Journal of Applied Sciences and Nanotechnology

Journal homepage: jasn.uotechnology.edu.iq

A Review of Structure, Properties, and Chemical Synthesis of Magnetite Nanoparticles

[1]Nwar A. Yousif*, [1]Selma M. H. Al-Jawad, [1]Ali A. Taha, [2]Haralambos Stamatis

[1]Department of Applied Sciences, University of Technology – Iraq
[2]Department of Biological Applications and Technologies (DBAT), University of Loannina – Greece

A R T I C L E I N F O

Article history:
Received: June, 17, 2022
Accepted: August, 29, 2022
Available online: June, 10, 2023

Keywords:
Nanoparticles,
Fe_3O_4,
Chemical methods

Corresponding Author:
Nwar A. Yousif
nwar.a.yousif@uotechnology.edu.iq

A B S T R A C T

In recent years, extensive studies have been devoted to iron oxide nanoparticles (IONPs). Iron oxides are chemical compounds that have various polymorphic forms, including maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), and Hematite (α-Fe_2O_3). Among them, the most important studied is magnetite (Fe_3O_4) due to its low cost and low toxicity and its unique magnetic and physicochemical characteristics, which qualify it for use in various biomedical and technological applications. Magnetic particles should be small and have a narrow size distribution for these applications. The smaller the size of the iron oxide particles, the greater their reactivity and biodegradability. In this review, we display summary information on magnetite (Fe_3O_4) nanoparticles in terms of structure, characteristics, and preparation methods. Because the prepared strategy has been proven to be critical for preferable control of the particle size and shape, in addition to producing monodispersed magnetite (Fe_3O_4) nanoparticles with a direct effect on their characteristics and applications, special attention will be placed on chemical preparation techniques including Hydrothermal synthesis, Coprecipitation technique, Sol-Gel process, and thermal decomposition method. This review offers specific information for selecting appropriate synthetic methods for obtaining appropriate sizes, shapes, and magnetic properties of magnetite (Fe_3O_4) nanoparticles (NPs) for target applications.

https://doi.org/10.53293/jasn.2022.5179.1178, Department of Applied Sciences, University of Technology - Iraq.

1. Introduction

Nanoparticles (NPs) have a higher surface area than macro-sized particles. At the atomic level (1–100) nm, NPs are referred to as controlled or manipulated particles. They exhibit size-related characteristics that vary significantly from bulk materials. Compared to similar materials in bulk dimensions, these structures have distinct and desirable chemical and physical properties, such as a unique surface area and optical, magnetic, electrical, thermal, and mechanical behaviour [1-6]. Magnetic nanoparticles (MNPs) contain numerous distinct magnetic properties, including high magnetic susceptibility, high coercivity, superparamagnetic, low Curie temperature, etc. [7]. MNPs have piqued the attention of researchers due to their fascinating properties and wide range of diverse applications in high-density data storage, ferrofluids, and catalysts. In bioapplications, containing detection of biological entities (viruses, bacteria, enzymes, nucleic acids, cells, protein, etc.) and magnetic bioseparation [7].

In addition, MNPs have been employed to create heat to treat hyperthermia, produce contrast influences for magnetic imaging, and dominate targeted drug delivery remotely [8]. Iron oxide nanoparticles have been identified as the best candidate for various factors. (1) abundance, (2) simple preparation, (3) simple access to several oxidation states and polymorphs, (4) a diverse range of electrical and magnetic properties, and (5) Iron oxide nanoparticles are an appropriate prototype of functional material with a varied spectrum of electrical and magnetic properties due to their low toxicity and spontaneous elimination [9]. In addition, due to their high biocompatibility, iron oxide nanoparticles are promising nanomaterials. The biocompatibility of iron oxide nanoparticles is the primary factor propelling significant research efforts to commercialise these nanoparticles for use in sophisticated medical technology applications [8, 10, 11]. Iron oxide can be found in variations of forms in nature. The most prevalent are hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4) [12, 13]. Magnetite (Fe_3O_4) is a promising candidate among known crystal polymorphs of iron (III) due to its biocompatibility and biodegradable activity [14]. Fe_3O_4 NPs exhibit either superparamagnetic (if the size is under 15 nm) or ferromagnetic behaviour [8]. Magnetite is a naturally occurring mineral that has been widely utilised in biological applications, including magnetic separation, magnetic drug delivery, magnetic resonance imaging, and magnetic hyperthermia [8, 15-20]. The physical, chemical, and biological approaches are the three most significant reported routes for creating Fe_3O_4 nanoparticles [21, 22]. Chemical methods have an advantage over physical and biological ones when developing new materials with higher chemical homogeneity by combining different precursors and carefully regulating nanoparticle size, shape, and content. The chemical pathway also saves time and money because it does not require expensive tools or ingredients, making it a suitable method for manufacturing nanoparticles. Yet, the chemical method has significant downsides, such as producing excess intermediates and contaminants and the possibility of colloidal agglomeration occurring during the synthesis process [23]. In this paper, we will focus on the influence of chemical synthesis on the geometries, sizes, and, thus, magnetic characteristics of magnetite NPs, in addition to the structure and summary of the properties of Fe_3O_4 nanoparticles.

2. Iron Oxides

There are eight known iron oxides [24]. Because of their polymorphism, which involves temperature-induced phase transitions, Hematite, maghemite, and magnetite are such widespread candidates among these iron oxides, and each one has distinct catalytic, magnetic, biochemical, and characteristics that make them suitable for a variety of biomedical and technical applications [25].

2.1 Hematite (α-Fe_2O_3)

With an antiferromagnetic order below Néel temperature and a corundum crystal structure, α-Fe_2O_3 is the most stable iron oxide phase (955 K). Two-thirds of the octahedral sites limited through the roughly ideal hexagonal close-packed Oxygen lattice are occupied by Fe^{3+} ions, as revealed in Fig. 1(a). Due to its inexpensive and high corrosion resistance, Hematite (α-Fe_2O_3) is commonly used in gas sensors, pigments, and catalysts and as a source for preparing magnetite and maghemite. Hematite is a 2.1 eV band gap n-type semiconductor under the circumstances of the environment [25- 27].

2.2 Magnetite (Fe_3O_4)

Magnetite has a face-centred cubic with an inverse spinel structure, set up on thirty-two Oxygen ions and packed closely along the direction [28]. Magnetite includes both divalent and trivalent iron, unlike most other iron oxides. Fe^{2+} ions occupy 1/2 octahedral positions, and the Fe^{3+} ions are distributed equally across the residual tetrahedral and octahedral positions. Fe^{3+} ions in the A and B positions are antiferromagnetically coupled, whilst Fe^{2+} ions in the B position participate in macroscopic ferromagnetic characteristics, as displayed in Fig. 1(b). Fe^{3+} ions within the A and B positions are coupled antiferromagnetically, while Fe^{2+} ions within the B position share macroscopic ferromagnetic characteristics. The divalent irons can be replaced partially or completely by another divalent ion (Zn, Mn, Co, etc). So, magnetite can be either p-type or n-type semiconductors. Due to its low band gap (0.1 eV), magnetite possesses the lowest resistivity among all iron oxides. Fe_3O_4 readily undergoes a phase transformation to maghemite at room temperature [25, 27].

