very low magnetization (1.685 emu/g).

Table (4.2.3)

Magnetic moment of elements.

Elements	μ_{so}^* / B.M.
Co^{2+}	3.88
Ni^{2+}	2.83
Cu^{2+}	1.73
Zn^{2+}	None

* μ_{so} where is Bohr magneton

(<http://wwwchem.uwimona.edu.jm/spectra/MagMom.html>)

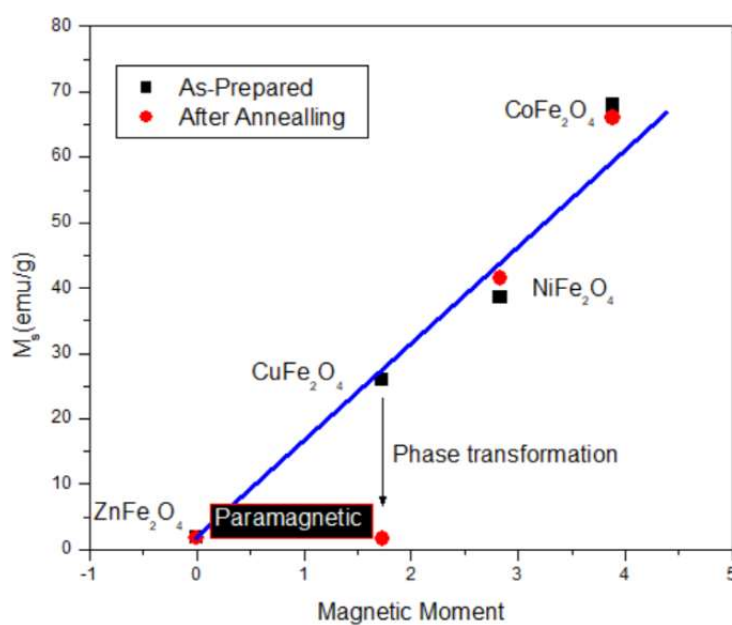


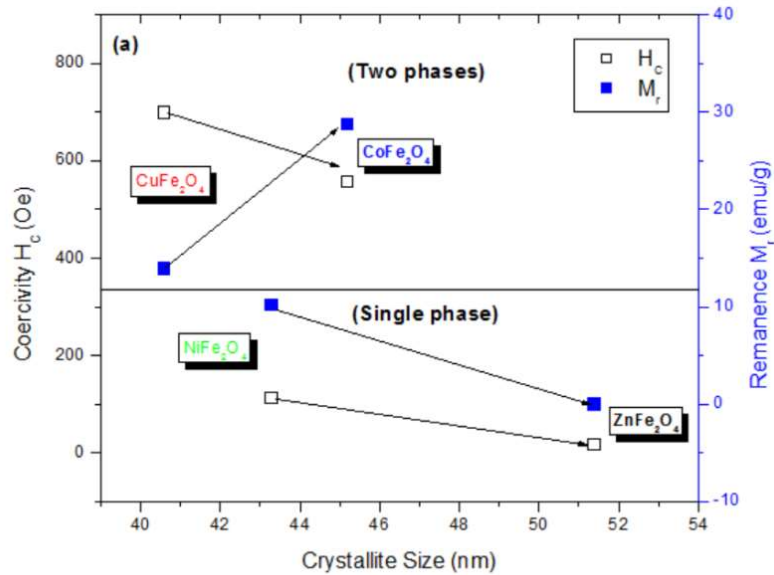
Figure (4.2.3)

Evolution of saturation magnetisation M_s vs. magnetic moment of ions (Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) for as-prepared and annealed MFe_2O_4 nanopowders

4.2.3 Correlation between Coercivity and Remanence versus Crystallite Size

Figure (4.2.4(a)) reveals a complex situation for the variation of H_c and M_r with the crystallite size that can be associated mainly with phase composition and nature of M (magnetic or non-magnetic), the following remarks can be drawn:

- (i) H_c decreases with increasing the crystallite size for all spinel phase.
- (ii) M_r decreases for single phase (M=Ni and Zn) while increases for two spinel phases (M= Co and Cu)
- (iii) After annealing, both H_c and M_r are inversely proportional to the crystallite size.



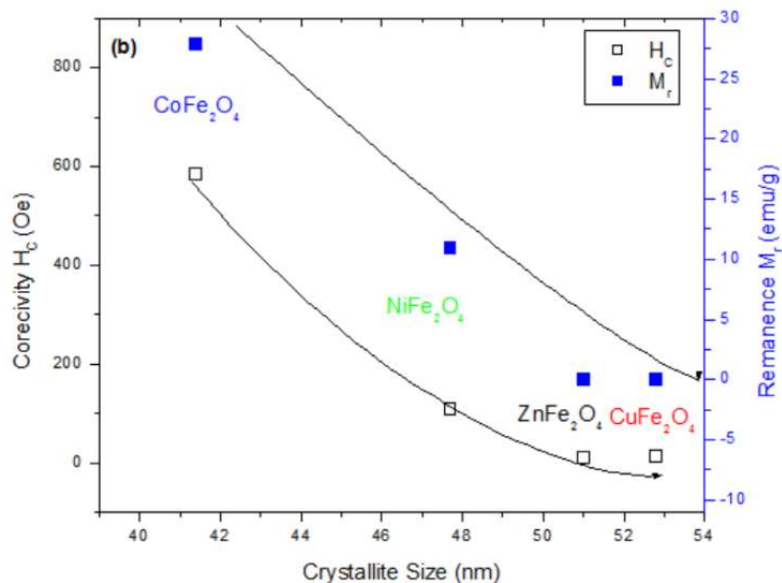


Figure (4.2.4)

**Evolution of Coercivity (H_c) and Remanence (M_r) versus crystallite size of:
(a) as prepared and (b) annealed MFe_2O_4 nanopowders**

4.2.4 Correlation between the products $H_c \cdot M_r$ versus crystallite size

For as prepared MFe_2O_4 nanopowders, with increasing the crystallite size, the product $H_c \cdot M_r$ increases for system ($M = \text{Cu}$ and Co) while decreases for system ($M = \text{Ni}$ and Zn).

