International Journal of Science and Research (IJSR)
ISSN: 2319-7064
Impact Factor 2023: 1.843

Magneto-Structural and Photocatalytic Degradation Towards Synthetic Dye Examinations of $MnFe_2O_4$ MNP's

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Abstract: ***This article focuses on the production of manganese ferrite ($MnFe_2O_4$) magnetic nanoparticles (MNP's) via green sol-gel auto-ignition process. The structural studies done through X-ray diffraction (XRD), microstructural through transmission electron microscopy (TEM), and vibrating sample magnetometry (VSM) were employed to examine magnetic properties. Investigation of the XRD outlines the development of a cubic spinel geometry deprived of any contamination. The average crystallite size was determined to be in the nanometer range, consistent with TEM results i.e. 32-33 nm. The magnetic entities, including saturation magnetization Ms = 20.57 emu/g, remanent magnetization Mr = 13.30 emu/g, and coercivity Hc = 804 Oe, were extracted from the M-H curve. The nanocrystalline sample displayed a dilute ferrimagnetic behavior. Manganese ferrite nanoparticles demonstrated remarkable oxidative degradation activity towards methyl orange synthetic dye, a compound regularly cast-off in the textile industry and recognized for its struggle to biodegradation.***

Keywords: manganese ferrite, green method, magnetic nanoparticles, photocatalyst.

1. Introduction

Now a days, spinel ferrite magnetic nanomaterials have gained recognition as effective candidates for environmental remediation, especially in the photodegradation of synthetic dyes [1]. These nanostructured materials possess distinctive magnetic characteristics and a high surface area-to-volume ratio, providing substantial benefits for water treatment applications. The general formula for spinel ferrites is MFe_2O_4, where M denotes a divalent metal ion such as Ni^{2+}, Co^{2+}, Zn^{2+}, or Mn^{2+} [2, 3]. The rising concentration of organic/synthetic dyes in industrial wastewater poses a significant environmental challenge due to their toxicity, persistence, and potential carcinogenic properties. Conventional water treatment techniques frequently prove inadequate in effectively eliminating these contaminants, highlighting the need for more efficient and sustainable solutions [4]. The photocatalytic degradation utilizing spinel ferrite nanomaterials has attracted considerable interest as an environmentally friendly and cost-effective remedy for this issue. Spinel ferrite nanoparticles demonstrate exceptional photocatalytic activity when exposed to both UV and visible light, rendering them suitable for solar-driven water treatment applications. Their magnetic properties facilitate straightforward separation and recovery from treated water, addressing a prevalent issue in nanomaterial-based water purification systems [5]. Furthermore, these materials can be customized through various synthesis techniques and compositional adjustments to improve their photocatalytic efficiency and stability.

Manganese spinel ferrite ($MnFe_2O_4$) with admirable magnetism and functional surface was widely used as an adsorbent for eliminating heavy metals in water solution. Yet, few studies were focused on azo dyes oxidative degradation process by directly employing $MnFe_2O_4$ nanoparticles as catalyst [6, 7].

Over the years, nanoferrites of zinc, cobalt and manganese have been extensively studied by worldwide researchers because of its unique size dependent physical and chemical properties as compared to bulk counterpart material [8, 9]. The nanoferrites are synthesized by the different methods such as chemical co-precipitation, hydrothermal, microemulsion, citrate-gel, etc. techniques [10, 11]. The wet chemical sol-gel technique is the utmost adaptable process to manufacture synthetic nanoparticles of spinel ferrites and having uncountable benefits over other methods for instance; requires low temperature, ecofriendly, desired nanoarchitecture, chemically stable product formation with desired morphology through modification of synthesis environments and parameters [12].

Recent research has focused on improving the photocatalytic activity of spinel ferrite nanomaterials through doping, surface modification, and creation of heterojunctions with other semiconductors.

In this study, nanocrystalline spinel-type manganese ferrite was produced through a green approach sol-gel auto-ignition method. The structural, microstructural, and magnetic properties were thoroughly examined. Afterward, the synthesized ferrite nanoparticles were employed as a catalyst for the oxidative photodegradation of methyl orange synthetic dye in an aqueous solution.