2.3 Maghemite (γ-Fe_2O_3)

Maghemite has a cubic structure; each unit of γ- Fe_2O_3 has 21⅓ Fe^{3+} ions, 2⅓ vacancies, and 32 O^{2-} ions. The O2− ions form a cubic packed close array, whilst the Fe^{3+} is spread between tetrahedral sites (8 Fe ions per unit cell) and octahedral positions (the residual iron ions and vacancies), as shown in Fig. 1 (c). Maghemite is oxidised magnetite and a 2.0 eV bandgap n-type semiconductor. An inexpensive technique can synthesise maghemite with good dispersivity in aqueous media. It is classified as a ferromagnetic oxide with a spinel structure nearly that of magnetite [25, 27].

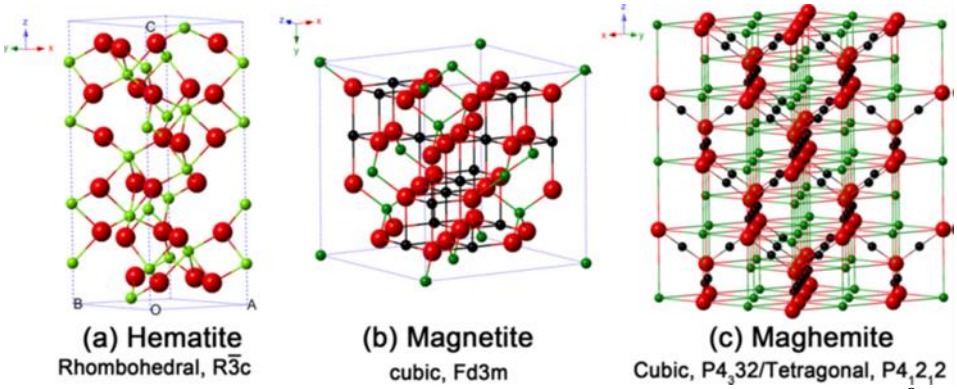

Figure 1: Crystal structure of the Hematite, Magnetite, and Maghemite (the black ball is Fe^{2+}, the green ball is $Fe^{3+,}$ and the red ball is O^{2-}) [25].

3. Properties of Magnetite (Fe_3O_4) Nanoparticles

The magnetic characteristics of Fe_3O_4 NPs are controlled via the size of the particle. When ferrimagnetic Fe_3O_4 NPs are small enough, they exhibit superparamagnetic attributes with a great response to the magnetic field applied. Fig. 2 depicts the transformation of ferrimagnetic to superparamagnetic characteristics, where the MNPs change to single-domain magnetism from multi-domain magnetism as their size decreases. The increase of coercivity to a maximum value is due to the reduction in size to a specific size called the critical diameter, Ds. At this point, the magnetic spins indicate the same direction, improving the magnetic property, and MNPs are typically hard to demagnetise due to their high coercivity. Decreasing size rapidly reduces the coercivity value until it equals zero; at this point, the NPs are said to be in a superparamagnetic state. Generally, Fe_3O_4 NPs with diameters less than 20 nm have superparamagnetic properties [8, 23].

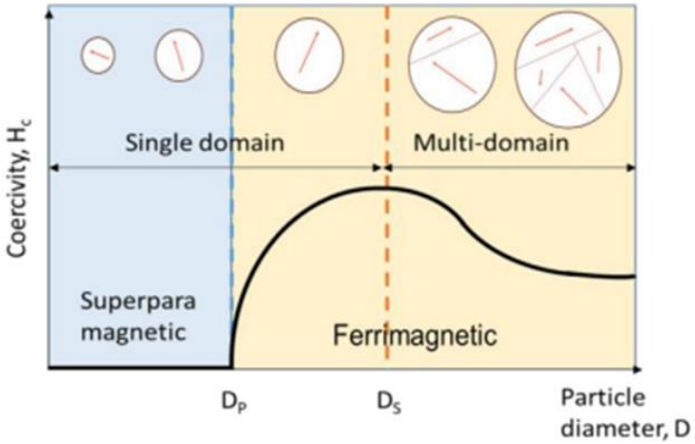

Figure 2: Relation between coercivity, HC, and magnetic particle diameter, D [23].

As displayed in Fig. 3, superparamagnetic Fe_3O_4 NPs differ from ferrimagnetic particles in that they lack coercive force and hysteresis loops because of single-domain magnetism, allowing them to be magnetised just in the existence of an external magnetic field. As a result, employing an external magnetic field to control these superparamagnetic Fe_3O_4 nanoparticles is simple. Superparamagnetic nanoparticles exhibit a stronger and quicker magnetic response to an external magnetic field, which is also worth noticing [23].

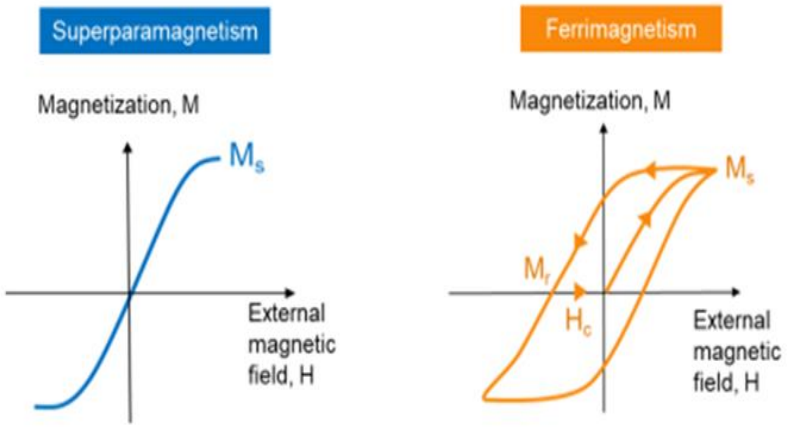

Figure 3: Magnetization vs the applied field (M–H) curve of the superparamagnetism (blue colour) and ferrimagnetism (orange colour) [23].

Table 1 displays the physical and magnetic properties of Fe_3O_4 NPs [24, 29, 30]. The saturation magnetisation values are the most important feature in the biological field. High saturation magnetisation values improve drug delivery to cancer cells, image projection resolution in MRI, and heat dissipation in MHT.

Table 1: Summary of the properties of Fe_3O_4 nanoparticles.

Property	Magnetite
Molecular formula	Fe_3O_4
Type of magnetism	Ferrimagnetic
Density (g/cm^3)	5.18
Curie temperature (K)	850
Saturation magnetisation (Ms) at 300K [$emug^{-1}$]	92–100
Melting point (^oC)	1583-1597
Standard Gibbs free energy of formation ($\Delta G_f 0$) [kJ/mol]	-1012.6
Structural type	Inverse spinel
Crystallographic system	Cubic
Lattice parameter (nm)	a = 0.8396
Lattice angles	$\alpha = \gamma = \beta = 90$
Band gap energy (Eg) [eV]	2.6
Color	Black
Formula units/unit cell	8
Hardness	5.5

4. Chemical Methods for Synthesis of Fe_3O_4 NPs

A typical magnetite preparation reaction is explained below by depicting the compound's composition [29].

$$\underset{\text{(Ferrous Oxide)}}{FeO} + \underset{\text{(Ferric Oxide)}}{Fe_2O_3} \longrightarrow \underset{\text{Magnetite}}{Fe_3O_4}$$

Much research has been developed in the last few decades to prepare iron oxide nanoparticles, and considerable studies have been published that describe efficient synthesis methods for producing stable, biocompatible, shape-controlled, and monodispersed iron oxide NPs. Hydrothermal synthesis [7], Coprecipitation [31], Sol-Gel, and thermal decomposition methods [28] are all Chemical methods for producing high-quality magnetite NPs.