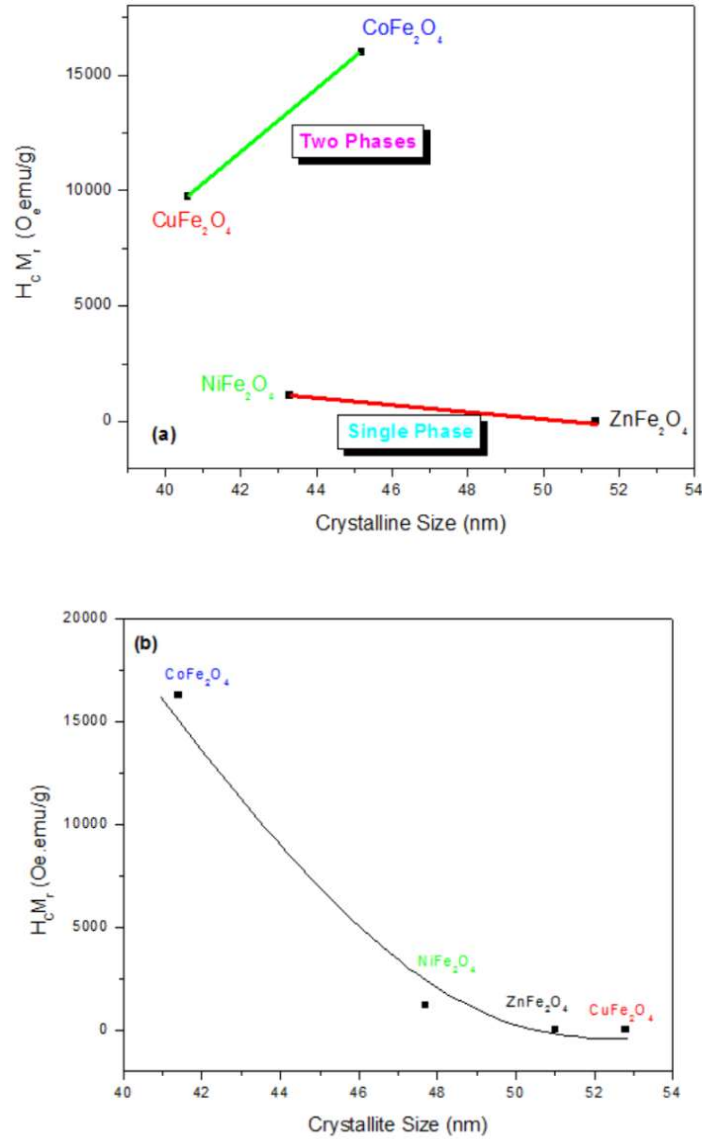


Figure (4.2.5)

Evolution of product of $H_c.M_r$ versus crystallite size for: (a) as-prepared and (b) annealed MFe_2O_4 nanopowders.

After annealing, an excellent inverse relationship in exponential manner is obtained as shown in Figure (4.2.5(b)).

$H_c.M_r$ represents the energy product, which can be considered as a new energy source and it is enhanced in increasing energy efficiency in the total energy life cycle. This energy is presented in many devices as; electric power

generation, conversion, transportation and condition, in which magnetic materials were used to improve the efficiency and the performance of devices. One example of using this energy consists on the replacement of oil-based fuel in transportation by electric motors, so the power can be changed from few watt to many hundreds of kilowatt and it is widely used in office and household appliances, transportation sector and industrial drives. This energy product is used in developed countries like USA; it decreases the consumption of electricity, saving money and reduction in CO₂ (Gulfleisch, O et al., 2011).

Chapter 4 - Section 3

SEM Analysis

Chapter 4-Section 3

4.3 SEM Scanning Electronic Microscopy Analysis

Figures (4.3.1 (a-h)) show SEM images as-prepared and annealed nanopowders of spinel ferrite MFe_2O_4 ($M=Co, Ni, Cu$ and Zn) prepared by MCM.

SEM observation of as prepared and annealed metal. SFs MFe_2O_4 ($M=Co, Ni, Cu$ and Zn) nanopowders prepared by MCM, are displayed in Figures 4.3.1(a-h). For as-prepared powders, SEM images (a-d) and (e-h) for annealed powders. SEM image (a) of $CoFe_2O_4$ shows particles with undefined shape, broad size particle distribution in the range (50-300 nm) without agglomeration while SEM image (b) for $NiFe_2O_4$ reveals particulate-network, undefined shape and broad particle size distribution in the range (30-200 nm) with high tendency to agglomeration. SEM images (c, d, g and f) for $CuFe_2O_4$ and $ZnFe_2O_4$ show particles, once again with undefined shape and ‘medium’ particle size distribution in the range (50-250 nm) with low agglomeration. In particular, SEM image (h) of annealed $ZnFe_2O_4$ reveals similar behaviour, except the particle size has quite narrow range (50-150 nm). SEM image (e) shows similar microstructure with very broad particle size distribution in the range (60-400 nm).

