CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter includes a brief literature survey on the possible tunability of Y-type barium hexaferrite (Co_2-Y) properties and the different ferrite systems utilized for all five (heterogeneous catalyst for oxidation, heterogeneous catalyst for reduction, photocatalyst for degradation of methyl orange, microwave absorber for EMI shielding, biocompatible hyperthermia agent) applications.

Since the discovery of hexagonal ferrites in the 1950s, hexaferrite has attracted scientists and engineers due to its broad range of applications, low cost, easy processing, and fine tunability of magnetic & electrical properties. The improved properties of these hexaferrite materials prove their suitability to be utilized within the field of permanent magnets, magnetic storage, microwave devices ultrahigh-frequency (UHF), and microwave shielding [(Mohsen *et al.*, 2017)]. The physical properties of these hexaferrite materials can be tuned according to the desired level using several approaches. It can be modified by the variations of synthesis methods, calcination temperature, and the substitution of appropriate elements at all three (Ba, Co, & Fe Site) possible sites to alter the structural parameters or the cationic distribution.

Till date, the Y-type hexaferrites are reported to be synthesized using limited number of processes likewise solid-state ceramic route [(Vinaykumar, Jyoti and Bera, 2018), (Wang *et al.*, 2012), (Fu *et al.*, 2019), (Mahmood *et al.*, 2015), (Baik, Shim and Kim, 2022), (Bierlich and Töpfer, 2012), (Kim, Rhee and Kim, 2012), (Salunkhe and Kulkarni, 2004)], sol gel method [(Chand Pramanik *et al.*, 2006), (Kamba *et al.*, 2010), (Iqbal and Barkat-ul-Ain, 2009)], sol-gel autocombustion [(Rashad *et al.*, 2018), (Nadeem *et al.*, 2022), (Alrebdi *et al.*, 2022), (Carol T *et al.*, 2022), (UL-AIN, AHMED and HUANG, 2013), (Bai *et al.*, 2006), (Odeh *et al.*, 2016), (Alrebdi *et al.*, 2022), (Iqbal and Liaqat, 2010), (Shakeel *et al.*, 2019), (Ahmad *et al.*, 2018), (Ali, Shaheen, *et al.*, 2014),

(Koutzarova *et al.*, 2012), (Warhate and Badwaik, 2020)], microwave assisted auto combustion method [(BADWAIK *et al.*, 2012)], flux method [(Wu *et al.*, 2022), coprecipitation method [(Jotania and Virk, 2012), (Chen *et al.*, 2011), (Nikzad *et al.*, 2015), (Lehlooh *et al.*, 2020), (Rashad *et al.*, 2018), (Daigle *et al.*, 2010)] & microemulsion method [(Ali, Islam, *et al.*, 2014)]. Two synthesis processes (solid-states ceramic method & sol-gel auto combustion method) govern all these processes. The adoption of the nitrate-citrate sol-gel auto combustion process for the synthesis of all pristine and substituted Co_2-Y hexaferrite within this research work can be explained due to its inexpensiveness, simple methodology, mild processing, homogeneity in terms of elemental distribution and phase formation, less reaction time & energy consumption, etc.

Many researchers have investigated the role of substituting different elements to enhance the magnetic and dielectric performances of the cobalt-based Y-type barium hexaferrite (Co_2-Y). The substitution of any foreign element into the hexaferrite system occupies the specific sites, and it is responsible for the modification of the physical properties. The magnetic properties of any ferrite system rely on the nature of substituting element and their preferential site occupancy. Apart from the nature of element and site occupancy, the deviation within the superexchange interactions also provides a crucial role in the finally achieved properties of Y-type hexaferrite [(Chandel *et al.*, 2020)].

2.1.1 Substitution at Ba-site in Co_2-Y barium hexaferrite

The substitution of Sr at the Ba site ($Ba_{2-x}Sr_xCo_2Fe_{12}O_{22}$) shows the variations within the particle sizes. The substitution results in the enhancement of the temperature-dependent dielectric constant value along with activation energy up to the x = 0.25 and decrease afterward [(Fu *et al.*, 2019)]. The substitution of Cr & Ni at the Ba site ($Ba_{2-2x}Cr_xNi_xCo_2Fe_{12}O_{22}$) shows the increasing trends in band gap (Eg), saturation

magnetization (M_s), coercivity (H_c), and magnetic retentivity up to the x = 0.1 and decrease afterward [(Carol T *et al.*, 2022)].

2.1.2 Substitution at Co-site in Co_2-Y barium hexaferrite

The substitution of Cr at the Co site ($Ba_2Co_{2-x}Cr_xFe_{12}O_{22}$) allows the formation of two secondary phases, $BaFe_{12}O_{19}$ and $BaCrO_4$, within the sample. The substitution increases the saturation magnetization value from 33.9 emu/g for pure Co_2-Y to 37.5 emu/g for Cr (x = 1) substituted ferrite [(Mahmood *et al.*, 2015)]. The substitution of Zn at the Co site ($Ba_2Co_{2-x}Zn_xFe_{12}O_{22}$) allows to decrease of both spin transition (T_{sp}) and Curie (Tc) transition temperatures. The room temperature hysteresis curve also suggests the increasing behavior of saturation magnetization (M_s) along with decreasing coercivity (H_c) up to x = 2 [(Kim, Rhee and Kim, 2012),(Odeh *et al.*, 2016), (Bierlich and Töpfer, 2012)]. The substitution of Mg at the Co site ($Ba_2Co_{2-x}Mg_xFe_{12}O_{22}$) permits the reduction of saturation magnetization, coercivity, magnetic hyperfine field, and spin transition temperature (T_{sp}) with increasing the substitution up to x = 0.5 [(Baik, Shim, and Kim, 2022)].

2.1.3 Substitution at Fe- Site in Co_2-Y barium hexaferrite

The substitution of Ga at the Fe site ($Ba_2Co_2Fe_{12-x}Ga_xO_{22}$) shows the increased value of saturation magnetization (M_s) and decreasing trend for both coercivity and magnetic retentivity (M_r) up to x = 1. The Mossbauer results suggest that the Ga ions are distributed at both sites (spin-up and spin-down), having a preference primarily for the spin-down state within the tetrahedral site of S & T blocks. The hyperfine fields associated with all three magnetic components are found to be decreased with the substitution [(Mahmood *et al.*, 2015)].

2.1.4 Substitution at both Ba & Fe- Site in Co_2-Y barium hexaferrite

The substitution of La at the Ba site and Zn at the Fe site ($Ba_{2-x}La_xCo_2Fe_{12-x}Zn_xO_{22}$) allow the formation of secondary phases such as $LaFeO_3$ & $LaFe_{12}O_{19}$ beyond x = 0.1. The room temperature magnetic study reveals that the values of magnetic saturation (M_s), coercivity field (H_c), magnetic retentivity (M_r) & initial permeability increase up to x=0.5 [(Vinaykumar, Jyoti, and Bera, 2018)]. The substitution of Sr at the Ba site and Al at the Fe site ($Ba_{0.8}Sr_{1.2}Co_2Fe_{12-x}Al_xO_{22}$) provides the diminished value of curie temperature and a significant enhancement of electrical polarization (from 21.3 to 37.7 $\mu C/m^2$) & magnetoelectric coefficient (from 1052 to 2516 ps/m) up to x = 1.08 measured at 100 K [(Wu *et al.*, 2022)].

2.1.5 Substitution at both Co & Fe- Site in Co_2-Y barium hexaferrite

The substitution of Mg at the Co site and Ga at the Fe site ($Ba_2CoMgFe_{11}GaO_{22}$) allow the formation of spinel-type barium ferrite ($BaFe_2O_4$) as a secondary phase. The substitution results in the decreasing value of saturation magnetization (from 33.9 to 26.6 emu/g), coercivity (from 123 to 81 Oe), and magnetic retentivity (from 7.90 to 5.81 emu/g) [(Mahmood *et al.*, 2015)].