4.1 Hydrothermal Synthesis

These reactions occur in aqueous media in autoclaves or reactors where the pressure (generally between 0.3 and 4 MPa) and temperature can be adjusted (in general from 130-250ºC. To achieve supersaturating, hydrothermal procedures depend on the capability of water to hydrolyse and dehydrate metal salts at extreme conditions, as well as the very low solubility of the resultant metal oxides in water at these limits [7, 32]. Iron oxide NPs with appropriate shape and size control are technologically significant because of the robust correlation between these parameters and magnetic characteristics [33]. The hydrothermal approach is environmentally friendly, inexpensive, and straightforward, and the reaction was carried out at relatively low temperatures. This technique controls particle size in crystallisation and morphology via reaction time and temperature, allowing for the creation of high-quality nanoparticles [28, 34-38]. The hydrothermal method is sometimes used to prepare single crystal particles free of dislocation defects, and grains created in this technique may possess higher crystallinity than grains formed in other methods, implying that hydrothermal synthesis is more likely to produce iron oxide NPs with highly crystalline [7]. Many researchers successfully fabricated iron oxide NPs by hydrothermal method [39-44]. In 2014 [40], conducted a comprehensive investigation of the influence of reaction time and temperature on particle size in this process. As stated by transmission electron microscopy examination, the size of the NPs increased from (14.5- 29.9) nm at a reaction temperature raised from 100 – 180°C for twelve hours. At 180°C, the size of nanoparticles grows from (20.6 –123.44) nm as the reaction time was raised from (1 – 48) h. This means that the reaction times had a more significant impact on the particle size than temperature. N. Gómez *et al*. [28] fabricated Fe_3O_4 NPs via a hydrothermal process. In addition, they investigated the influence of reaction temperature on the morphology, phase structure, particle size, and shape of products. The X-ray diffraction pattern displayed that all the NPs were Fe_3O_4 in a pure magnetite phase. The produced NPs had uniform morphology with a high level of crystallinity at all temperatures, as noticed by TEM. Fig. 4 revealed a TEM image of NPs prepared at 120ºC. As a result, by elevating the temperature to 120°C, 140°C, and 160°C, it was feasible to create quasi-spheres, octahedrons, and cubes in the nanometric regime. The hydrothermal method was chosen by S. Ni et al. [44] to produce well-dispersed, well crystallised and high-purity Fe_3O_4 nanoparticles, which this method can quickly obtain. The product was received at 90 C for 24 h with an average diameter of approximately 160 nm in the presence of sodium sulfate. S. Ahmadi *et al*. [43] have used a facile hydrothermal technique to fabricate highly crystallite Fe_3O_4 nanocrystals. The calculated average crystallite sizes are 13.4, 20.8, and 22.8 nm for the magnetite formed at 100, 150, and 200ºC, sequentially. It is suggested that elevated temperature is desirable for preparing bigger magnetite NPs. Both crystallite and average particle sizes of the magnetite NPs are identical, showing the single-crystal structure of the crystals. The formed magnetite nanocrystals have superparamagnetic behaviour, whereas the saturation magnetisation and the coercivity increment with the increment of the hydrothermal temperature. The increment of both the saturation magnetisation and the coercivity of the magnetite nanocrystals can be referred to as the spin canting influence and the reduced ratio of the surface-to-volume of the nanocrystals. Fig. 5 displays the hydrothermal synthesis of IONPs.

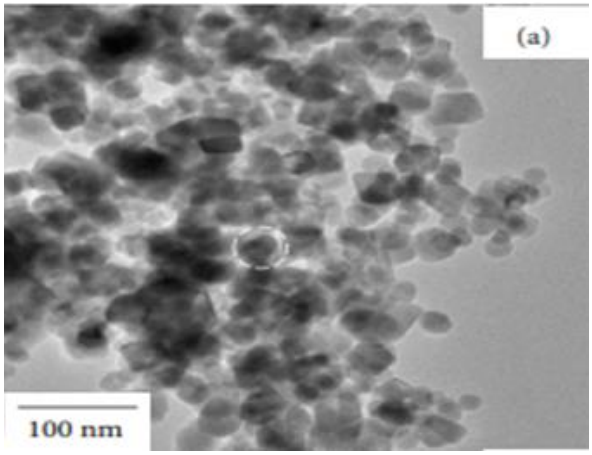

Figure 4: TEM image of the Fe_3O_4 NPs at 120ºC [28].

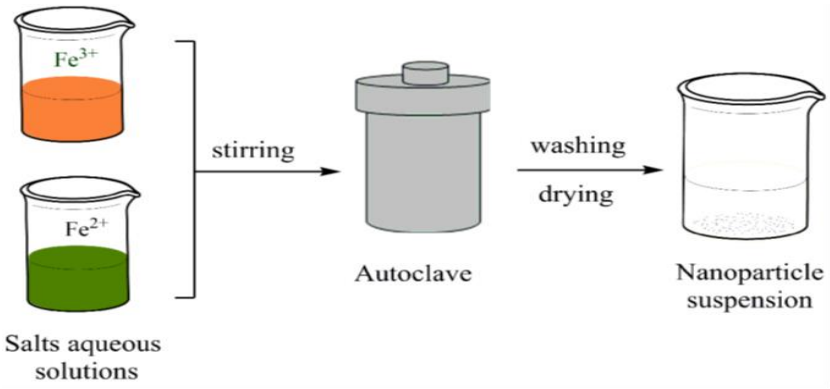

Figure 5: Hydrothermal synthesis of IONPs [45].

4.2 Coprecipitation

Coprecipitation is the most generally utilised method for producing Fe_3O_4 because of its advantages, including an inexpensive and simple synthetic procedure, a high-yield product with exceptional magnetic and crystal characteristics, and an inorganic reactant. This process involves mixing ferric and ferrous ions in fundamental solutions at elevated or room temperatures in a 2:1 molar ratio. The morphology and size of the Fe_3O_4 NPs rely on the type of salt utilised (e.g. nitrates, perchlorates, chlorides, sulfates, etc.), ionic strength of the media, the PH value, the growth temperature, the ferric and ferrous ions ratio, and the other factors (e.g. dropping speed of basic solution, stirring rate) [46-48]. Fig. 6 reveals a schematic representation of Fe_3O_4 NPs formation during chemical coprecipitation. S. ISLAM *et al*. [47] investigated the comparative formation of Fe_3O_4 NPs by coprecipitation and hydrothermal methods. The results reveal that the coprecipitation method is better in terms of particle size, saturation values of magnetisation, and heat dissipation capability. In contrast, the hydrothermal method is better regarding absorbance (reflectance) and particle shape.

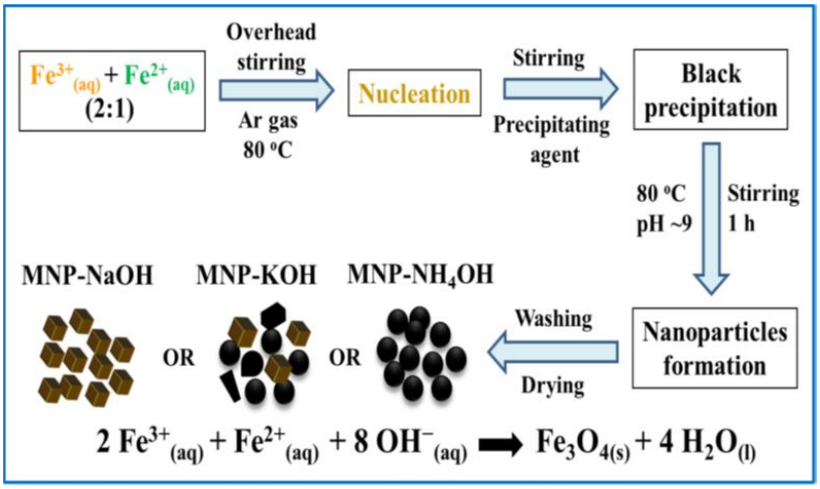

Figure 6: Schematic representation of SPIONs formation during chemical coprecipitation [49].