From SEM observations, it is evident that both as-prepared and annealed SFs powders have high tendency to agglomeration and this will cause the following; (i) decrease of surface area as well as (ii) reduction of available adsorption sites as reported by (B. Al-Najar et al.2017), where SG : sol gel ethod, SGM: sol gel modified, see Figure (4.3.2).

This will be detrimental to the adsorption of heavy metal ions from aqueous solutions.

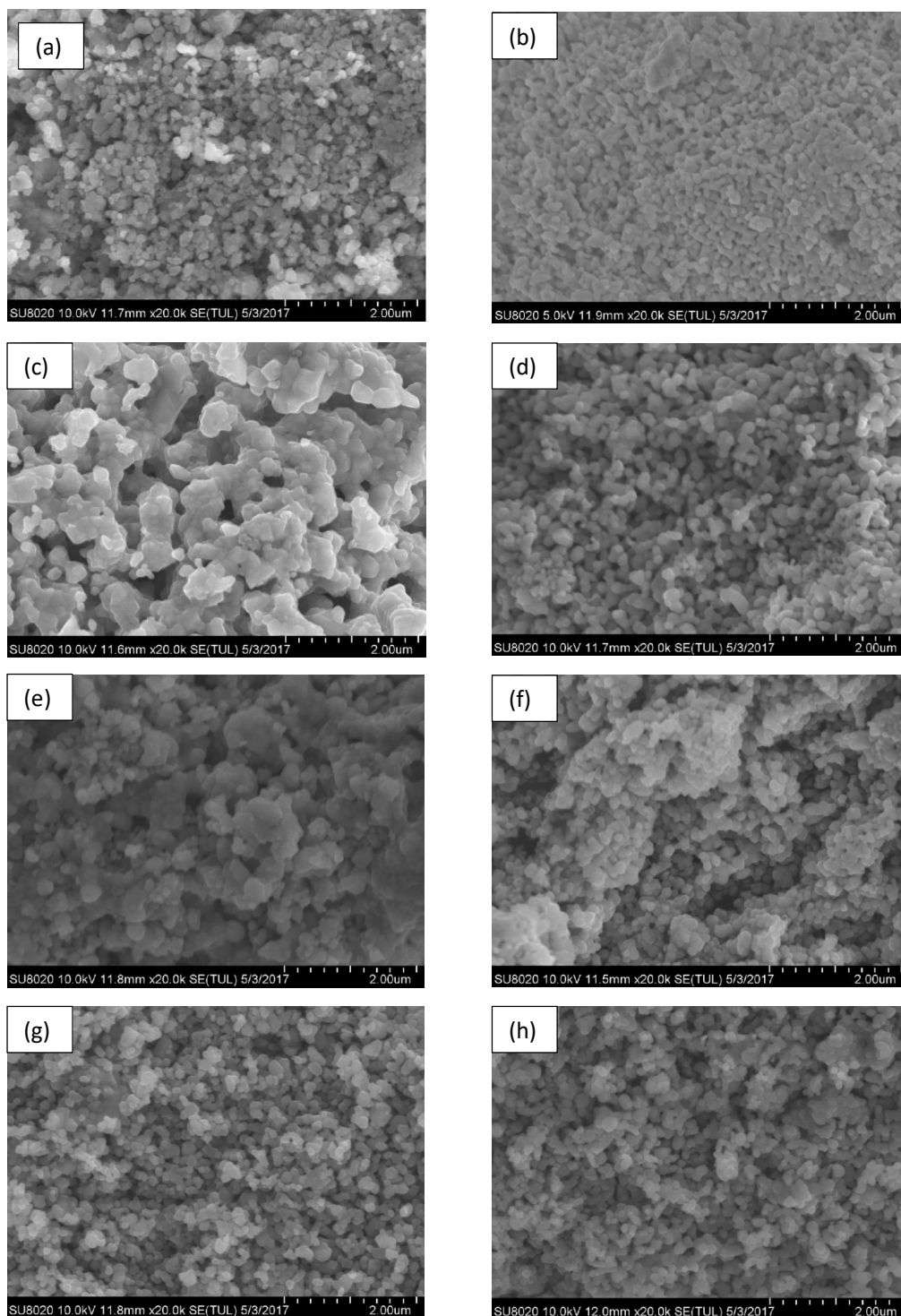


Figure (4.3.1)

SEM images of nanopowders of as-prepared (a) CoFe_2O_4 ; (b) NiFe_2O_4 ; (c) CuFe_2O_4 ; (d) ZnFe_2O_4 and annealed (e) CoFe_2O_4 ; (f) NiFe_2O_4 ; (g) CuFe_2O_4 ; (h) ZnFe_2O_4