2. Experimental

Highly pure (99.99%) analytical reagent grade (Merk) manganese nitrate $Mn(NO_3)_2.6H_2O$, ferric nitrate $Fe(NO_3)_3.9H_2O$ and l-ascorbic acid $C_6H_8O_7$ were utilized as raw materials and used without any extra processing.

Fabrication:
Nanocrystalline *$MnFe_2O_4$* spinel ferrite was effectually produced using eco-friendly sol-gel auto ignition technique

and l-ascorbic acid as a fuel. The AR grade nitrate and l-ascorbic acid ($C_6H_8O_6$), serving as a fuel, were each dissolved in 100 ml of deionized water to create a uniform solution. The precursor metal nitrates were combined with the minimum necessary volume of deionized water to achieve a clear solution. The reaction was conducted in an open-air environment, without the use of inert gas protection. The ratio of metal nitrates to l-ascorbic acid i.e. fuel was maintained at 1:3. Liquor ammonia was added gradually to stabilize the pH at neutral i.e 7. An auto-ignition reaction occurred after several hours of continuous heating at 100 ˚C, resulting in the desired product. The uncalcined powder sample was subsequently sintered at 600 ˚C for 6 hours and was then employed for further investigations into its structural, microstructural, magnetic, and catalytic properties.

Instrumentation: Table 1 gives the specifications of the instrumentation employed in the current investigation.

Table 1: Characterization techniques employed in the current study

Characterizations Tools	Model/Make	Specifications
XRD	Miniflex 600, Rigaku-Japan	2θ range of 20˚ - 80˚ at room temperature using Cu-Kα radiation having wavelength λ=1.5405 Å, scanning rate: 0.02 º.
VSM	Lakeshore VSM 7410	applied magnetic field of 7 kOe
TEM	Philips CM-200	Operating voltages: 20–200 kV, Resolution:2.4 Ao.

Photocatalytic Activity Test

At first, 0.1 g of $MnFe_2O_4$ nanoparticles were introduced into 250 ml of a methyl orange solution at a concentration of 30 mg/L. The subsequent aqueous suspension was exposed to stirring for a duration of 40 minutes to enhance both dispersion and adsorption efficacy prior to the degradation process. The pH of the methyl orange solution was modified to 3 through the gradual addition of hydrochloric acid (HCl). Succeeding this adjustment, 1 ml of hydrogen peroxide (H_2O_2) was incorporated as an oxidizing agent. At intervals of 0.5 hours during the degradation process, a small aliquot of the solution was extracted for analysis, with absorbance measured at 507 nm using a spectrophotometer. The degradation rate of methyl orange was subsequently calculated. Subsequently, the degradation rate of methyl orange is estimated by:

$$D\ (in\ \%) = \frac{(C_i - C_t)}{C_i} \times 100 \qquad (1)$$

Where, D was the degradation rate of methyl orange, C_i is the initial concentration of methyl orange and C_t is the concentration of methyl orange at time t.

3. Results and Discussion

Fig. 1 displays the powder XRD diffractograms of cobalt spinel ferrite nanoparticles produced by the eco-friendly sol-gel combustion route. Entire reflections appeared in diffraction pattern agreeably indexed with monophasic cubic spinel geometry with space group *Fd*-3*m* (JCPDS Card #74-2403) lacking any impurity phase for all the product samples [13].

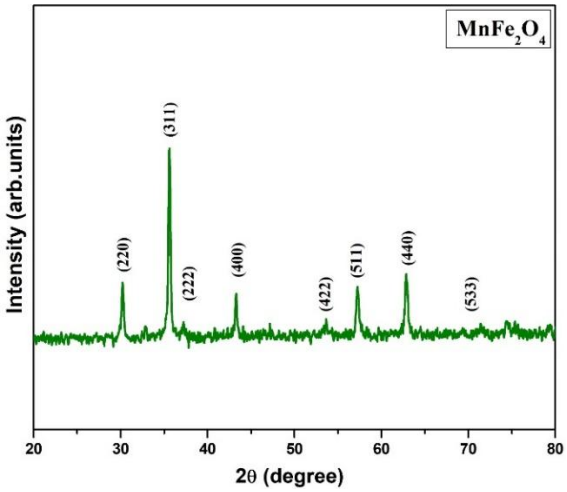

Figure 1: XRD pattern of manganese ferrite nanoparticles

The lattice constant (a), Unit cell volume (V) and X-ray density (d_x) value was conducted utilizing standard relations, with the results compiled in Table 2 [14];