M. Tajabadi and M. E. Khosroshahi [50] reported the influence of alkaline medium temperature and concentration on significant properties of Fe_3O_4 NPs. Ferrous chloride hexahydrate and ferric sulfate heptahydrate are used as iron sources. At two different temperatures, i.e. 25 and 70°C, NH_4OH with (0.9-2.1) M concentration was utilised as an alkaline precursor. These results display that the particles prepared at higher temperature (70°C) and minimum alkaline concentration (0.9 M) possess the largest saturation magnetisation, at 70°C around 68 emu/gr, in comparison with the smallest particle size at 25°C about 63 emu/gr. R. Rahmawati *et al*. [51] studied the influence of the frequency of ultrasonic waves and the stirring rate on the particle size of magnetite NPs prepared via coprecipitation protocol. Until 700 rpm, the average crystallite size of Fe_3O_4 NPs reduced from 24.0 to 22.3 nm, then incremented to 25 nm up to 900 rpm. TQ. Bui *et al*. [52] prepared monodisperse magnetite nanoparticles

by an ultrasonically enhanced coprecipitation process. The TEM images revealed that the magnetite had homogeneously spherical nanoparticles in the form of nanoparticle agglomerates with an average diameter of 10 nm, as revealed in Fig. 7. Their research indicated that the magnetic responsiveness of Fe_3O_4 NPs generated by coprecipitation is dependent on the particle sizes and that the magnetic responsiveness increment as the particle size decreases.

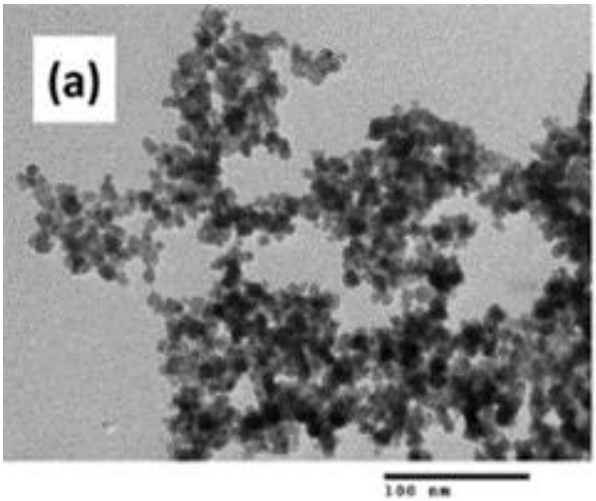

Figure 7: TEM image of Fe_3O_4 NPs [52].

4.3 Sol-gel

The sol-gel technique is popular because of its inexpensive cost, low sintering temperature, and capability to modify the particle size with homogeneous components [53-58]. The Sol-gel process starts with hydrolysis and poly-condensation to make a gel. Fig. 8 shows a schematic diagram of the sol-gel process for producing nanopowders. This process is an appropriate wet chemical technique for producing metal oxide nanoscale with particular characteristics [27, 30, 59]. One of the most significant disadvantages of this approach is accumulation during the washing operation, which makes it incapable of producing monodispersed nanoparticles [60]. Many researchers successfully prepared monodispersed and non-agglomerated nanoparticles utilising this strategy to overcome this drawback [27, 61-68]. Hydrolysis and condensation rates are important parameters that influence the characteristics of final particles. Slower and more controlled hydrolysis generates smaller particle sizes and more distinct characteristics. The solvent should be removed after the solution has condensed into a gel. Higher calcination temperatures are typically required to decompose the organic precursor. The size of the sol particles is determined by the composition of the solution, pH, and temperature [30, 54]. P. Hu *et al*. [63] synthesised monodisperse Fe_3O_4 NPs with 3-20 nm size via an explosion-assisted sol-gel method. According to the XRD and XPS, the products were well-crystallised, highly pure Fe_3O_4 NPs. The influence of various temperatures of (5, 128, and 300) K on how magnetic behaves was thoroughly investigated. Their finding displayed weakened hysteresis behaviour at the temperature increment. At (the Verwey transition) temperature TV, saturation magnetisation (Ms) of 86.2emu/g is the highest. Coercivity (Hc) decreases with temperature, while Initial susceptibility (ca) increases. O.M. Lemine *et al*. [64] synthesised Fe_3O_4 particles with an average size of 8 nm and well crystallinity, which have been prepared via an adjusted sol-gel method under supercritical conditions of ethyl alcohol (EtOH). XRD and Mössbauer analysis indicate that the NPs are single phases. The presence of spherical NPs with homogeneous size distribution is revealed by TEM analysis, as displayed in Fig. 9. At room temperature, SQUID measurements confirm the nanoparticles' ferromagnetic behaviour, with a saturated magnetisation of 47 emu/g. S. Shaker *et al*. [54] studied the influence of different annealing temperatures of 200, 300, and 400ºC on the particle size. These results reveal that the size of magnetite NPs can change by varying the annealing temperature.

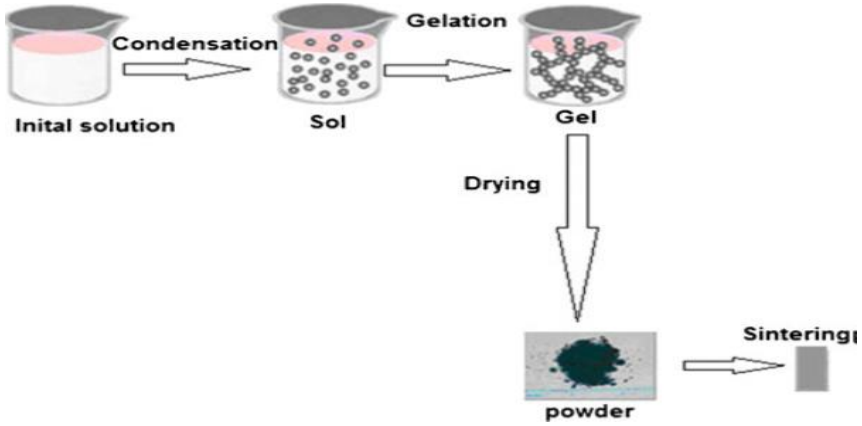

Figure 8: Schematic diagram of sol gel process for production nanopowders [65].

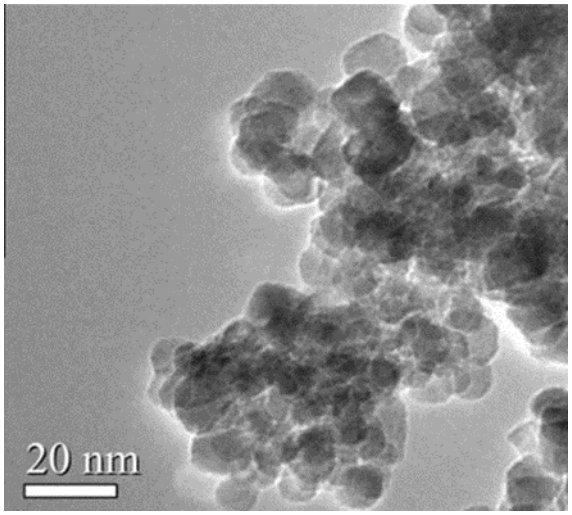

Figure 9: TEM images of the NPs [64].