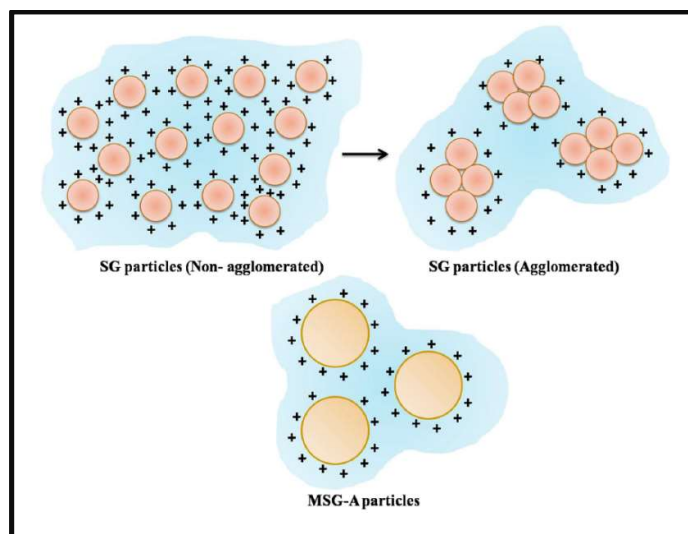


Figure (4.3.2)

Effect of agglomeration of SG and MSG-A nanopowders on the uptake of ions (Al- Najar,B et al., 2017)

Chapter 4 - Section 4
Adsorption of Heavy Metal Ions from Aqueous Solutions
Analysis

Chapter 4 - Section 4

4.4.1 Heavy metal ions removal by using MNPs

The up take tests of heavy metal ions Cd^{2+} and Pb^{2+} by MFe_2O_4 ($\text{M}=\text{Co}$, Ni , Cu and Zn) nanopowders as prepared by MCM and after annealing at 800°C for 16 h were investigated.

The residual (C_e), removal and adsorption capacity (q_e) of Cd^{2+} and Pb^{2+} in aqueous solution are reported in Tables (4.4.1(a-c)) when using of 10, 20 and 30 mg of MNPs with fixed initial concentration (C_0) of 25ppm for of Cd^{2+} and Pb^{2+} in aqueous solution before the addition of MNPs . Table(b) is obtained from Table(a) by substitution in adsorption equation, From Table (b), it is clear that for Cd^{2+} , both 10 and 20 mg, the % removal is above 50% (reaching even 59% for 20 mg for annealed NiFe_2O_4), then suddenly drops to around 44% for 30 mg. While for Pb^{2+} , the situation is different, the adsorption capacity decreases in general slightly, but indicates some enhancement after annealing: for 10 mg, we obtain 19 % for as-prepared CoFe_2O_4 then got double to 38% for annealed; while 27.7 % for as-prepared ZnFe_2O_4 then increases to 38.1% for annealed. In this study, the highest obtained adsorption capacity is 59% (31.5 mg/g) for 20 mg annealed NiFe_2O_4 and 38% (47.1 mg/g) for 10 mg annealed ZnFe_2O_4 for Cd^{2+} and Pb^{2+} , respectively.

Hereafter, a comparison of the adsorption capacity for same heavy metal ions (Cd^{2+} and Pb^{2+}) for other material as reported in the literature. For example, the removal efficiency of Cd^{2+} from aqueous solutions was found nearly same as our results; i.e. 36.48 mg/g by MgFe_2O_4 synthesized by sol-gel method and 32.48 mg/g by MgFe_2O_4 synthesized by modified sol-gel method) at RT and pH 7 (AL Najar et al., 2017). While the adsorption capacity was found much lower for maghemite $\gamma\text{-Fe}_2\text{O}_3$ prepared by wet chemical method (Ahmadi et al., 2014); it increased from 9.37 to 14.26 % when pH changed from 4.5 to 7.5, respectively. Another study (Barakat et al., 2015) reported around 48.8 mg/g of Cd^{2+} removal

when using porous magnetic silica composite prepared by surface assisted template approach at pH 6.5. Another detailed study by Bououdina et al. (Khezami et al., 2015) used milled goethite and the adsorption capacity reached an optimum value of 66.11 mg/g at pH 7, while decreases up to 30.21, 33.02, 6.11, 7.80 mg/g for pH 4, 6, 7 and 8, respectively. In addition, nanocrystalline Ni doped Fe_2O_3 at pH 6.5 (Lemine et al., 2014) adsorbed 65.462 mg/g for an optimum Ni doping of 15%. For the removal of Pb^{2+} , much higher values are obtained, reaching up to 99.63% by poly (γ -glutamic acid)-coated Fe_3O_4 MNPs (Jing et al., 2013). Meanwhile, for maghemite $\gamma\text{-Fe}_2\text{O}_3$ Prepared by wet chemical method (Ahmadi et al., 2014), the removal capacity increased from 71.29 to 92.47% by increased pH from 4.5 to 7.5, respectively. However, much lower capacity was obtained in another study (Barakat et al., 2015); about 32 mg/g at pH 6.5 for porous magnetic silica composite prepared by surface assisted template approach.

It can be concluded, as mentioned earlier, that the adsorption selectivity is intrinsic to the nature of the used material, while the capacity is dependent on several experimental parameters mainly pH and temperature of solutions; as well as shape/size (surface area), the amount of magnetic nanoparticles and surface functionalization using polymeric/porous materials.