2.1.6 Substitution at all three sites (Ba, Co & Fe) in Co_2-Y barium hexaferrite

The substitution of Ca at Ba site, Zn at Co site, and Nd at Fe site ($BaCaCo_{2-x}Zn_xNd_yFe_{12-y}O_{22}$) improve the bulk density, enhance the saturation magnetization (25.8 to 51.1 emu/g), magnetic retentivity (14.4 to 28.5 emu/g) and coercivity values up to x = y =1 [(Nadeem *et al.*, 2022)]. The substitution of Ce at the Ba site, Zn & Cu at the Co site, and Ni at the Fe site ($Ba_{2-x}Ce_xCo_{0.7}Zn_{0.7}Cu_{0.6}Fe_{12-y}Ni_yO_{22}$) allows the formation of $NiFe_2O_4$ & Fe_3O_4 as secondary phases. The substitution increases the bulk density, saturation

magnetization (M_s), retentivity (M_r), coercivity (H_c), magnetic anisotropy constant (K_1), and decreases the dielectric constant and band gap value (2.35 to 2.13 eV) up to x = 1 [(Alrebdi *et al.*, 2022)].

In summary, it can be seen that the structural and physical properties of cobalt-based Y-type barium hexaferrite (Co_2-Y) can be tuned easily using the substitutional approach for achieving the desired properties suitable for the required applications.

2.2 Trends for utilization of ferrite materials in versatile applications

As the theme of this research work deals with five versatile applications for concerned ferrite (cobalt-based Y-type barium hexaferrite), the literature review can be categorized accordingly within five sections as given below:

2.2.1 Utilization of ferrites as a heterogeneous catalyst for oxidation of styrene

Benzaldehyde, the simplest member of the aromatic aldehyde group, is being widely utilized in several chemical industries [(Tong *et al.*, 2016), (Oliveira *et al.*, 2017)]. It can be produced using various methods, including direct oxidation of toluene, benzyl alcohol, hydrolysis of benzyl chloride & hydrogenation of benzoic acid [(Yadav and Haldavanekar, 1997), (Nasrollahzadeh, Bagherzadeh, and Karimi, 2016), (Cheng *et al.*, 2008), (Lv *et al.*, 2010)]. To date, owing to its modest reaction procedure, direct oxidation of styrene has become an advantageous method for manufacturing benzaldehyde [(Narayanan *et al.*, 2016)]. The oxidation of styrene can also be achieved using homogeneous catalysts such as cobalt-tetraphenyl porphyrins [(Haber, Kłosowski and Połtowicz, 2003)] & transition metal-based Schiff base complexes [(X. Wang *et al.*, 2016)], but it is limited due to utilization of expensive chemicals, intricate separation processes for products and catalysts, poor recycling and less conversion of styrene [(Liu *et al.*, 2018)].

Nowadays, it becomes crucial importance to achieve a suitable catalyst that can support the oxidation reaction of styrene at side chains for both theoretical research and applicable for the industrially adoptable process [(Dhakshinamoorthy, Alvaro and Garcia, 2011)]. The products of this reaction include benzaldehyde (C_6H_5CHO), which is a priceless chemical that has extensive applications in organic synthesis related to pharmaceuticals, perfumery, agrochemical industries, dyestuffs, and the production of various other aldehydes [(Nemanashi and Meijboom, 2013), (Justinus and Satrio, 2001)]. Generally, several spinal ferrite-based catalysts have been employed to catalyze the oxidation of styrene and synthesize benzaldehyde as a concerned product.

In 2003, magnesium doped nanosized spinel ferrite ($Mg_xFe_{3-x}O_4$) is employed as a heterogeneous catalyst for the oxidation reaction of styrene. The result suggests that $Mg_{0.4}Fe_{2.6}O_4$ shows its excellency with 66.7 mol% of benzaldehyde selectivity and 40.6 mol% conversion of styrene in the presence of equimolar H_2O_2 as an oxidizer, using acetone as a solvent [(Ma *et al.*, 2003)].

In 2005, nanosized spinel ferrite Fe_3O_4 is used as a heterogeneous catalyst for the oxidation reaction of styrene. The result recommends that the 68.4 mol% of benzaldehyde selectivity is achieved with 36.5 mol% conversion of styrene in the presence of equimolar H_2O_2 as an oxidizer and acetone as a solvent [(Guin, Baruwati and Manorama, 2005)]. Nanosized spinel ferrite $ZnFe_2O_4$ is also applied as a heterogeneous catalyst for the oxidation reaction of styrene. The result endorses that the 50.4 mol% of benzaldehyde selectivity is achieved with 26.1 mol% conversion of styrene in the presence of equimolar H_2O_2 as an oxidizer and acetone as a solvent [(Guin, Baruwati and Manorama, 2005)].

In 2007, nanocrystalline spinel ferrite $NiFe_{2-x}Gd_xO_4$ is utilized as a heterogeneous catalyst for the oxidation reaction of styrene. The result validates that $NiFe_{0.4}Gd_{1.6}O_4$ shows its excellency with 100 mol% of benzaldehyde selectivity and 56.8 mol% conversion of

styrene in the presence of H_2O_2 to styrene ratio of 2:1, using acetonitrile as a solvent [(Ramanathan and Sugunan, 2007)].

In 2010, nanocrystalline spinel ferrite $CaFe_2O_4$ is employed as a heterogeneous catalyst for the oxidation reaction of styrene. The result recommends that the 91 mol% of benzaldehyde selectivity is achieved with 38 mol% conversion of styrene in the presence of equimolar H_2O_2 as an oxidizer, using acetone as a solvent [(Pardeshi and Pawar, 2010)].

In 2011, spinel ferrite $SrFe_2O_4$ is employed as a heterogeneous catalyst for the oxidation reaction of styrene. The result proposes that it can achieve 63.7 mol% selectivity of benzaldehyde along with 51.0 mol% conversion of styrene in the presence of equimolar H_2O_2 using water as a solvent [(Pardeshi and Pawar, 2011)].

In 2014, nanocrystalline spinel ferrite $Mg_{1-x}Cu_xFe_2O_4$ is availed as a heterogeneous catalyst for the oxidation reaction of styrene. The result advises that $Mg_{0.5}Cu_{0.5}Fe_2O_4$ shows its excellency with 87.6 mol% of benzaldehyde selectivity and 17.2 mol% conversion of styrene in the presence of H_2O_2 to styrene ratio of 5:2, using water as a solvent [(Cai *et al.*, 2014)].

In 2018, nanocrystalline spinel ferrite $MnFe_2O_4$ is employed as a heterogeneous catalyst for the oxidation reaction of styrene. The result proposes that the 93.2 mol% of benzaldehyde selectivity is attained with 84.4 mol% conversion of styrene in the presence of t-BuOOH (70%) as an oxidizer under the irradiation of 10 W micro-wave irradiation [(Martins, Pombeiro and Martin, 2018)].

The catalytic efficiencies of all above-mentioned ferrite materials can be explained due to the redox characteristics along with facile magnetic separation & recycling nature. The catalytic efficiency of any ferrite system is due to the capability of metallic ions to wander among the sub-lattices without destroying the initial structure. Moreover, there is a need to come up with reusable catalysts that can be better selective, active, and more facile

to separate [(Tasca *et al.*, 2012)]. All the ferrite materials being utilized for the above application are dominated by the spinel-type of ferrites, so analyzing the performance of Co_2-Y hexaferrite material for this application may offer fruitful outcomes.