4.4 Thermal Decomposition

Therm decomposition is one of the most widely utilised methods for producing monodisperse and highly crystalline IONPs [27]. Thermolysis, or thermal decomposition, is the process of treating a substance with heat. The thermal decomposition temperature is the temperature at which the chemical decomposes. This is an endothermic reaction because heat breaks the chemical bonds [66]. Fig. 10 displays a schematic diagram of magnetite nanoparticle synthesis by thermal decomposition. With the technique, iron oxide NPs have been prepared to utilise the decomposition of organometallic precursors, i.e. $Fe(cup)_3$ (cup = N-nitroso phenylhydroxylamine), $Fe(acac)_3$ (acac = acetylacetonate), or $Fe(CO)_5$ (co= carbonyls), after that, oxidation can result in monodispersed aloft -quality iron oxide NPs. However, this necessitates typically higher temperatures and a more complicated procedure [7, 67]. D. Maity *et al*. [68] reported the fabrication of water-dissoluble Fe_3O_4 NPs via the thermal decomposition of iron (III) acetylacetonate, Fe(acac)3 in tri(ethylene glycol). TEM points out that Fe_3O_4 NPs are relatively monodispersing with an average crystallite of 10.7 nm, as revealed in Fig. 11. The Size and the composition of the product particles are relayed on factors such as the temperature, the surfactant molecule length, and the reaction time [69]. N. J. Orsini *et al*. [70] have reported succeeding in preparing Fe_3O_4 NPs with diameters d, $7nm \leq d \leq 12nm$, by thermal decomposition of $Fe(acac)_3$. The structural and magnetic characteristics of nanocrystals were studied concerning different reaction conditions. The heating rate is the most essential parameter controlling the final particle size prepared by thermal decomposition. Table 2 displayed different methods and morphology of magnetite of Fe_3O_4 nanoparticles.

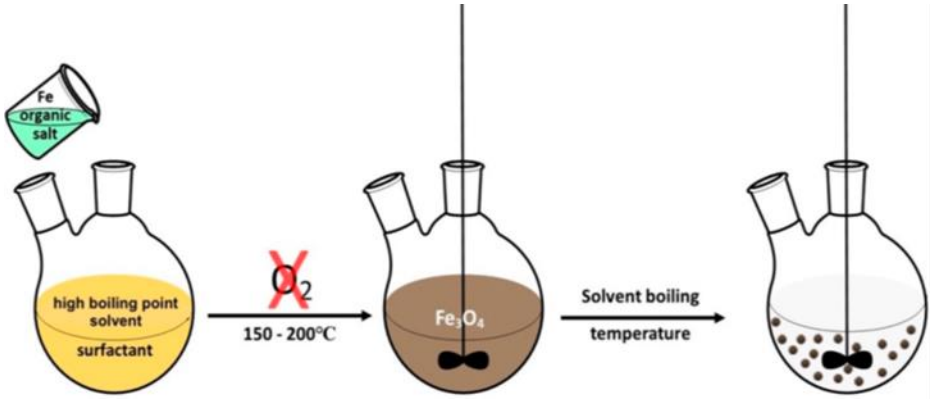

Figure 10: Synthesis of MNPs by thermal decomposition [71].

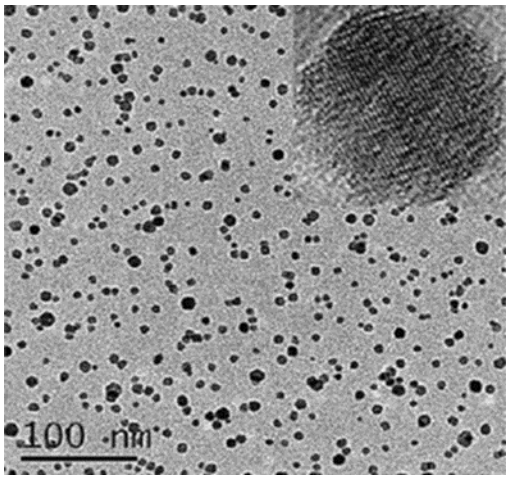

Figure 11: TEM image of the Fe_3O_4 NPs. Inset is the HRTEM image of individual Fe_3O_4 nanocrystals [68].

Table 2: Different methods and morphology of magnetite of Fe_3O_4 nanoparticles.

Method of Synthesis	Precursor	Morphology	Ref.
Hydrothermal	$Fe_3O(OCOCH_3)6NO_3$, $FeCl_2{\cdot}4H_2O$.	Spherical NPs, with an average diameter of 10 nm, were prepared at 180°C for 20 h, and the pH value is 8.6.	[72]
Hydrothermal	Fe3O(OCOCH3)6NO3, $FeCl_2{\cdot}4H_2O$.	Nanorods have an average width of about 25nm and a length of about 200nm.	[72]
Coprecipitation	$FeCl_3{\cdot}6H_2O$ $FeCl_2{\cdot}4H_2O$	Nanoparticles were nearly spherical and non-aggregated, with a mean size of 10 nm.	[73]
thermal decomposition	Iron acetylacetonate (acac) iron oleate complexes	Uniform nanoparticles comprise triangular, cubic, and diamond-shaped particles with an average particle size of 11 nm.	[74]
thermal decomposition	Fe $(NO_3)_3{\cdot}9H_2O$	Ultrafine particles, which are closely packed form nano-aggregates (≤ 100 nm). There is a powerful aggregation of NPs with a size of 10 nm.	[75]
sol–gel	Fe $(NO_3)_3{\cdot}9H_2O$	Nanoparticles had been agglomerated, particles of grain dimensions ranging from 15–30 nm.	[76]
Solvothermal	$FeCl_3 \cdot 6H_2O$	A spherical shape of Fe_3O_4 particles has uniform sizes and good dispersibility with a mean diameter of 326 nm.	[77]

5. Conclusions

Nowadays, magnetic NPs have piqued researchers' attention due to their intriguing properties and diverse applications. Many chemical synthesis routes, including sol-gel, thermal decomposition, hydrothermal, and coprecipitation, have revealed some benefits and disadvantages for the preparation of nanoparticles. Magnetite nanoparticles' (sizes and geometries) and magnetic properties are two important properties that can be obtained using suitable synthetic approaches. As a result, the sizes and shapes of magnetic Fe_3O_4 NPs are critical structural factors that influence many NPs' characteristics and capabilities in various applications.

Acknowledgement

Thanks to the Department of Applied Sciences for their help and support.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

[1] A. Azizi, "Green Synthesis of Fe_3O_4 Nanoparticles and Its Application in Preparation of Fe_3O_4/Cellulose Magnetic Nanocomposite: A Suitable Proposal for Drug Delivery Systems," *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 30, p. 3552-3561, 2020.

[2] A. Sirelkhatim, S. Mahmud, A. Seeni, N. H. M. Kaus, L. C. Ann, S. k. M. Bakhori, H. Hasan and D. Mohamad, "Review on Zinc Oxide Nanoparticles: Antibacterial Activity and Toxicity Mechanism," *Nano-Micro Lett*., vol. 7, p. 219-242, 2015.