Figure (4.4.1(a)) reveals that all as-prepared MFe_2O_4 nanopowders possess the ability to adsorb both Cd^{2+} and Pb^{2+} ions but obviously with some critical differences, due to several factors including the initial concentration of MNPs. Among the studied initial concentrations of MNPs (10, 20 and 30 mg) in this study, surprisingly and interesting, the lowest amount of 10 mg is shows the highest adsorption capacity of 69.4 and 47.1 mg/g for Cd^{2+} and Pb^{2+} , respectively. Meanwhile, the highest amount of 30 mg has the lowest adsorption capacities. For that reason, we opted to investigate the effect of much lower amount of MNPs; i.e. 5 mg and the results are reported in Table (4.4.1(d)). Once again, the obtained results are interesting, the value of adsorption capacity almost double

for Cd^{2+} (120 -122) compared to 10 mg (52-60) mg/g, while no considerable effect has been noticed for Pb^{2+} .

Additionally, Figure (4.4.1(c)) indicates that 5mg of MNPs are more efficient to remove Cd^{2+} than Pb^{2+} (almost 12 times). This means that, higher adsorption capacity for Cd^{2+} can be efficiently achieved only by small amount of MNPs. Figure (4.4.1(b)) indicates that for Cd^{2+} , the used concentration of MNPs possess different adsorption capacities, especially for 10 mg.

Table (4.4.1(a))

The residual of heavy metal ions (Cd^{2+} and Pb^{2+}) from aqueous solutions.

C_e (ppm)						
	Cd^{2+}			Pb^{2+}		
Concentration (mg)	10	20	30	10	20	30
CoFe₂O₄ as-prepared	12.2	12.0	14.6	20.2	23.3	23.1
NiFe₂O₄ as-prepared	11.9	11.9	14.6	20.3	22.0	21.8
CuFe₂O₄ as-prepared	11.9	11.4	14.4	21.4	22.9	22.3
ZnFe₂O₄ as-prepared	11.8	10.8	14.1	18.0	23.5	23.6
CoFe₂O₄ Annealed	11.9	11.1	14.3	15.6	21.5	22.0
NiFe₂O₄ Annealed	11.7	10.1	14.1	16.5	22.9	23.0
CuFe₂O₄ Annealed	11.9	11.5	14.4	19.5	22.5	15.2
ZnFe₂O₄ Annealed	11.9	11.5	14.3	15.5	22.7	22.4

Table (4.4.1(b))
The % removal efficiency of heavy metal ions (Cd^{2+} and Pb^{2+}) from aqueous solutions.

% Removal efficiency of heavy metal ions of Cd^{2+} and Pb^{2+}						
	Cd^{2+}			Pb^{2+}		
Concentration (mg)	10	20	30	10	20	30
CoFe_2O_4 as-prepared	51.2	51.8	41.6	19.2	6.8	7.5
NiFe_2O_4 as-prepared	52.3	52.3	41.6	18.8	11.9	12.6
CuFe_2O_4 as-prepared	52.3	54.5	42.4	14.3	8.4	11.0
ZnFe_2O_4 as-prepared	52.8	56.8	43.5	27.7	6.2	5.8
CoFe_2O_4 Annealed	52.5	55.5	42.8	37.6	14.0	12.0
NiFe_2O_4 Annealed	53.4	59.5	43.7	33.9	8.4	7.9
CuFe_2O_4 Annealed	52.5	53.9	42.6	22.1	10.0	39.1
ZnFe_2O_4 Annealed	52.4	54.1	42.7	38.1	9.4	10.5

Table (4.4.1(c))

Adsorption capacities of heavy metal ions (Cd^{2+} and Pb^{2+}) from aqueous solutions.

q_e (mg/g)						
	Cd^{2+}			Pb^{2+}		
Concentration (mg)	10	20	30	10	20	30
CoFe₂O₄ as-prepared	64.0	30.0	15.9	18.9	4.2	3.1
NiFe₂O₄ as-prepared	56.0	30.0	16.0	23.1	7.4	5.1
CuFe₂O₄ as-prepared	59.4	29.5	17.7	17.5	9.2	4.5
ZnFe₂O₄ as-prepared	69.4	32.9	16.9	33.6	3.8	5.0
CoFe₂O₄ Annealed	66.3	32.9	16.6	43.5	8.0	2.4
NiFe₂O₄ Annealed	56.1	31.5	16.0	41.9	5.2	3.3
CuFe₂O₄ Annealed	60.8	33.4	16.8	26.8	6.0	16.1
ZnFe₂O₄ Annealed	52.9	30.2	16.3	47.1	10.8	4.4

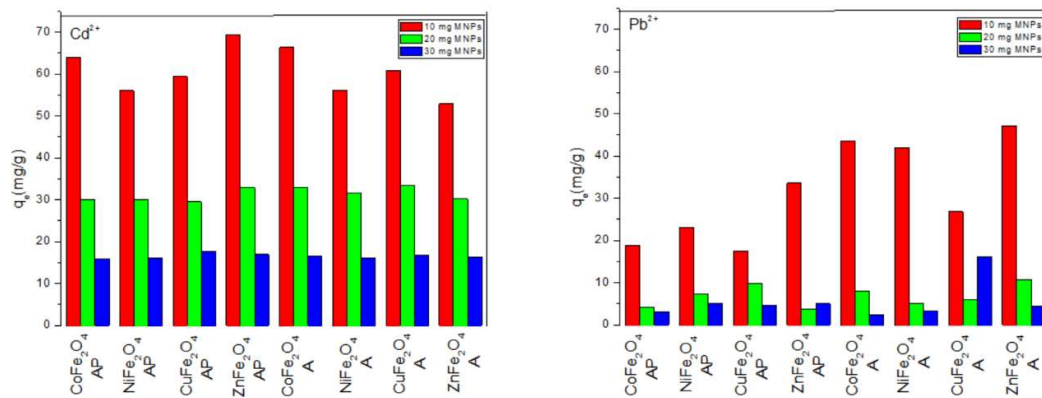


Figure (4.4.1(a))

Adsorption capacities of heavy metal ions of Cd^{2+} and Pb^{2+} at varies MNPs concentrations.