2.2.2 Utilization of ferrites as a heterogeneous catalyst for reduction of toxic nitro-organic pollutants

The rapid growth of several industries such as plastics, paper, agriculture, textile, pharmaceutical, and paint results in the environment's pollution due to the discharge of dangerous chemicals into the ecosystem. These industries utilize various toxic organic compounds like nitroaromatic compounds, phenols, aromatic hydrocarbons, and sulphonamides as a precursor, solvents, or intermediates. The direct disposal of this industrial waste to the environment causes severe threats to human health and aquatic life [(Gupta, Rishi, and Gupta, 2021)]. Nitrobenzene (NB) is one of the significant nitro-compound widely applicable in manufacturing paper pulp, explosives, colorants, pesticides, pharmaceuticals, synthetic rubber, perfumes, plastics, and dyes [(Y. Zhang *et al.*, 2014), (Srilakshmi, Saraf and Shivakumara, 2015)]. It is found as one of the major pollutants in water due to its high durability and solubility [(Gupta, Rishi, and Gupta, 2021), (Y. Zhang *et al.*, 2014), (Srilakshmi, Saraf and Shivakumara, 2015), (Bhaduri *et al.*, 2019)]. It is a carcinogenic pollutant [(Mu *et al.*, 2004)] in the water. This pollutant causes nausea, coordination disorders, vomiting, burning feeling in the mouth & throat, dizziness, cyanosis, dropped blood pressure, restlessness, collapse, tachycardia, unconsciousness, paralysis, and coma in human bodies [(Hartwig, 2018)]. Removing these nitroaromatic compounds from the wastewater is essential to make it more ecological. Conservatively, these nitroaromatic compounds may be processed through physical, chemical, and biological techniques, but all these methods can be limited due to secondary pollution

(byproducts due to adsorption and biodegradation), which leads to high processing costs [(Alfredo Reyes Villegas *et al.*, 2020), (Jeong *et al.*, 2018)].

It is known that nitrobenzene is a non-biodegradable compound, so it is essential to develop a catalyst that can either reduce or oxidize toxic substances to less harmful compounds such as aminobenzene. The as-prepared aminobenzene can be used both as intermediates and starting materials to manufacture a variety of chemicals such as analgesic & antipyretic drugs, wood stains, dyeing agents, photographic developers, pesticides, herbicides, explosives, cosmetics, surfactants, and corrosion inhibitors in paints [(Goyal *et al.*, 2015)]. Conventionally, reducing nitrobenzene requires heavy-duty mineral acids & metal, which enforces risky environmental consequences with lesser conversion yield [(Gupta, Rishi, and Gupta, 2021)]. Recently, there have been several advanced procedures, such as photo-assisted reduction, heterogenous & homogenous catalytic-transfer hydrogenation, electrolytic-reduction, and direct reducing mediators like hydrazine hydrates & hydrazine, metal or acid-based reduction, suggested through which nitrobenzene can be transformed to constituent amino benzene [(Gupta, Rishi, and Gupta, 2021), (Taghavi *et al.*, 2011)]. All these methods have a significant drawback related to the recovery or the reusability of the catalyst, which can be eliminated by using magnetic ferrite materials. Therefore to develop a large-scale and cost-effective process, it is suggested to study the ferrite materials as catalysts for their suitability to reduce the toxic nitrobenzene to useful amino benzene [(Kharisov, Dias and Kharissova, 2019), (Astruc, Lu and Aranzaes, 2005)]. Till date, several spinal ferrite-based catalysts have been employed to catalyze the reduction of toxic nitro-organic pollutants, especially nitrobenzene.

In 2011, nanosized spinel Fe_3O_4 ferrite is employed as a heterogeneous catalyst for the reduction of nitrobenzene. The result suggests that it provides complete conversion of nitrobenzene along with 99% selectivity for aniline, utilizing 4 equivalent of hydrated

hydrazine & ethanol as a solvent [(Kim, Kim, and Kim, 2011)]. Rhodium-based heterodimer nanocrystals of Fe_3O_4 (Rh nanoparticles of 2–3 nm attached with Fe_3O_4 having 16 nm size) are also used as a heterogeneous catalyst for the reduction of nitrobenzene. The result recommends that it is achieved 99% isolated yield for the concerned product, i.e., aniline, utilizing 6 equivalent of hydrazine [(Jang *et al.*, 2011)].

In 2012, nanosized magnetic particles of Fe_3O_4-Ni are applied as a heterogeneous catalyst for the reduction of 4-methoxy nitrobenzene. The result proposes that it is achieved 94% isolated yield for 4-methoxyaniline, utilizing glycerol as both solvent and hydrogen donor [(Gawande *et al.*, 2012)].

In 2013, nanosized Mg_xMn_1-xFe_2O_4 ferrites are utilized as a heterogeneous catalyst for the reduction of 4-methoxy nitrobenzene. The result advises that $MnFe_2O_4$ can completely decompose the nitrobenzene solution (concentration of 50 ppm), utilizing UV radiation exposure of 125 W mercury vapor lamp [(Pathak *et al.*, 2013)].

In 2014, nickel substituted cobalt ferrite ($Co_{1-x}Ni_xFe_2O_4$) is availed as a heterogeneous catalyst for the decomposition of 4-nitrophenol. The result proposes that 30 mol% of $Co_{0.4}Ni_{0.6}Fe_2O_4$ can decompose the 4-nitrophenol within 20 minutes, utilizing water as a solvent & 25 equivalent of $NaBH_4$ as a reducing agent [(Singh, Goyal and Singhal, 2014)]. The superparamagnetic graphene-based hybrid nanocomposite ($CuFe_2O_4$–G) is also engaged as a heterogeneous catalyst for the conversion of p-nitrophenol to p-nitroaniline as a product. The result advises that $CuFe_2O_4$–G(0.25) shows its excellency utilizing 5 equivalent of $NaBH_4$ as a reducing agent with an equal ratio of ethanol & water as a solvent [(H. Zhang *et al.*, 2014)].

In 2015, spinel $CoM_{0.2}Fe_{1.8}O_4$ (where M = Co, Zn, Cu & Ni) ferrites are extended as a heterogeneous catalyst for the decomposition of aromatic nitro compounds. The result recommends that $CoCu_{0.2}Fe_{1.8}O_4$ can completely decompose 2-nitrophenol, 3-nitrophenol,

and 4-nitrophenol with a rate constant of 3.12, 1.08 & 2.10 min^{-1} utilizing $NaBH_4$ as a reducing agent [(Goyal *et al.*, 2015)]. The fine Fe_3O_4 (obtained from electric arc furnace dust) is also employed as a heterogeneous catalyst for the reduction of nitrobenzene. The result suggests that it can convert 86% of nitrobenzene (within 60 minutes) to aniline as a product. This catalytic performance can be attributed to the presence of Fe^{2+} and Fe^0 on the catalytic surface [(de Paula *et al.*, 2015)].

In 2017, bismuth substituted cobalt ($CoFe_{2-x}Bi_xO_4$) ferrites are addressed as a heterogeneous catalyst for the reduction of 4-nitrophenol from 4-aminophenol as a product. The result advises that $CoFe_{1.9}Bi_{0.1}O_4$ can easily convert the 4-nitrophenol (just within 2.25 minutes for sample synthesized using combustion process and 3.38 minutes for sample synthesized using the coprecipitation method) utilizing water as a solvent & excessive $NaBH_4$ as a reducing agent [(Kiran and Sumathi, 2017)]. Cube-shaped $NiFe_2O_4$ magnetic nanoparticles are also examined as a heterogeneous catalyst for the conversion of 4-nitrophenol to 4-aminophenol as a product. The result proposes that it can efficiently convert 4-nitrophenol (concentration of $4.3x10^{-4}$ M) at a rate constant of 0.1238 min^{-1}, utilizing water as a solvent & $NaBH_4$ as a reducing agent [(Dey *et al.*, 2017)].

In 2019, cobalt-attached nanoparticles of cobalt (Co-$CoFe_2O_4$) ferrite is applied as a heterogeneous catalyst for the reduction of p-nitrophenol to p-aminophenol as a product. The result recommends that $CuFe_2O_4$ can completely decompose the p-nitrophenol with a rate constant of 0.0170 s^{-1} utilizing excessive $NaBH_4$ as a reducing agent [(Zhang *et al.*, 2019)]. Co_3O_4 formed over $CoFe_2O_4$ is employed as a heterogeneous catalyst for the reduction of 4-nitrophenol to 4-aminophenol as a product. The result advises that $CoFe_2O_4$-2.0 can completely convert the p-nitrophenol with a rate constant of 0.34 s^{-1} utilizing water as a solvent & excessive $NaBH_4$ as a reducing agent [(Ortiz-Quiñ Onez and Pal, 2019)].