[3] L. Xie, R. Jiang, F. Zhu, H.Liu and G. Ouyang," Application of functionalised magnetic nanoparticles in sample preparation," *Anal Bioanal Chem*., vol. 406, p. 377-399, 2014.

[4] Z. S. Sh. Khedaer, D. S. Ahmed and S. M. H. Al- Jawad," Investigation of Morphological, Optical, and Antibacterial Properties of Hybrid ZnO-MWCNT Prepared by Sol-gel," *Journal of Applied Sciences and Nanotechnology*, Vol. 1, p. 66- 77, 2021.

[5] A.M. Mousa, A. J. Haider and S. M.H. Al-Jawad," Optical Properties of Nanostructure in CdS at Different Condition Bath Deposition," *Journal of Materials Science and Engineering*, vol. 5, p. 184-491, 2011.

[6] R. A. Ismail, S. M. H. Al-Jawad and N. Hussein," preparation of n-ZnO/p-Si solar cells by oxidation of zinc nanoparticles: effect of oxidation temperature on the photovoltaic properties," *Appl. Phys. A*, vol. 117, p. 1977–1984, 2014.

[7] W. Wu, Q. He and C. Jiang," Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalisation Strategies," *Nanoscale Res Lett*. Vol. 3, p. 397- 415, 2008.

[8] M. D. Nguyen, H.Tran, S. Xu and T. R. Lee," Fe_3O_4 Nanoparticles: Structures, Synthesis, Magnetic Properties, Surface Functionalisation, and Emerging Applications," *Appl. Sci.* vol. 11, p. 11301, 2021.

[9] A. Ruiz, P. C. Morais, R. B. Azevedo, Z. G. M. Lacava, A.Villanueva and M.P. Morales," Magnetic nanoparticles coated with dimercaptosuccinic acid: development, characterisation, and application in biomedicine," *J Nanopart Res.* Vol. 16, p. 2589, 2014.

[10] S. Albukhaty, H.N. Manesh, T. Tiraihi and M. S. Jabir," Poly-L-lysine-coated superparamagnetic nanoparticles: a novel method for the transfection of pro-BDNF into neural stem cells," *Artificial Cells, Nanomedicine, and Biotechnology*, vol. 46, p. S125–S132, 2018.

[11] S. Albukhaty, S. Al-Musawi, S. A. Mahdi, G. M. Sulaiman, M. S. Alwahibi, Y. H. Dewir, D. A. Soliman and H. Rizwana, Investigation of Dextran-Coated Superparamagnetic Nanoparticles for Targeted Vinblastine Controlled Release, Delivery, Apoptosis Induction, and Gene Expression in Pancreatic Cancer Cells," *Molecules*, vol. 25, p. 4721, 2020.

[12] S. F. Hasany, I. Ahmed, Rajan J and A. Rehman," Systematic Review of the Preparation Techniques of Iron Oxide Magnetic Nanoparticles," *Nanoscience and Nanotechnology*, vol. 2, p. 148-158, 2012.

[13] N. Ajinkya, X. Yu, P. Kaithal, H. Luo, P. Somani and S. Ramakrishna," Magnetic Iron Oxide Nanoparticle (IONP) Synthesis to Applications: Present and Future," *Materials*, vol. 13, p. 4644, 2020.

[14] J. B. Mamani, L.F. Gamarra and G. E.d.S. Brito," Synthesis and Characterisation of Fe_3O_4 Nanoparticles with Perspectives in Biomedical Applications," *Materials Research.* Vol. 17, p. 542-549, 2014.

[15] S. Zhang, W. Wu, X. Xiao, J. Zhou, F. Ren and C. Jiang," Preparation and characterisation of spindle-like Fe_3O_4 mesoporous nanoparticles," *Nanoscale Research Letters*, vol. 6, p. 89, 2011.

[16] Y. Tian, B. Yu, X. Li and K. Li," Facile solvothermal synthesis of monodisperse Fe3O4 nanocrystals with precise size control of one nanometre as potential MRI contrast agents," *Journal of Materials Chemistry*, vol. 21, p. 2476, 2011.

[17] Y. Zhang, J. Liu, S. Ma, Y. Zhang, X. Zhao, X. Zhang and Z. Zhang," Synthesis of PVP-coated ultra-small Fe_3O_4 nanoparticles as a MRI contrast agent," J *Mater Sci: Mater Med*, vol. 21, p. 1205–1210, 2010.

[18] V. Vijayakanth and C. Krishnamoorthi," Effect of Zwitterionic Surfactant Ligand Monolayer on MagneticHyperthermia Properties of Monosize Fe_3O_4 Nanoparticles," *Journal of Superconductivity and Novel Magnetism*, vol. 34, p. 623–632, 2021.

[19] C. Li, R. Wei, Y. Xu, A. Sun and L. Wei," synthesis of hexagonal- and triangular Fe_3O_4 nanosheets via seed-mediated solvothermal growth," *Nano Res*., vol. 7, p.536-543, 2014.

[20] A. Mohammadi, M. Barikani and M. Barmar," Effect of surface modification of Fe3O4 nanoparticles on thermal and mechanical properties of magnetic polyurethane elastomer nanocomposites," *Journal of Materials Science*, vol. 48, p.7493- 7502, 2013.

[21] J. K. Xu, F. F. Zhang, J. J. Sun, J. Sheng, F. Wang and M. Sun," Bio and Nanomaterials Based on Fe_3O_4," Molecules, vol. 19, p. 21506-21528, 2014.

[22] J. K. Xu, F. F. Zhang, J. J. Sun, J. Sheng, F. Wang and M. Sun," Application of Iron Magnetic Nanoparticles in Protein Immobilization," *Molecules*, vol. 19, p. 11465-11486, 2014.

[23] K. N. Koo, A. F. Ismail, M. H. D. Othman, M. A Rahman and T. Z. Sheng," Preparation and characterisation of superparamagnetic magnetite (Fe_3O_4) nanoparticles: A short review," *Malaysian Journal of Fundamental and Applied Sciences*, Vol. 15, p. 23-31, 2019.

[24] R.M. Cornell, U. Schwertmann, The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses: Wiley-VCH, 2003.

[25] W. Wu, Z. Wu, T. Yu, C. Jiang and W.S. Kim," Recent progress on magnetic iron oxide nanoparticles: synthesis, surface functional strategies and biomedical applications," *Science and Technology of Advanced Materials*, vol. 16, p. 023501, 2015.

[26] I. Mimouni, A. Bouziani, Y. Naciri, M. Boujnah, M. A. El Belghiti1 and M. El Azzouzi ," Effect of heat treatment on the photocatalytic activity of α-Fe_2O_3 nanoparticles: towards diclofenac elimination," *Environmental Science and Pollution Research*, vol. 29, p. 7984–7996, 2022.

[27] O. A. Noqta, A. Abdul Aziz, I. A.Usman and M. Bououdina," Recent Advances in Iron Oxide Nanoparticles (IONPs): Synthesis and Surface Modification for Biomedical Applications," *Journal of Superconductivity and Novel Magnetism*, vol. 32, p. 779–795, 2019.

[28] N. T. Gómez, O. Nava, L. A. Figueroa, R. G. Contreras, A. B. Barrera and A. R. V. Nestor," Shape Tuning of Magnetite Nanoparticles Obtained by Hydrothermal Synthesis: Effect of Temperature," *Journal of Nanomaterials*, Vol. 2019, p. 1-15, 2019.