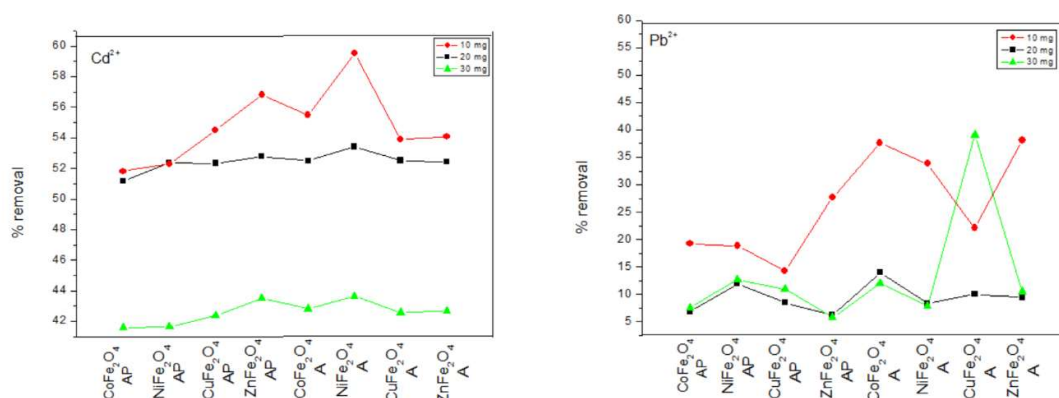


Figure (4.4.1(b))

Effect of the MFe_2O_4 (M=Co, Ni, Cu and Zn) on the removal efficiency of heavy metal ions of Cd^{2+} and Pb^{2+} .

Table (4.4.1(d))

Adsorption capacities of 5 mg MFe₂O₄ (M=Co, Ni, Cu and Zn) for heavy metal ions from aqueous solution: Cd²⁺ and Pb²⁺ in pH =2

5 mg of MFe₂O₄ to remove Cd²⁺ and Pb²⁺						
	Cd²⁺			Pb²⁺		
Mass (mg)	C_e (ppm)	removal %	q_e (mg/g)	C_e (ppm)	Removal %	q_e (mg/g)
CoFe₂O₄ as prepared	12.9	48.5	121.3	24.4	2.6	6.4
NiFe₂O₄ as prepared	12.9	48.5	121.2	24.5	2.0	5.2
CuFe₂O₄ as prepared	12.8	48.8	122.1	24.9	0.3	0.7
ZnFe₂O₄ as prepared	12.7	49.4	123.5	24.2	3.1	7.7
CoFe₂O₄ Annealed	12.9	48.3	120.8	23.3	7.0	17.5
NiFe₂O₄ Annealed	12.8	48.7	121.7	24.1	3.5	8.7
CuFe₂O₄ Annealed	12.8	48.7	121.8	23.7	5.2	13.1
ZnFe₂O₄ Annealed	12.9	48.6	121.4	24.0	3.9	9.7

Table (4.4.1(e))

Adsorption capacities of 5 mg MFe₂O₄ (M=Co, Ni, Cu and Zn) of heavy metal ions from aqueous solution: Cd²⁺ and Pb²⁺ in pH =12

5 mg of MFe₂O₄ to remove Cd²⁺ and Pb²⁺						
	Cd²⁺			Pb²⁺		
Concentration (mg)	C_e (ppm)	removal %	q_e (mg/g)	C_e (ppm)	Removal %	q_e (mg/g)
CoFe₂O₄ as prepared	11.5	54.0	135.1	23.6	5.5	13.8
NiFe₂O₄ as prepared	10.5	57.9	144.9	22.2	11.4	28.5
CuFe₂O₄ as prepared	11.5	54.1	135.3	22.9	8.4	21.1
ZnFe₂O₄ as prepared	10.6	57.5	143.7	22.9	8.3	20.8
CoFe₂O₄ Annealed	10.4	58.4	146.1	18.7	25.3	63.1
NiFe₂O₄ Annealed	10.9	56.5	141.3	22.3	10.8	27.0
CuFe₂O₄ Annealed	9.2	63.1	157.7	21.9	12.4	31.1
ZnFe₂O₄ Annealed	11.5	54.0	135.1	21.8	12.7	31.9

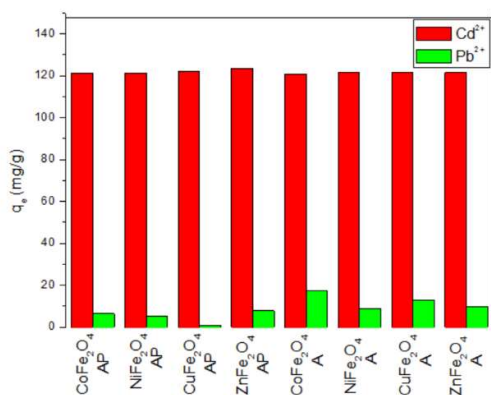


Figure (4.4.1(c))

Adsorption capacities of heavy metal ions Cd²⁺ and Pb²⁺ by using 5 mg of MNPs.