In 2020, spinel ferrite $CuFe_2O_4$ is used as a heterogeneous catalyst for the decomposition of 4-nitrophenol to 4-aminophenol as a product. The result proposes that $CuFe_2O_4$ can completely decompose the nitrobenzene solution ($1.35x10^{-4}$ M) with a rate constant of 0.6684 min^{-1} utilizing $NaBH_4$ ($1x10^{-3}$ M)) as a reducing agent [(Dey *et al.*, 2020)].

In 2021, nanosized spinel $MnFe_2O_4$ ferrite is employed as a heterogeneous catalyst for the reduction of 4-nitrophenol. The result indicates that it can decompose 4-nitrophenol (concentration of 0.005 mol/L) at a reaction rate of 0.0013 s^{-1} within the presence of excess $NaBH_4$ (0.1 mol/L) at a pH level of 9 [(Gupta, Rishi, and Gupta, 2021)]. The nanosized spinel $CuFe_2O_4$ ferrite is applied as a heterogeneous catalyst for the reduction of 4-nitrophenol. The result proposes that it can decompose 4-nitrophenol (concentration of 0.005 mol/L) at a reaction rate of 0.0031 s^{-1} within the presence of excess $NaBH_4$ (0.1 mol/L) at a pH level of 9 [(Gupta, Rishi, and Gupta, 2021)]. The nanosized $CuFe_2O_4$ ferrite is utilized as a heterogeneous catalyst for the decomposition of 4-nitrophenol to 4-aminophenol as a product. The result recommends that $CuFe_2O_4$ can completely decompose the nitrobenzene solution at a rate constant of 0.9906 min^{-1} utilizing $NaBH_4$ as a reducing agent [(Ramu *et al.*, 2021)].

It is found that all the ferrite materials utilized for this specific application are dominated by the spinel-type of ferrites, so analyzing the performance of Co_2-Y hexaferrite material for this application may offer fruitful outcomes.

2.2.3 Utilization of ferrites as a photocatalyst for treatment of methyl orange contaminated wastewater

Water quality is an essential question in the present scenario due to the increasing rate of pollution. Although plenty of water is available over the earth's surface, only a

fraction of it (around 0.03% of total water bodies) is convenient for human activities. Water, a vital part of living beings, is deteriorating day by day with rapid industrial growth [(Shah *et al.*, 2022)]. This rapid industrial growth allows the discharge of various pollutants into the water bodies, adversely affecting water quality. Most of these industries, especially concerned with paper, textile, leather, pharmaceuticals, food and packaging, and cosmetics, consume a huge number of dyes annually. Various chemicals are being utilized in industrial processing, from inorganic compounds to harsh organic and complex polymers. The textile industries occupy the largest share (around 60%) of the total consumption of organic dyes and harmful chemicals during the aqueous processing of clothes [(Hai, Yamamoto, and Fukushi, 2007)]. The water bodies exposed to the untreated discharge of industrial waste contain several toxic, mutagenic, carcinogenic, and threatening compounds that cause esthetical pollution and perturbations to the aquatic life (for both microbiological & fishes) and human life [(Shah *et al.*, 2022), (Hai, Yamamoto and Fukushi, 2007)].

The dyes are composed of skeleton, chromophore (groups having unsaturated or multiple bonding), auxochrome (doesn't produce color themselves, enhances the color density), and soluble part (presence is optional, helps to dissolve within solvent) [(Auld, 1907)]. These dyes can be categorized over different applications as direct dyes, vat dyes, acidic dyes, basic dyes, azoic dyes, pigment-based dyes, natural dyes, and dispersed dyes [(Benkhaya, Sara, and Ahmed, 2017)]. Among all these dyes, only half (45 to 47%) of these dyes are found to be biodegradable. The remaining (53 to 55%) portion of these dyes are toxic to the ecosystem and have become an issue of concern these days [(Muhd Julkapli, Bagheri, and Bee Abd Hamid, 2014)]. Due to above mentioned adverse impact on the ecological system and human life, it has become crucial to develop a facile methodology to degrade these water-polluting agents, i.e., non-biodegradable dyes.

Methyl orange (MO) or orange III (dark red crystalline, odorless powder) is an anionic azo-based organic non-biodegradable dye (carcinogenic in nature), having a general molecular formula of $C_{14}H_{14}N_3NaO_3S$ (molecular weight 327.34 g. mol^{-1}), density: 1.28 g/cm^3, solid, melting point >300 °C (573 K), solubility in water: 0.5 g/100 mL (20 °C). The structure of MO consists of the chromophore, auxochrome, and water-soluble parts [(Aroke *et al.*, 2020)]. It is widely utilized in the textile and printing industries. Approximately 10 to 15% of the initial concentration is disposed of directly into the water bodies or open environment while performing industrial processes [(Aroke *et al.*, 2020)]. The increasing utilization of MO in textile & analytical industries and untreated disposal of these industrial waste within water bodies have become a major concern for researchers.

To date, several strategies have been explored by the researchers to degrade these non-biodegradable organic dyes, i.e., Fenton-based reaction, flocculation, photocatalysis, precipitation, treating with hydrogen peroxide, adsorption on activated carbon, treating with intense ultrasonic waves, air drag or inverse osmosis, oxidization using ozone, degradation using UV light irradiation within an aqueous solution, electrochemical degradation and electron beam irradiation [(Shah *et al.*, 2022), (Valero-Luna, Palomares-Sanchéz, and Ruíz, 2016)]. However, these processes may vary in expenditure, degradation effectiveness, and environmental issues. Among these, photo-Fenton-based degradation has been recognized as an outstanding technique due to its reasonably mild conditions, facile processing, and almost complete degradation of water-soluble organic dyes from water [(Valero-Luna, Palomares-Sanchéz, and Ruíz, 2016)].

Traditionally, the homogenous Fenton technology has several drawbacks with a narrow range of acceptable pH levels, utilization of expensive precursors, and producing a huge amount of iron sludge at the end of the process. To overcome these flaws, heterogeneously catalyzed Fenton technology is developed. Till date, heterogeneously

catalyzed Fenton technology (inexpensive, utilization of semiconducting ferrite materials which facilitate the separation, a broad range acceptance for pH level) has become the most effective and largely adaptable, advanced catalytic oxidation process for the treatment of industrial wastewater. Furthermore, the degradation rate is accelerated by the UV–vis light irradiation [(Valero-Luna, Palomares-Sanchéz, and Ruíz, 2016), (Fallmann *et al.*, 1999), (Wang *et al.*, 2014)]. The process involves the generation of exceedingly reactive hydroxyl radicals ($HO^{\bullet}$) by the catalytic dissociation of hydrogen peroxide (H_2O_2) within the presence of iron. The as-generated hydroxyl radicals ($HO^{\bullet}$) have a higher oxidation potential of 2.80 V and can easily oxidize or mineralize most of the organic molecules to produce H_2O, CO_2, and other small molecules. It attacks most non-biodegradable organic compounds (especially unsaturated compounds) with zero selectivity [(Valero-Luna, Palomares-Sanchéz, and Ruíz, 2016),(Liu *et al.*, 2011)]. In continuation, many researchers are focused on the photo-Fenton-based degradation of complex organic compounds, using iron-containing material systems (as a heterogeneous catalyst) having excellent redox configuration and moderate magnetic properties to facilitate the separation after completion of the reaction. Till date, several spinal ferrite-based catalysts have been employed to decompose non-biodegradable dyes from wastewater bodies.