Table 2: Lattice constant (a), unit cell volume (V), X-ray density (d_x), average particle size (t) from XRD and average particle size (D) from TEM of manganese spinel ferrite nanoparticles

Sample	*a (Å)*	*V (Å³)*	*d_x (g/cm³)*	*t nm*	*D (nm)*
$MnFe_2O_4$	8.3572	583.69	5.62	33.4	32.44

From the TEM micrographs, the average crystallite size (D) was estimated with the aid of ImageJ software and was obtained to be ~32.44 nm. The transmission electron microscopy (TEM) analysis illustrated (Fig. 2) that uniform, round nanocrystalline powders were successfully synthesized. The grains displayed a morphology characterized by agglomerated spherical and cubic shapes in the organized samples.

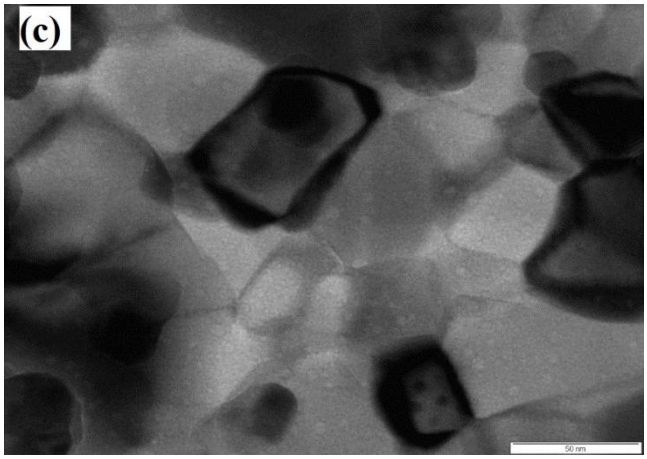

Figure 2: TEM micrograph of manganese ferrite nanoparticles

Magnetic characteristics

To investigate the magnetic properties of the synthesized sample in response to an external magnetic field, the field-dependent magnetization at 300 K was assessed using a Vibrating Sample Magnetometer (VSM). Figure 3 illustrates the M-H curve for the synthesized manganese ferrite sample, which displays a well-defined hysteresis loop characteristic of ideal soft ferrimagnetic materials. Manganese ferrite sample shows magnetic values of including saturation magnetization Ms = 20.57 emu/g, remanent magnetization Mr = 13.30 emu/g, and coercivity Hc = 804 Oe.

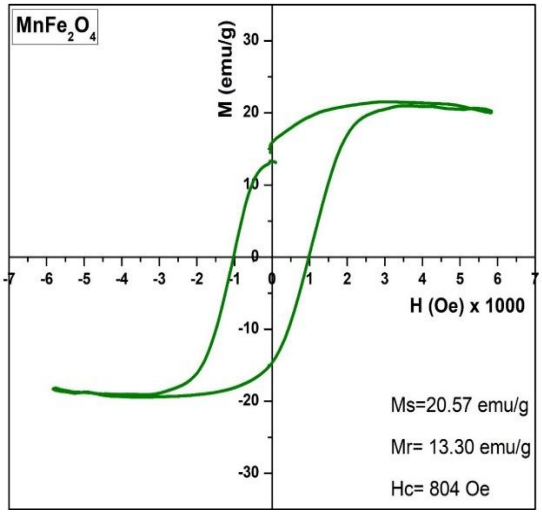

Figure 3: *M-H* hysteresis loop for manganese ferrite

Photocatalytic Activity Studies

Figure 4(a) depicts the UV-Vis spectral changes and degradation efficiency of methyl orange in the presence of $MnFe_2O_4$ nanocrystalline catalyst and H_2O_2. The characteristic absorption peak of methyl orange gradually decreased in intensity during the catalytic reaction.