[29] L. S. Ganapathe, M. A. Mohamed, R. M. Yunus and D. D. Berhanuddin," Magnetite (Fe_3O_4) Nanoparticles in Biomedical Application: FromSynthesis to Surface Functionalisation," magnetochemistry, vol. 6, p. 68, 2020.

[30] A. S. Teja and P. Y. Koh," Synthesis, properties, and applications of magnetic iron oxide nanoparticles," Progress in Crystal Growth and Characterization of Materials, vol. 55, p. 22-45, 2009.

[31] H. Bae, T. Ahmad, I. Rhee, Y. Chang, S. U. Jin and S. Hong," Carbon-coated iron oxide nanoparticles as contrast agents in magnetic resonance imaging," Nanoscale Research Letters, vol. 7, p.44, 2012.

[32] S. F. Hasany, N. H. Abdurahman, A.R. Sunarti and R. Jose," Magnetic Iron Oxide Nanoparticles: Chemical Synthesis and Applications Review," Current Nanoscience, Vol. 9, p. 1-15, 2013.

[33] F. Ozel, H. Kockar and O. Karaagac," Growth of Iron Oxide Nanoparticles by Hydrothermal Process: Effect of Reaction Parameters on the Nanoparticle Size," J Supercond Nov Magn, vol. 28, p. 28:823–829, 2015.

[34] F. Ozel and H. Kockar," A Simple Method of Synthesis and Characterizations of Oleate-Coated Iron Oxide Nanoparticles," J Supercond Nov Magn, vol.30, p. 2023- 2027, 2017.

[35] K.H. Aboud, N. J. Imran and S. M. H. AL-Jawad," Structural, Optical and Morphological Properties Cadmium Sulfide Thin Films Prepared by Hydrothermal Method," *Journal of Applied Sciences and Nanotechnology*, Vol. 1, p. 49- 57, 2021.

[36] H. K. Judran, N. A. Yousif, and S. M. H. AL-Jawad, "Preparation and characterisation of CdS prepared by hydrothermal method," J. Sol-Gel Sci. Technol., vol. 97, pp. 48–62, 2021.

[37] S. M. H. Al-Jawad, M. M. Ismail, and S. F. Ghazi, "Characteristics of Ni-doped TiO_2 nanorod array films," J. Aust. Ceram. Soc., vol. 57, pp. 295–304, 2021.

[38] S. M.H. Al-Jawad, O. N. Salman, N. A. Yousif," influence of titanium tetrachloride concentration and multiple growth cycles of TiO_2 nanorod on photoanode performance in dye sensitised solar cell," *Photonics and Nanostructures - Fundamentals and Applications*. Vol. 31, p. 81–88, 2018.

[39] N. Mizutani, T. Iwasaki, S. Watano, T. Yanagida, H. Tanaka and T. Kawai," Effect of ferrous/ferric ions molar ratio on reaction mechanism for hydrothermal synthesis of magnetite nanoparticles," *Bull. Mater. Sci.*, Vol. 31, p. 713- 717, 2008.

[40] M. Ma, Y. Zhang, Z. Guo and N. Gu." Facile synthesis of ultrathin magnetic iron oxide nanoplates by Schikorr reaction," *Nanoscale Research Letters*, vol. 8, p.16, 2013.

[41] L. M. Cursaru, R. M. Piticescu, D. V. Dragut, R. Morel, C. Thébault, M. Carrière, H. Joisten and B. Dieny," One-Step Soft Chemical Synthesis of Magnetite Nanoparticles under Inert Gas Atmosphere. Magnetic Properties and In Vitro Study," *nanomaterials*, vol. 10, p. 1500, 2020.

[42] C.Y. Haw, F. Mohamed, C.H. Chia, S. Radiman, S. Zakaria, N.M. Huang and H.N. Lim," Hydrothermal synthesis of magnetite nanoparticles as MRI contrast agents," *Ceramics International*, vol. 36, p. 1417–1422, 2010.

[43] S. Ahmadi, C. H. Chia, S. Zakaria, K. Saeedfar and N. Asim," Synthesis of Fe3O4 nanocrystals using hydrothermal approach," Journal of Magnetism and Magnetic Materials, vol. 324, p. 4147–4150, 2012.

[44] S. Ni, X. Wang, G. Zhou, F. Yang, J. Wang, Q. Wang and D. He," Hydrothermal synthesis of Fe3O4 nanoparticles and its application in lithium ion battery," *Materials Letters*, vol. 63, p. 2701–2703, 2009.

[45] M. B.Torres, D. R. Fierro, J. E. Nuñez, B. A.Vera, E. C. Proaño and E. Bucio," Polymeric Composite of Magnetite Iron Oxide Nanoparticles and Their Application in Biomedicine: A Review," *Polymers*, vol. 14, p. 752, 2022.

[46] A. V. Samrot, N. Shobana, P. D. Sruthi and C. S. Sahithya ," Utilisation of chitosan-coated superparamagnetic iron oxide nanoparticles for chromium removal," *Applied Water Science*, vol.8, p. 192, 2018.

[47] M. S. Islam, Y. Kusumoto, J. Kurawaki, M. A. AL-Mamun and H. Manaka," A comparative study on heat dissipation, morphological and magnetic properties of hyperthermia suitable nanoparticles prepared by coprecipitation and hydrothermal methods," *Bull. Mater. Sci.*, Vol. 35, p. 1047–1053, 2012.

[48] M. I. Khalil," coprecipitation in aqueous solution synthesis of magnetite nanoparticles using iron (III) salts as precursors," *Arabian Journal of Chemistry*, vol. 8, p. 279–284, 2015.

[49] S. Ali, S. A. Khan, Z. H. Yamani, M. T. Qamar, M. A. Morsy and S. Sarfraz," shape- and size-controlled superparamagnetic iron oxide nanoparticles using various reducing agents and their relaxometric properties by Xigo acorn area," *Applied Nanoscience*, vol. 9, p. 479–489, 2019.

[50] M. Tajabadi and M. E. Khosroshahi," Effect of Alkaline Media Concentration and Modification of Temperature on Magnetite Synthesis Method Using FeSO4/NH4OH," *International Journal of Chemical Engineering and Applications,* Vol. 3, p. 206-210, 2012.

[51] R. Rahmawati, M. G. Permana , B.Harison, Nugraha, B. Yuliartoa, Suyatmana and D. Kurniadia," Optimisation of Frequency and Stirring Rate for Synthesis of Magnetite (Fe_3O_4) Nanoparticles by Using Coprecipitation- Ultrasonic Irradiation Methods," *Procedia Engineering* , vol. 170, p. 55 – 59, 2017.

[52] T. Q. Bui, S. N.Ton, A. T. Duong and H. T. Tran," Size-dependent magnetic responsiveness of magnetite nanoparticles synthesised by coprecipitation and solvothermal methods," *Journal of Science: Advanced Materials and Devices,* vol. 3, p. 107-112, 2018.

[53] A. Hakeem, T. Alshahrani, G. Muhammad, M.H. Alhossainy, A. Laref, A. R. Khan, I. Ali, H. M. T. Farid, T. Ghrib, S. R. Ejaz and R. Y. Khosa," Magnetic, dielectric and structural properties of spinel ferrites synthesised by sol-gel method," *journal of materials research and technology*, vol. 11, p. 158-169, 2021.

[54] S. Shaker, S. Zafarian, CH. S. Chakra and K.V. Rao," preparation and characterisation of magnetite nanoparticles by sol-gel method for water treatment*," international journal of innovative research in science, engineering and technology*, Vol. 2, p. 2969-2973, 2013.