In 2011, sulfated $ZnFe_2O_4$ is used as a heterogeneous catalyst (photo-Fenton) to decompose the reactive black KN-GR (100 mg L^{-1}) under exposure to UV-Visible. The result proposes that $ZnFe_2O_4$ calcinated at 773 K (termed as S773 catalyst) can remove 90% of total organic carbon content & nearly 100% decolorization utilizing 9.8 mM of H_2O_2 and catalyst loading of 0.5 gL^{-1} at a pH value of 6 [(Liu *et al.*, 2011)]. Activated carbon impregnated $FeFe_2O_4$ (Fe_3O_4/AC-H) is employed as a heterogeneous Fenton oxidation of methyl orange. The result recommends that it can provide 100% degradation

of MO (having a concentration of 50 mg L^{-1}) & 59% total organic carbon removal, using H_2O_2 as a scavenger [(Nguyen *et al.*, 2011)].

In 2014, mesoporous copper ferrite ($CuFe_2O_4$) is utilized as a heterogeneous catalyst for the decomposition of imidacloprid (an insecticide mostly applied in agricultural fields). The result confirms that $CuFe_2O_4$ can completely decompose imidacloprid (10 mg L^{-1}) with a rate constant of 1.0445 hr^{-1}, utilizing 40 mM H_2O_2 at a pH value of 3 [(Wang *et al.*, 2014)]. Mesoporous cobalt ferrite ($CoFe_2O_4$) is applied as a heterogeneous catalyst for the decomposition of imidacloprid. The result proposes that $CoFe_2O_4$ can completely decompose imidacloprid (10 mg L^{-1}) with a rate constant of 0.7214 hr^{-1}, utilizing 40 mM H_2O_2 at a pH value of 3 [(Wang *et al.*, 2014)].

In 2015, magnetic bimetallic nano-spinel $NiFe_2O_4$ is used as a photocatalyst for the decomposition of methyl blue (MB) in an aqueous solution. The result suggests that 0.5 g L^{-1} amount of $NiFe_2O_4$ can degrade methyl blue dye (aqueous solution having a concentration of 10 mg L^{-1}) at a rate constant of 0.138 min^{-1} while maintaining the molar ratio of MB/ferrite/ H_2O_2 at 0.001/0.065/1 [(Sharma, Bansal and Singhal, 2015)].

In 2020, spinel nanoparticles of $MgFeCrO_4$ are utilized as a photocatalyst for the decomposition of direct black 122 dye in an aqueous solution. The result advises that 0.04 g L^{-1} of catalyst loading can degrade DB122 dye (aqueous solution having a concentration of 20 mg L^{-1}) at a rate constant of 0.0533 s^{-1} [(Moradnia *et al.*, 2020)].

The problems associated with the poor thermo-chemical stability of these spinal ferrites restrict the utilization of these catalysts in a wide-scale application [(Suthar *et al.*, 2020)]. Researchers have investigated a few hard ferrite magnetic materials due to their excellent thermo-chemical stability to overcome these issues. The M-type strontium hexaferrite ($SrFe_{12}O_{19}$) is utilized to degrade the toluidine blue dye with a poor degradation rate (3 x 10^{-3} min^{-1}) [(Farghali, Khedr, and Moustafa, 2008)]. In comparison, M-type

barium hexaferrite ($BaFe_{12}O_{19}$) results in the poor degradation (70.8%) of methylene blue [(Valero-Luna, Palomares-Sanchéz, and Ruíz, 2016)].

All the ferrite materials utilized for this specific application are dominated by the spinel-type of ferrites, so analyzing the performance of Co_2-Y hexaferrite material for this application may offer fruitful outcomes.

2.2.4 Utilization of ferrites as a microwave absorber for EMI shielding application

Hexaferrites are technologically significant ceramics widely used in numerous applications. They are composed of oxides with ferrimagnetic nature, where metal cations and oxygen anions are placed in a specific pattern. The hexaferrite materials containing barium or strontium cations are crucial members of this category [(Pullar, 2012)]. The performance of these materials depends upon their permittivity, permeability, and electrical resistivity behavior at the operational frequency for several applications [(Duggal and Aul, 2014), (Pubby *et al.*, 2018)]. The hexaferrites are typically used as permanent magnets. It also offers data storage and magnetic recording media, components in electrical devices, primarily operating at widespread microwave/GHz frequencies.

These ferrites principally owe the widespread range of applications in the higher frequency due to the preferred plane of magnetization and the subsequent higher ferromagnetic resonance frequency (FMR) compared to spinel or soft ferrites. This characteristic allows the persistence of reasonable values of permittivity and permeability up to the cut-off frequency limit. Moreover, the permeability and permittivity spectra can be tuned by the compositional variation in these ferrites. Thus, numerous hexaferrite compounds, primarily based on planar W, M, U, Z, and Y-type, are expansively employed in the research for high-frequency applications [(Stergiou and Litsardakis, 2016), (Meena, Bhattachrya, and Chatterjee, 2010), (Geiler *et al.*, 2012)].

Numerous essential applications, likewise broadcasting, satellite/radio communications, radars, wireless networks, GPS, and mobile phones, are operated worldwide within the lower band of microwave frequency (1–18 GHz). In the actual operating conditions, the effectiveness of these systems can be tainted by unwanted emissions or reflections. At the same time, the health risk alarms also impose a restraint on the electromagnetic (EM) waves. Nowadays, high-frequency electromagnetic radiation has arisen as one of the pollutions in the atmosphere [(Chandra Babu Naidu, RoopasKiran and Madhuri, 2017)]. These radiations can generate health issues such as loss of immunity, damage to DNA structure, and restlessness. In mandate to overcome such problems, EMI shielding is essential. EMI shielding is mainly conducted by both absorption and reflection processes. Intense research has been driven on materials for EMI suppression. Many metals and metal-based alloys are established for the suppression of these EM radiations. Usually, metals with better electrical conductivity and high initial permeability give better EMI shielding efficiency, but they need to be substituted with ferrites due to higher cost and density. Till date, several ferrites have been investigated for their microwave absorbing properties for EMI shielding applications.

In 2007, the combination of $(Ni_{1-x-y}Co_xZn_y)Fe_2O_4$ spinel ferrites and paraffin wax (5:1), is characterized for evaluating their microwave absorbing properties within the frequency range of 0.5 to 14 GHz. The result suggests that $(Ni_{0.407}Co_{0.207}Zn_{0.386})Fe_2O_4$ provides the uppermost performance in terms of EM wave absorbing capability within a frequency range of 8.64 to 11.2 GHz & a matching thickness of 3.15 mm [(Xie *et al.*, 2007)].

In 2013, copper-doped NiZn ($Cu_xNi_{0.4-x}Zn_{0.6}Fe_2O_4$) ferrites are considered for evaluating their electromagnetic interference shielding properties within the frequency range of 1 MHz–1.8 GHz. The result confirms that the reflection losses are shifted towards

the lower frequencies with increasing copper content (x). All samples possess the reflection loss ($|R_L|$) greater than 20 dB (99% absorption for the input signal), $|R_L|$ values for all the samples are above 35 dB, providing considerable shielding effectiveness within a moderate attenuation bandwidth from 2 MHz to 40 MHz [(Ruiz, Bercoff and Jacobo, 2013)]. Nanosized barium ferrite blended with novolac phenolic resin (NPR) matrix ($BaFe_{12}O_{19}$-NPR) is analyzed to evaluate their electromagnetic interference shielding properties within the X band (frequency range of 8.2 to 12.4 GHz). The result recommends that the composite (2 mm thickness) having 50 wt% of NPR achieves uppermost reflection loss of −37.06 dB corresponding to 9.5 GHz along with a dual bandwidth of 1.04 GHz and 1.01 GHz showing −10 dB absorption, which can be proposed as a promising candidate for developing a thin magnetic absorber [(Ozah and Bhattacharyya, 2013)].