4.4.2 Effect of pH on Adsorption of Heavy Metal Ions

The effect of pH on the removal of Cd^{2+} and Pb^{2+} is tested by changing the value of pH from 2 to 12 at room temperature using 5 mg of MNPs are reported in Table (4.4.1(e)). The results are shown in Figure (4.4.1(d)). It is evident that the adsorption capacity in basic media is better than acidic media for both Cd^{2+} and Pb^{2+} , but Pb^{2+} has relatively more important change, almost more than double; (6.4 to 13.8, 5.2 to 28.5, 0.7 to 21.1, 7.7 to 20.8, 17.5 to 63.1, 8.7 to 27.0, 13.1 to 31.1 and 9.7 to 31.9) for as-prepared CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 , ZnFe_2O_4 , annealed CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 , ZnFe_2O_4 , respectively. The pH value is important parameter in adsorption, because it enhances to change the conformation of molecular structure, influences the stability and speciation of metals (Jing et al., 2013).

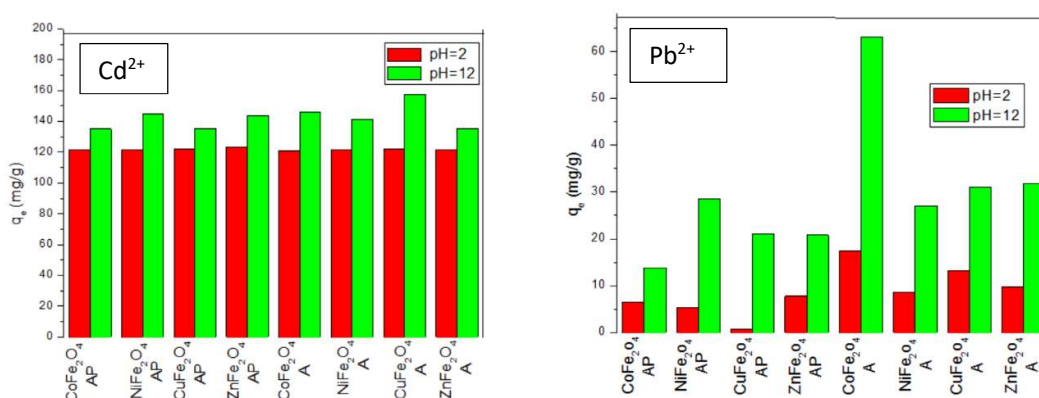


Figure (4.4.1(d))

Adsorption capacities of for heavy metal ions Cd^{2+} and Pb^{2+} by using 5 mg of MNPs in pH=2 and pH=12.

Chapter 5

**SUMMARY, CONCLUSIONS AND FUTURE
RESEARCH WORK**

Summary, Conclusion and Future Research Work

My MSc thesis consists of four main chapters. Chapter 1 presents a general introduction, starting by discussing nanotechnology and its applications; Advantages of nanomaterials; water scarcity and water pollution; types and main causes of wastewater contamination and the diseases that may be related to water pollution. After that, a description of the crystal structure of spinel ferrites (SFs) and their properties with potential applications. Iron-based spinel system was adopted in this study (MFe_2O_4 where M is Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}). Previous studies showed that Ferrites have great potential in the adsorption of heavy metal ions from aqueous solutions. Both aim and objective of this project are presented.

Chapter 2 describes the Structure and Magnetic Properties of MFe_2O_4 nanoparticles (NPs); the adsorption technique which is widely used in wastewater treatment; followed by a literature review about Properties and applications of AB_2O_4 were compared with data obtained from the literature.

In Chapter 3, the synthesis of MFe_2O_4 (M = Zn, Cu, Ni, Co) NPs by microwave combustion method (MCM) is presented, followed by annealing at 800 C° for 16 hours in order to enhance crystallinity, better chemical homogeneity, phase composition and magnetic properties. In addition, both fundamental background and procedure of the different characterization techniques used in this project were presented including X-ray diffraction technique (XRD), vibrating scanning microscope (VSM) and Scanning Electron Microscopy (SEM). The adsorption of heavy metal ions by MNPs by batch technique for Cadmium and Lead up-take, is adopted where the effects of MNPs concentration and pH were investigated.

The analysis of the obtained results are discussed in chapter 4. In- depth analysis and correlation between different structural (lattice parameters, volume) and microstructural (particles morphology and size) parameters with the corresponding magnetic properties (coercivity, remanence, saturation

magnetisation) is presented. Heavy metal ions (cadmium and lead) were removed by using MNPs at various MFe_2O_4 quantities (10, 20 and 30 mg) and among these quantities 10 mg was detected to have the best adsorption capacity. Moreover, the adsorption capacity is influenced by pH; a basic media is found to be better than acidic for both Cd^{2+} and Pb^{2+} , but Pb^{2+} shows a much higher capacity (almost double).

The obtained results indicate that (MCM) method is very suitable to prepare Ni and Zn spinel ferrite (single phase), while Co and Cu spinel ferrite reveal the presence of some amounts of a secondary phase even after annealing. The as-prepared spinel ferrite nanopowders display excellent removal of Cd^{2+} and Pb^{2+} from aqueous solutions, with a maximum adsorption of Cd^{2+} and Pb^{2+} of 69.4 and 47.1 mg/g at pH 2, respectively. The selectivity of Cd^{2+} and Pb^{2+} adsorption onto CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 and ZnFe_2O_4 MNPs was in advantage to Cd^{2+} . Therefore, the studied spinel ferrite nanopowders can be considered as potential candidates for Cd^{2+} and Pb^{2+} removal for wastewater.