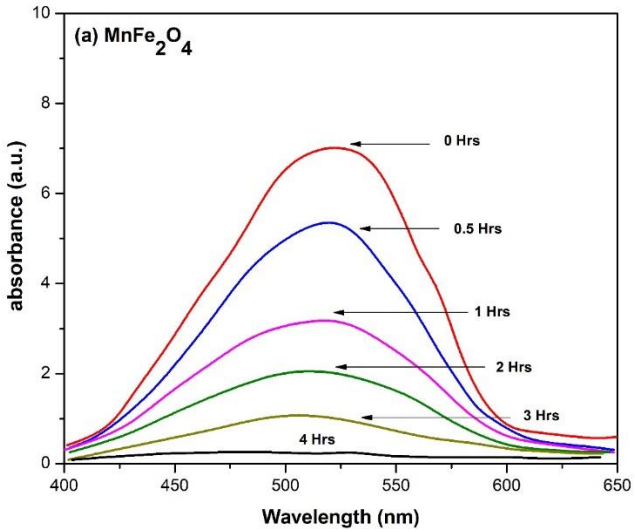

Figure 4. (a): UV-Vis absorbance spectra of methyl orange solution with reaction time (with manganese ferrite)

After approximately four hours, this peak had nearly vanished, with no additional peaks emerging or significant shifts observed in the primary peak. This indicates that almost 98% of methyl orange was effectively degraded, as shown in Fig. 4(b). The exceptional catalytic performance can be attributed to several factors: 1. High specific surface area of the nanoparticles 2. Presence of active absorbed oxygen species 3. Ion transfer between various valence states of A and B site ions within the nanoparticles. These properties collectively facilitated the degradation process, demonstrating that manganese ferrite nanoparticles exhibit outstanding oxidative degradation activity towards methyl orange. Spinel ferrite magnetic nanomaterials have emerged as promising candidates for environmental remediation, particularly in the photodegradation of organic dyes. Their general formula is MFe_2O_4, where M represents a divalent metal ion (e.g., Ni^{2+}, Co^{2+}, Zn^{2+}, or Mn^{2+}).

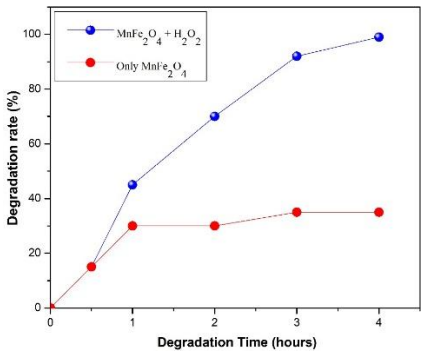

Figure 4. (b): Degradation efficiency of methyl orange for $MnFe_2O_4$ catalyst

These materials offer several advantages in water treatment applications viz. unique magnetic properties, high surface area-to-volume ratio, photocatalytic activity under both UV and visible light, easy separation and recovery due to their magnetic nature, tailorable properties through various synthesis methods and compositional modifications The photodegradation mechanism typically involves the generation of reactive oxygen species (ROS) such as hydroxyl radicals (-OH) and superoxide anions (O^{2-}) upon light irradiation. These reactive species then break down dye

molecules into less harmful or mineralized products. Recent research has focused on improving the photocatalytic activity of spinel ferrite nanomaterials through: doping, surface modification, creation of heterojunctions with other semiconductors. These approaches aim to enhance light absorption, reduce electron-hole recombination, and increase the overall efficiency of the photodegradation process.

4. Conclusions

In this investigation, $MnFe_2O_4$ nanoparticles were successfully synthesized using an environmentally friendly sol-gel auto-ignition method, with l-ascorbic acid serving as the combustion agent. The study conducted a thorough analysis of the structural, microstructural, magnetic, and photocatalytic properties of the synthesized nano-ferrite. X-ray diffraction (XRD) analysis confirmed the formation of fine nanoparticles with a cubic spinel structure, belonging to the space group *Fd-3m*, without any impurity phases. The average crystallite size, calculated using the Debye-Scherrer equation, was estimated to be 32 nm. Transmission electron microscopy (TEM) analysis revealed spherical, uniform nanocrystalline powder, corroborating the XRD-derived nanoparticle size of approximately 33 nm. The magnetic hysteresis (M-H) plot indicated soft ferrimagnetic material properties. The synthesized manganese ferrite nanoparticles demonstrated remarkable oxidative degradation activity towards methyl orange, achieving a degradation efficiency of approximately 98%. UV-Vis spectral analysis showed a gradual decrease in the characteristic absorption peak of methyl orange during the catalytic reaction, with nearly complete disappearance after four hours.

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