In 2014, lanthanum-modified NiCoZn-ferrites ($Ni_{0.35}Co_{0.15}Zn_{0.5}La_xFe_{2-x}O_4$) are considered for evaluating their microwave absorbing properties within the frequency range of 2 to 18 GHz. The result suggests that the sample having a general formula of $Ni_{0.35}Co_{0.15}Zn_{0.5}La_{0.02}Fe_{1.98}O_4$ shows its excellency by achieving a minimum of −34 dB along with a broad bandwidth of 5.5 GHz corresponding to reflection loss of −10 dB [(Ren and Xu, 2014)].

In 2016, a blend of multiwalled carbon nanotubes and manganese zinc ferrite ($MnZnFe_2O_4$) is performed to evaluate their electromagnetic interference shielding properties within the X-band frequency range (8 - 12 GHz). The result advises that the addition of both MWCNTs and $MnZnFe_2O_4$ (3:1) as fillers within the epoxy matrix achieves the uppermost EMI shielding (dominated by absorption mechanism) performance [(Phan, Mariatti, and Koh, 2016)]. The lanthanum-modified Ni–Zn ($Ni_{0.8}Zn_{0.2}La_xFe_{2-x}O_4$) ferrites are characterized for evaluating their microwave absorbing properties within the frequency range of 2 to 18 GHz. The result suggests that the reflection loss value for sample

$Ni_{0.8}Zn_{0.2}La_{0.06}Fe_{1.94}O_4$ achieves below −10 dB within the frequency range of 3.1 to 5.9 GHz having its minima at 5.1 GHz (R_L = −15.43 dB). Consequently, the La^{3+} incorporation within the ferrite system improves the microwave absorption capability [(Y. Wang *et al.*, 2016)].

In 2017, magnesium-modified nickel ferrite ($Ni_{1-x}Mg_xFe_2O_4$) is analyzed to evaluate its electromagnetic interference shielding properties within the X-band frequency range (8 - 12 GHz). The result confirms that the high EMI shielding effectiveness of 17 dB for $Ni_{0.6}Mg_{0.4}Fe_2O_4$, 14.3 dB for $Ni_{0.5}Mg_{0.5}Fe_2O_4$ & 12.3 dB for $Ni_{0.4}Mg_{0.6}Fe_2O_4$ are achieved at 8.4 GHz, which are desirable for EMI shielding for desktop & laptop systems. All these three materials possess superior dielectric & magnetic losses at 12 GHz, suggesting their promising microwave absorbing capabilities[(Chandra Babu Naidu, RoopasKiran and Madhuri, 2017)].

All the ferrite materials utilized for this specific application are dominated by the spinel-type of ferrites, so analyzing the performance of Co_2-Y hexaferrite material for this application may offer fruitful outcomes.

2.2.5 Utilization of ferrites as a biocompatible hyperthermia agent

The magnetic excitation and easy controllability behavior of ferrite materials within an external frequency-dependent field allow an extensive range of biomedical applications such as medical diagnostic tools, tracers for MRI, targeted drug carriage, and hyperthermic destruction of cancerous tissues [(Hiergeist *et al.*, 1999), (Fayazzadeh *et al.*, 2020), (He *et al.*, 2018)]. The utilization of ferrite materials for destroying unwanted biological tissues and tumors (malignant cells) is a well-known application. It has widely been studied for the last five decades [(Hiergeist *et al.*, 1999)]. Considering the toxicity of several transition metals (with higher magnetization and eddy current losses), the ferrite shows its promising

candidacy due to its better biocompatibility [(Rashid *et al.*, 2013)]. The principle of magnetic hyperthermia involves the oscillation of magnetic moment within the presence of an externally applied AC magnetic field, which converts magnetic energy loss into the form of heat. The heat produced during this process is utilized to destroy the cancerous cells by achieving a temperature of around 42 to 46^{o}C without affecting healthy tissues. The concept of local and externally controllable heat generation also favors the use of ferrite nanomaterials [(Dutz and Hergt, 2014)]. The heat energy evolved during the hyperthermia process may be due to the hysteresis losses, eddy current losses, Neel & Brownian relaxation in the case of single domain ferrite, and frictional losses due to flipping of nanoparticles with surrounding [(Najafinezhad *et al.*, 2018)].

The magnetic nanoparticles with significant heating performance and good stability may be promising to be used within the field of magnetic hyperthermia. Considering size and stability within the colloidal state, the nanoparticles with a superparamagnetic state (above blocking temperature) are superior. The smaller particle size minimizes the magnetic dipolar interactions with neighboring particles; it doesn't allow the segregation of magnetic nanoparticles within the applied magnetic field. It results in better colloidal stability. The limitation of these superparamagnetic nanoparticles arises due to less heating capability, which is quite good with larger magnetic particles [(Obaidat, Issa and Haik, 2015), (Mehdaoui *et al.*, 2011)]. The selection of a suitable magnetic material is quite intricate due to its simultaneous dependency on several factors such as geometrical parameters (particle size, shape, distribution, availability of anisotropic axes), intraparticle interactions (exchange and superexchange interactions within the atomic magnetic moments for single-domain particles, multi-domain magnetic interactions, the interaction of surface moments with moments available at the core), inter particles interactions (dipole to dipole interactions with the net magnetic moment, direct exchange interactions at the

surface, superexchange interactions between the particles isolated within the non-magnetic matrix), and interaction with the applied magnetic field (interaction of surface moments and magnetic domains with applied magnetic field) [(Obaidat, Issa and Haik, 2015),(Barrera *et al.*, 2020)].

The heating efficiency of any magnetic material may be explained in terms of the specific loss power (SLP) or specific absorption rate (SAR), which can be derived from the following relation [(Hergt and Dutz, 2007)];

$$\text{SAR} = \frac{P_L(H_{AC},f)}{\rho_m} = \left(\frac{1}{\rho_m}\right)\mu_o \pi \chi'' f\, H_{AC}^2 \qquad (2.1)$$

Where H_{AC} represents the strength of applied AC magnetic field at a frequency (f), μ_o is free space permeability, χ'' is an imaginary part of susceptibility, and ρ_m signifies the mass density of the material. In practical application, a higher SLP value is required for any magnetic nanomaterial as a hyperthermia agent. It can generate the desired temperature level while overcoming the absorption of heat energy by an aqueous medium within the human body. According to equation (2.1), it is clear that the SAR value can be increased by enhancing the frequency (f) or the applied AC magnetic field intensity (H_{AC}). Still, it is required to consider an upper limit value of both these parameters. As the human body consists of water-based organs, which are conductors in nature, the excess applied AC magnetic field may generate an eddy current within the human body, damaging these organs [(Obaidat, Issa, and Haik, 2015)]. The Brezovich criterion suggests that the product of frequency and the magnetic field intensity ($H_{AC}.f$) should be limited up to 4.85×10^8 $Am^{-1}s^{-1}$; in consideration of the severity and lesser exposing body area and time, it can also be exceeded up to a maximum value of 5×10^9 $Am^{-1}s^{-1}$ [(Hergt and Dutz, 2007), (Kita *et al.*, 2010)]. Till date, several ferrites have been investigated, and their magnetic hyperthermia capabilities can be analyzed in terms of SAR (specific absorption rate) and SLP (specific loss power) values.

In 2013, mixed-phase composites of $SrFe_{12}O_{19}/MgFe_2O_4/ZrO_2$ are characterized for evaluating their hyperthermia capability at an applied field of 22 Oe at 214 kHz frequency. The result suggests that the sample having 16 weight percentage of Mg and Zr content shows its excellency by obtaining the SAR value of 0.72 W/g [(Rashid *et al.*, 2013)].

In 2014, maghemite phase nanoparticles (γ-Fe_2O_3) are analyzed to evaluate their hyperthermia capability at an applied field of 190 Oe at a frequency of 110 kHz. The result confirms that the γ-Fe_2O_3 achieves the SAR value of 29 W/g [(Lemine *et al.*, 2014)].