[55] Z. I. Takai, M. K. Mustafa, S. Asman and K. A. Sekak," Preparation and Characterisation of Magnetite (Fe_3O_4) nanoparticles By Sol-Gel Method," *International Journal of Nanoelectronics and Materials*, Vol. 12, p. 37-46, 2019.

[56] SM H. AL-Jawad, S. H. Sabeeh, A. A. Taha, H. A. Jassim," Studying structural, morphological and optical properties of nanocrystalline ZnO:Ag films prepared by sol–gel method for antimicrobial activity," *Journal of Sol-Gel Science and Technology*, vol. 87, p. 362–371, 2018.

[57] S. M. H. AL-Jawad, AB. K. Elttayf and A. S. Saber," influence of annealing temperature on the characteristics of nanocrystalline SnO_2 thin films produced by Sol–Gel and chemical bath deposition for gas sensor applications," *Journal of Sol-Gel Science and Technology*, vol. 24, p. 1750140, 2017.

[58] S. M. H. AL- Jawad, S. H. Sabeeh, A. A. TAHA and H. A. Jassim," synthesis and characterisation of Fe–ZnO thin films for antimicrobial activity," *Surface Review and Letters*, Vol. 26, p. 1850197, 2019.

[59] M. I. A. Abdel Maksoud, R. A.Fahim, A. G. Bedir, A. I. Osman, M. M. Abouelela, G. S. El-Sayyad, M. Abd Elkodous, A. S. Mahmoud, M. M. Rabee, A. H. Al-Muhtaseb and David W. Rooney," Engineered magnetic oxides nanoparticles as efficient sorbents for wastewater remediation: a review," *Environmental Chemistry Letters*, vol. 20, p. 519- 562, 2022.

[60] Q. H. Zhang, Y. Biao, L.C. Kui and LU Wei," synthesis and characterisation of water-soluble magnetite nanocrystals via one-step sol-gel pathway," *Science China Physics, Mechanics & Astronomy*, vol. 54, p. 1239–1243, 2011.

[61] Y. Lu, Y. Yin, B. T. Mayers, and Y. Xia," Modifying the Surface Properties of Superparamagnetic Iron Oxide Nanoparticles through A Sol−Gel Approach," *Nano Letters*, Vol. 2, p. 183-186, 2002.

[62] Y. H. Deng, C. C. Wang, J. H. Hu, W. L. Yang and S. K. Fu," Investigation of formation of silica-coated magnetite nanoparticles via sol–gel approach," *Colloids and Surfaces A: Physicochem. Eng. Aspects,* vol. 262, p. 87–93, 2005.

[63] P. Hu, T. Chang, W. J. Chen, J. Deng, S. L. Li, Y. G. Zuo, L. Kang, F. Yang, M. Hostetter and A. A. Volinsky," Temperature effects on magnetic properties of Fe_3O_4 nanoparticles synthesised by the sol-gel explosion-assisted method," Journal of Alloys and Compounds, vol. 773, p. 605- 611, 2019.

[64] O.M. Lemine, K. Omri, B. Zhang, L. E. Mira, M. Sajieddine, A. Alyamani and M. Bououdina," Sol–gel synthesis of 8 nm magnetite (Fe_3O_4) nanoparticles and their magnetic properties," Superlattices and Microstructures, vol. 52, p. 793–799, 2012.

[65] C. Aydın, O.A. Al-Hartomy, A. A. Al-Ghamdi, F. Al-Hazmi, I. S. Yahia, F. El-Tantawy and F. Yakuphanoglu," Controlling of crystal size and optical band gap of CdO nanopowder semiconductors by low and high Fe contents," *J Electroceram,* vol. 29, p. 155–162, 2012.

[66] A. V. Samrot, C. S. Sahithya, J. Selvarani A, S. K. Purayil and P. Ponnaiah," A review on synthesis, characterisation and potential biological applications of superparamagnetic iron oxide nanoparticles," *Current Research in Green and Sustainable Chemistry*, vol. 4, p.100042, 2021.

[67] F. Ozel, H. Kockar, S. Beyaz, O. Karaagac and T. Tanrisever," Superparamagnetic iron oxide nanoparticles: effect of iron oleate precursors obtained with a simple way," *J Mater Sci: Mater Electron,* vol. 24, p. 3073-3080, 2013.

[68] D. Maity, S.N. Kale, R. K. Ghanekar, J. M. Xue and J. Ding," Studies of magnetite nanoparticles synthesised by thermal decomposition of iron (III) acetylacetonate in tri (ethylene glycol)," *Journal of Magnetism and Magnetic Materials*, vol. 321, p. 3093- 3098, 2009.

[69] K. Simeonidisa, S. Mourdikoudisa, M. Moullab, I. Tsiaoussisa, C. Martinez-Boubetaa, M. Angelakerisa, C. Dendrinou-Samarab, O. Kalogiroua," Controlled synthesis and phase characterisation of Fe-based nanoparticles obtained by thermal decomposition," *Journal of Magnetism and Magnetic Materials*, vol. 316, p. e1–e4, 2007.

[70] N. Jović Orsinia, B. Babić-Stojića, V. Spasojevića, MP Calatayudb, N. Cvjetićaninc and G.F. Goyab," Magnetic and power absorption measurements on iron oxide nanoparticles synthesised by thermal decomposition of $Fe(acac)_3$," *Journal of Magnetism and Magnetic Materials*, Vol. 449, P. 286-296, 2018.

[71] Kinga Mylkie, Pawel Nowak, Patryk Rybczynski and Marta Ziegler-Borowska," Polymer-Coated Magnetite Nanoparticles for Protein Immobilization," *Materials,* vol. 14, p. 248, 2021.

[72] Q. Dong, N. Kumada, Y. Yonesaki, T. Takei and N. Kinomura," Hydrothermal synthesis of Fe_3O_4 particles with shapes," *J. of the Ceramic Society of Japan*, vol. 117, p. 881- 886, 2009.

[73] K. D. Kim, S. S. Kim, Y. H. Choa, and H. T. Kim," Formation and Surface Modification of Fe_3O_4 Nanoparticles by Coprecipitation and Sol-gel Method," *J. Ind. Eng. Chem.*, Vol. 13, p. 1137-1141, 2007.

[74] A. G. Roca, M. P. Morales, K. O. Grady and C. J. Serna," Structural and magnetic properties of uniform magnetite nanoparticles prepared by high temperature decomposition of organic precursors," *Nanotechnology,* vol. 17, p. 2783–2788, 2006.

[75] B. Aslibeiki, P. Kameli, I. Manouchehri and H. Salamati," Strongly interacting superspins in Fe_3O_4 nanoparticles," *Current Applied Physics,* vol. 12, p. 812- 816, 2012.

[76] V. T. Geetha, G. Puthilibai and S. Induja," A starch-assisted innovative synthesis of spinel-structured and ferromagnetic behaviour of Fe_3O_4 nanoparticles catalytic activity evaluated in the selective oxidation," *SN Applied Sciences*, vol. 1, p. 472, 2019.

[77] H. Yana, Z. Liping, H. Weiwei, L. Xiaojuan, L. Xiangnong and Y. Yuxiang," A Study on Synthesis and Properties of Fe_3O_4 Nanoparticles by Solvothermal Method,", *Glass Physics and Chemistry*, Vol. 36, p. 325–331, 2010.