Difficulties and Challenges

- 1- The use of samples of MFe_2O_4 nanopowders for the adsorption of Cadmium and Lead from aqueous solution after long time from being characterized.
- 2- It was difficult to weigh small amounts of magnetic nanoparticles by the digital scale available in Chemistry Department (4 digits).
- 3- Magnetic Stirrer couldn't be set for one period of 12 hours, so it was rather divided for two periods of 6 hours.

Recommendations

- 1- Perform adsorption measurements using small amounts of MNPs.
- 2- Adsorption measurements should be performed immediately after characterisations (XRD and VSM); or the nanopowders should be stored in glove box under inert gas (Nitrogen or Argon) in order to avoid any contamination (nanopowders have high surface area and can up-take oxygen from air and form oxides layer on surface of particles and thereby reduce their activity).
- 3- Make sure of the availability of AAS lamps before adopting heavy metal ions.

Conclusions

My MSc research project has successfully achieved its objectives; the removal of heavy metal ions (Cd^{2+} and Pb^{2+}) from aqueous solution by adsorption method. The as-prepared spinel ferrites nanopowders were subjected to annealing at 800 C for 16 hours, then fully characterized by XRD, VSM and SEM. Annealing achieved the transformation of CuFe_2O_4 to single phase. The magnetic properties (saturation magnetization, remanence and coercivity) were found to slightly change after annealing, except CuFe_2O_4 exhibited a major change as it transformed from ferromagnetic to superparamagnetic due to phase transformation from tetragonal to cubic. The adsorption process has been found to be dependent on the initial concentration of MNPs, annealing temperature, time and pH and all experimental parameters had been fixed, while varying pH value. Finally, it can be concluded that adsorption as an inexpensive, easy and rapid method (take only 12 hours, or even less), can be adopted for the removal of heavy metal ions (in this study Cd^{2+} and Pb^{2+}) from wastewater.

Aspirations for Future Research Work

- Increasing the removal efficiency of heavy metal ions from aqueous solutions via adsorption process by the development of composites based on our spinel ferrite nanopowders.
- Perform adsorption measurements for other heavy metals such as mercury (Hg), arsenic (As), chromium (Cr), nickel (Ni), cobalt (Co), etc.
- Perform adsorption tests on aqueous solutions containing mixed heavy metal ions.
- Conduct treatment of wastewater from other contaminants such as inorganic compounds and organic compounds by using the as- prepared spinel ferrite nanopowders.

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الملخص:

في هذا البحث تم تحضير مواد الإسبينيل فريت النانوية بواسطة طريقة الإحتراق الميكرويفية, من نترات المعادن الكوبلت , النيكل, النحاس والزنك مع نترات الحديد كمفاعلات مؤكسدة مع وقود اليوريا. بالنسبة لتحليل المواد بواسطة أنماط حيود الأشعة السينية وجد أن مادة الكوبلت والنحاس الإسبينيل فريت مواد ثنائية الطور ، بينما وجد ان مواد النيكل والزنك الإسبينيل فريت أحادية الطور. حجم البلورات يتراوح بين 40-51 نانومتر. بعد تسخين المواد عند حرارة 800 درجة سيليزيه لمدة زمنية 16 ساعة وجد أن جميع المواد أصبحت أحادية الطور ماعدا مادة الكوبلت الإسبينيل فريت. تم تحليل المواد وإجراء القياسات باستخدام تقنيات عديدة مثل: حيود الأشعة السينية وجهاز قياس المغناطيسية للمواد بالاهتزازات و المجهر الإلكتروني الماسح. كشفت منحنيات الحقل المغناطيسي نوعية المواد المغناطيسية لكل مادة حيث وجد إن الكوبلت, النيكل والنحاس الإسبينيل فريت مواد فيرومغناطيسية بينما الزنك الإسبينيل فريت مادة بارامغناطيسية وبعد تسخين المواد تحولت مادة النحاس الإسبينيل فريت من فيرومغناطيسية إلى بارامغناطيسية نتيجة التحول في الطور من رباعي الأضلاع إلى مكعب الناتج من التسخين عند درجة حرارة عالية. يمكن الإستنتاج إن طريقة التحضير بواسطة الإحتراق الميكرويفية مناسبة جدا لتحضير هذه المواد. المواد المحضرة النانوية استخدمت في إختبار إزالة أيونات المعادن السامة من الوسط المائي مثل أيونات الكاديوم والرصاص عند تركيزات مختلفة من المواد النانوية 10 و 20 و 30 ملغرام ودرجة حموضة الوسط المائي مختلفة 2 و 12. ووجد أن كمية الأمتصاص تزداد عند كمية 10 ملغرام . ووجد أن قدرة الإمتزاز تتأثر بدرجة حموضة الوسط المائي و أن الوسط القلوي أفضل من الوسط الحمضي في قدرة الإمتزاز حيث تصل إلى الضعف.

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قسم الفيزياء

كلية العلوم



وصف وإزالة أيونات المعادن الثقيلة بواسطة إستخدام مواد نانوية من مياه الصرف

رسالة بحث لإستكمال متطلبات الحصول على درجة الماجستير في الفيزياء التطبيقية

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