In 2016, zinc-modified magnetite nanoparticles ($Zn_xFe_{3-x}O_4$) are performed to evaluate their hyperthermia capability at an applied field of 34.3 Oe at a frequency of 700 kHz. The result proposes that the sample $Zn_{0.9}Fe_{2.1}O_4$ shows its excellency by obtaining the SAR value of 36 W/g [(Hanini *et al.*, 2016)].

In 2017, magnetic nanoparticles of zinc-modified magnesium ferrite ($Mg_{1-x}Zn_xFe_2O_4$) are considered to evaluate their hyperthermia capability at an applied field of 10.2 kA/m at a frequency of 354 kHz. The result advises that the sample $Mg_{0.9}Zn_{0.1}Fe_2O_4$ & $Mg_{0.7}Zn_{0.3}Fe_2O_4$ show their suitability by obtaining the SAR value of 10.29 W/g & 18.73 W/g [(Reyes-Rodríguez *et al.*, 2017)].

In 2020, hematite (α-Fe_2O_3) is characterized for evaluating its hyperthermia capability at an applied field of 170 Oe at a frequency of 332.8 kHz. The result recommends that the hematite achieves the SAR value of 3.5 W/g [(Lemine *et al.*, 2020)]. The Zn–Co–Cr ($Zn_{0.54}Co_{0.46}Cr_{0.6}Fe_{1.4}O_4$) ferrite nanoparticles are analyzed to evaluate their hyperthermia capability at an applied field of 16 kA/m at a frequency of 100 kHz. The result advises that the sample achieves the SAR value of 9.3 W/g after annealing at 500 °C for 2 hrs [(Yu *et al.*, 2020)]. The nickel ($NiFe_2O_4$) ferrite nanoparticles are considered for evaluating their hyperthermia capability at an applied field of 170 Oe at a frequency of

332.8 kHz. The result proposes that the $NiFe_2O_4$ achieves the SAR value of 4.5 W/g [(Lemine *et al.*, 2020)].

In 2022, magnetite (Fe_3O_4) nanoparticles are characterized for evaluating their hyperthermia capability at an applied field of 13.9 kA/m at a frequency of 276 kHz. The result recommends that the Fe_3O_4 achieves the SAR value of 81 W/g & ILP of 1.5 nHm^2/Kg [(Jalili *et al.*, 2022)].

Based on the above-studied ferrite systems for hyperthermia applications, the limited value of SAR allows the researchers to develop other ferrite systems having improved performance. For the single relaxation mode of ferrite nanoparticles in the presence of a sufficiently small external field (within linear response), it is assumed that the average power dissipation of any ferrite system may be governed by the following relationship [(Verde *et al.*, 2012)];

$$P_d^{LRT} = 2\pi^2 \chi_0 \mu_0 H_{AC}^2 f^2 \left[\frac{\tau}{1+(2\pi f\tau)^2}\right] \quad (2.2)$$

Where P_d^{LRT} is power dissipation from linear response theory, χ_0 is susceptibility value at equilibrium, τ is for Neel-Brown relaxation time, which can be described as follows;

$$\tau = \tau_0 \left(\frac{\pi k_B T}{4V_{ef}}\right)^{1/2} . e^{\left(\frac{V_p K_{eff}}{2k_B T}\right)} \quad (2.3)$$

Where τ_0 varies within the 10^{-12} to 10^{-8} s, k_B is Boltzmann constant, T and V_p are temperature and volume of particle, respectively, and K_{eff} is for effective anisotropy (magnetic) value. Apart from LRT (linear response theory), the Stoner-Wohlfarth model also suggests that engineering the anisotropy energy barrier for magnetization reversal within a ferrite system may determine the obtained SAR value. This anisotropy energy barrier is found to be proportional to the product of particle volume and uniaxial anisotropy. The product of these two parameters determines the temperature and frequency-dependent hysteresis behavior [(He *et al.*, 2018)]. Both of these relations propose that the increasing

value of magnetic anisotropy may enhance the SAR value of the ferrite system. Investigators have focused on cobalt-based spinal ferrite with a higher magnetic anisotropy value of 2.0×10^5 J/m^3 [(He *et al.*, 2018)].

In 2007, cobalt ferrite nanoparticles ($CoFe_2O_4$) are characterized to evaluate their hyperthermia capability at an applied field of 24.8 kA/m at a frequency of 700 kHz. The result suggests that the sample exhibits an SLP value of 40 W/g [(Fortin *et al.*, 2007)]. The cobalt ferrite nanoparticles ($CoFe_2O_4$) are also analyzed to evaluate their hyperthermia capability at an applied field of 15 kA/m at a frequency of 300 kHz. The result proposes that the sample shows its excellency by obtaining a SAR value of 37 W/g [(Pradhan *et al.*, 2007)].

In 2018, zinc-modified cobalt ($Co_{1-x}Zn_xFe_2O_4$) ferrite nanoparticles are considered for evaluating their hyperthermia capability at an applied field of 10 Oe at a frequency of 200 kHz. The result recommends that these samples show inferior SAR performance with less than 0.03 W/g [(Ghayour *et al.*, 2018)].

In 2019, cobalt ferrite ($CoFe_2O_4$) nanoparticles are characterized to evaluate their hyperthermia capability at an applied field of 24.4 mT at a frequency of 10 kHz. The result confirms that the $CoFe_2O_4$ achieves the SLP value of 40 W/g [(Lucht *et al.*, 2019)]. The cobalt ferrite nanoparticles ($CoFe_2O_4$) are also used to evaluate their hyperthermia capability at an applied field of 27 Oe at a frequency of 92 kHz. The result advises that the sample achieves the SAR value of 0.37 W/g & ILP of 0.87 nHm^2/Kg [(Jalili *et al.*, 2019)]. The oleic acid-coated $CoFe_2O_4$ (OA-$CoFe_2O_4$) nanoparticles are considered for evaluating their hyperthermia capability at an applied field of 95.6 kA/m at a frequency of 329 kHz. The result proposes that the sample shows a remarkable SAR value of 76 W/g [(Munjal *et al.*, 2019)].

In 2020, cobalt ferrite ($CoFe_2O_4$) is characterized for evaluating its hyperthermia capability at an applied field of 100 Oe at 200 kHz frequency. The result advises that the sample $CoFe_2O_4$ synthesized using the hydrothermal method at 160 ^oC (CFO-160) shows its excellency by obtaining the SAR value of 10.63 W/g & ILP of 0.84 nHm^2/Kg [(Fayazzadeh *et al.*, 2020)].

In 2021, gadolinium substituted cobalt ferrite ($CoFe_{2-x}Gd_xO_4$) is considered to evaluate their hyperthermia capability at an applied field of 25 mT with a frequency of 765 kHz. The result confirms that the sample $CoFe_{1.95}Gd_{0.05}O_4$ shows its excellency by obtaining the specific power loss value of 20 W/g [(Koutsoumbou *et al.*, 2021)]. The mesoporous core-shell cobalt ferrite/hydroxyapatite ($CoFe_2O_4$ + HA) nanocomposite is performed to evaluate their hyperthermia capability at an applied field of 150 Oe at a frequency of 200 kHz. The result recommends that the combination of $CoFe_2O_4$-50 wt% HA achieves the SAR value of 27.9 W/g [(Hassanzadeh-Tabrizi *et al.*, 2021)]. The zinc substituted cobalt ferrite ($Co_{1-x}Zn_xFe_2O_4$) is characterized for evaluating their hyperthermia capability at an applied field of 12 kA/m at a frequency of 183 kHz. The result suggests that the sample $Co_{0.95}Zn_{0.05}Fe_2O_4$ shows its excellency by obtaining a SAR value of 52.6 W/g [(Albino *et al.*, 2019)].

In 2022, cubic-shaped cobalt ferrite nanoparticles ($CoFe_2O_4$) are considered to evaluate their hyperthermia capability at an applied field of 13.9 kA/m at 276 kHz. The result suggests that the $CoFe_2O_4$ achieves the SAR value of 5.2 W/g & ILP of 0.1 nHm^2/Kg [(Jalili *et al.*, 2022)]. The enlarged SAR value associated with cobalt ferrite systems is due to the larger effective anisotropy value. The result indicates the further need to investigate the hard ferrite materials for improving the SAR values.

The use of hard ferrite materials, having a significant anisotropy value ($3.3x10^5$ Jm^{-3} in the case of M-type hexaferrite) [(Koutzarova *et al.*, 2009)], is restricted because of the

larger coercivity value. At a particular frequency, the applied magnetic field is insufficient to achieve saturation; thus, no relaxation and hysteresis losses arise. The excess values of magnetic anisotropy decrease SAR value, lowering the interaction between the ferrite particles, resulting in fewer dipole alignments towards the direction of the applied field [(Najafinezhad *et al.*, 2018)]. According to the linear response theory (LRT), the SAR values are proportional to the hysteresis area under the applied AC magnetic field; thus, the larger coercivity value ($Hc >> H_0$) degrades the SAR performance of the materials [(Najafinezhad *et al.*, 2018), (Carrey, Mehdaoui and Respaud, 2011)]. The particle volume is the second important parameter of concern to achieve the larger SAR value. According to the LRT theory, the optimum volume for the ferrite may be selected using the following relation [(Carrey, Mehdaoui and Respaud, 2011)];

$$V_{opt} = \left(\frac{k_B.T}{K_{eff}}\right).\ln(\pi f \tau_0) \qquad (2.4)$$

The SAR values are found to be less while lowering the particle volume below its optimum volume due to the superparamagnetic response of ferrite nanoparticles. The ferrite nanoparticles within the superparamagnetic state provide a fully reversible hysteresis loop with an applied AC magnetic field; thus, negligible power loss occurs. As the particle volume increases, a ferromagnetic hysteresis loop provides maximum hysteresis area under the applied AC magnetic field, achieving its highest value of SAR at optimum volume. Further enlargement of particle volume enhances the coercivity field, far beyond the applied field. The magnetic reversal becomes intricate as the coercivity field becomes dominant, resulting in minor hysteresis losses and less SAR value [(Rashid *et al.*, 2013), (Carrey, Mehdaoui, and Respaud, 2011)]. So, based on the magnetic anisotropy and optimum volume of ferrite particles, it is desired to develop a ferrite material with a larger value of effective magnetic anisotropy and an optimum coercivity (*Hc*) value similar to the

soft ferrite materials. So analyzing the performance of Co_2-Y hexaferrite material for this application may offer fruitful outcomes.

2.3 Summary of literature review

The literature review suggests that several researchers have focused on these applications using spinel-type ferrites. The drawbacks associated with utilizing a soft ferrite material within these five applications (mentioned above) explain the need for exploration of new materials which exhibit better performance. The Co_2-Y hexaferrite may show its candidacy as a prominent replacement for soft ferrite materials. The magnetic profile compared to soft ferrite is shown in Table 2.1. It shows enhanced magnetic anisotropy (good in terms of using it within microwave absorbing material and as a hyperthermia agent), better thermochemical stability along with similar redox configuration (advantageous in terms of using it as a heterogeneous catalyst) & low value of band gap (facilitating the visible light absorption explaining its application as a photocatalyst).

Table 2.1 Comparative performance of Co_2-Y hexaferrite with spinel ferrite materials.

S.No.	Parameter	Soft ferrite	Y-type hexaferrite
1	Saturation magnetization (M_s)	High	Moderate (below 50 emu/g)
2	Coercivity (H_c)	Low	Moderate (below 500 Oe)
3	Redox configuration	Yes	Yes
4	Magnetic anisotropy (K_1)	Low	Highest with Co_2-Y
5	Thermal stability	Poor	Excellent
6	Chemical stability	Poor	Excellent
7	Efficiency within process	Moderate	Not yet discovered

The literature review also suggests that one can stimulate the physical properties of Co_2-Y hexaferrite by selecting a suitable elemental substitution. The selectivity of elements for the substitution in Co_2-Y hexaferrite to overcome the existing issues is explained below:

A. There are two major issues with existing spinel ferrite as a heterogeneous catalyst for styrene oxidation. First, it has poor thermochemical stability, and second, it arises with a poor conversion efficiency of styrene or less selectivity of the concerned product, i.e., benzaldehyde. It may be eliminated by using Co_2-Y hexaferrite with excellent thermochemical stability. The substitution of Ce^{3+} ions at the Ba^{2+} site in Co_2-Y hexaferrite may facilitate the existence of multivalency ions within the structure and enhance the redox configuration of the system. It may also encourage the formation of oxygen vacancies & may form a minor impurity phase CeO_2 over the surface of the catalyst. These features may boost up oxidative reactivity combinedly.

B. Concerning a spinel ferrite as a heterogeneous catalyst for the reduction of nitro organic compounds, there are two major issues with existing ferrite materials. First, it has poor thermochemical stability, which may be eliminated using Co_2-Y hexaferrite material. The second issue arises with a poor conversion efficiency of nitrobenzene or less selectivity of the concerned product, i.e., aniline. The substitution of Ce^{3+} ions at the Fe^{3+} site in Co_2-Y hexaferrite may facilitate the existence of multivalency ions within the structure and enhance the redox configuration of the system. It may also encourage the formation of oxygen vacancies and increase the reducing reactivity combinedly.

C. Concerning a spinel ferrite as a photocatalyst for the treatment of methyl orange contaminated wastewater, there are two major issues with existing ferrite materials. First, it has poor chemical stability, which may be excluded from using Co_2-Y

hexaferrite material. The second issue arises with the poor degradation efficiency of the non-biodegradable dye. The substitution of Ti^{4+} at the Fe^{3+} site in Co_2-Y hexaferrite may facilitate the existence of multivalency ions within the structure by enhancing the redox configuration. It may also encourage the formation of oxygen vacancies and enhance photocatalytic reactivity combinedly.

D. There are two major issues with existing spinel ferrite as a microwave absorbing material for EMI shielding material. The first one is lower working frequency & poor environmental stability, which may be eliminated by using Co_2-Y hexaferrite material. The second issue arises with the poor absorbing capability of the material. The substitution of La^{3+} at the Ba^{2+} site & substitution of Mg^{2+} at the Co^{2+} site in Co_2-Y hexaferrite may improve the EMI shielding efficiency by improving intrinsic magnetic properties & magnetocrystalline anisotropy

E. There are two major issues with existing spinel ferrite as a hyperthermia agent. The first one is associated with poor biocompatibility and thermochemical stability, which may be eliminated using Co_2-Y hexaferrite material. The second issue arises with the poor heating capability of the material. The substitution of Cr^{3+} at the Fe^{3+} site in Co_2-Y hexaferrite may be expected to improve the heating capability.

2.4 Objectives of the work

In consideration of the literature outcomes, the present research work aims to achieve the following objectives:

(a) Synthesize pure and substituted Co_2-Y hexaferrite using nitrate-citrate sol-gel auto combustion process.

(b) Investigate the role of Ce^{3+} substitution at the Ba^{2+} site in Co_2-Y and evaluate its performance as a heterogeneous catalyst for the oxidation of styrene.

(c) Explore the role of Ce^{3+} substitution at the Fe^{3+} site in Co_2-Y and evaluate its performance as a heterogeneous catalyst for the reduction of toxic nitro-organic pollutants.

(d) Analyze the role of Ti^{4+} substitution at the Fe^{3+} site in Co_2-Y and evaluate its performance as a photocatalyst for the treatment of methyl orange contaminated wastewater.

(e) Study the role of La^{3+} substitution at Ba^{2+} site & Mg^{2+} substitution at Co^{2+} site in Co_2-Y and evaluate its performance as a microwave absorber for EMI shielding application.

(f) Examine the role of Cr^{3+} substitution at the Fe^{3+} site in Co_2-Y and evaluate its performance as a biocompatible hyperthermia agent.