Active Photo-Catalytic Characteristics towards Methyl Orange Synthetic Dye for Eco-Friendly Produced Cobalt Ferrite Nanoparticles

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Abstract: ***In this article, pristine cobalt ferrite ($CoFe_2O_4$) nanoparticles were fabricated via ecofriendly sol-gel auto-ignition procedure. X-ray diffraction (XRD), transmission electron microscopy (TEM), and vibrating sample magnetometry (VSM) were employed to examine the structural, microstructural, and magnetic properties, respectively. Analysis of the XRD patterns indicates the development of a cubic spinel phase without any contamination peaks. The average crystallite size was determined to be in the nanometer range, consistent with TEM results i.e. 33 nm. The magnetic properties of the sample were assessed using VSM at room temperature (300 K). Key magnetic parameters, including saturation magnetization Ms = 31.44 emu/g, remanent magnetization Mr = 19.18 emu/g, and coercivity Hc = 830.5 Oe, were extracted from the M-H curve. The nanocrystalline sample exhibited a soft ferrimagnetic behavior. Cobalt ferrite nanoparticles demonstrated remarkable oxidative degradation activity towards methyl orange azo dye, a compound commonly used in the textile industry and known for its resistance to biodegradation.***

Keywords: cobalt ferrite, sol-gel, nanoparticles, magnetic, photocatalyst

1. Introduction

The growing enthusiasm for technological advancement in recent years has led to significant research into spinel ferrites. These materials exhibit remarkable properties, including electrical, dielectric, magnetic, and photocatalytic characteristics, which render them highly valuable in a variety of technical applications [1].

Ferrites are ceramic materials formed from the combination of iron oxide and divalent metal ions. Their significance has increased due to their unique dielectric and magnetic properties [2]. Advanced electronics utilize these materials due to their versatile characteristics and potential uses in various applications, including magnetic storage systems, transducers, actuators, sensors, microwave and high-frequency devices, transformer cores, magnetic resonance imaging, spintronics devices, among others [3].

Altering the chemical composition of spinel ferrite nanoparticles can potentially influence their electric, dielectric, magnetic, and catalytic characteristics. The properties of spinel ferrites are determined by various factors, including the preparation method, sintering temperature, sintering duration, and chemical composition. Mixed metal oxides with the stoichiometric formula MFe_2O_4 (where M represents Ni, Cu, Co, Zn, etc.) and exhibiting a spinel structure are among the most commonly utilized magnetic materials. [4, 5]. Their significance is underscored by their diverse applications across multiple domains. These materials are employed in microwave devices, radio frequency applications, transformer cores, antenna rods, and memory chips, owing to their high electrical resistivity, minimal eddy current and dielectric losses, as well as their chemical stability. [6].

The significant toxicity and high solubility of these synthetic dyes necessitate the exploration of various methods for their removal, including adsorption, filtration, sedimentation, and catalytic processes. Methyl orange is a water-soluble azo dye is utilized in dyeing and printing textiles as a dyestuff [7].

Recent advancements have been made in the field of photocatalytic activity under both UV and visible light. Azo dyes, commonly utilized in the textile industry, are known for their high toxicity, mutagenicity, and carcinogenic properties, posing significant risks to both environmental and human health. Consequently, it is crucial to degrade these dyes prior to their release into the environment. Photocatalytic degradation has emerged as one of the most efficient techniques for wastewater treatment. [8].

Cobalt ferrite semiconductor photocatalysts have been extensively utilized for the degradation of organic pollutants, contributing to the remediation of hazardous waste, the treatment of contaminated groundwater, and the management of toxic air pollutants [9]. The potential of cobalt ferrite in harnessing solar energy and its sensitivity to visible light further enhance its applicability. Over the past decade, its chemical and thermal stability has established cobalt ferrite as a significant material in various domains, including magnetic applications, catalysis, and adsorption technologies [10].

In this study, nanocrystalline spinel-type cobalt ferrite was produced through an environmentally friendly sol-gel auto-ignition method. The structural, microstructural, and magnetic properties were rigorously analyzed. Subsequently, the synthesized ferrite nanoparticles were employed as a catalyst for the oxidative degradation of methyl orange (MO) in an aqueous solution.

2. Experimental

Processing of $CoFe_2O_4$ spinel ferrite nanoparticles

2.1 Materials

Highly pure (99.99%) analytical reagent grade (AR) cobalt nitrate $Co(NO_3)_2.6H_2O$, 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.

2.2 Synthesis

Nanocrystalline $CoFe_2O_4$ 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 (C6H8O6), 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 fuel (l-ascorbic acid) was maintained at 1:3. Ammonia solution was added gradually to stabilize the pH at 7. An auto-ignition reaction occurred after several hours of continuous heating at 110 ˚C, resulting in the desired product. The uncalcined powder sample was subsequently sintered at 800 ˚C for 5 hours and was then employed for further investigations into its structural, microstructural, magnetic, and catalytic properties.

2.3 Characterizations

X-ray diffraction (XRD) analyses were conducted within a 2θ range of 20º to 80º at ambient temperature utilizing Cu-Kα radiation. The examination of surface morphology and microstructure was carried out through transmission electron microscopy (TEM) using a Philips CM200 instrument. Magnetic properties of the materials were assessed at room temperature employing a vibrating sample magnetometer (VSM) (Lakeshore VSM 7410) with an applied magnetic field of 7 kOe. Additionally, the UV-Vis light absorption spectrum of the methyl orange solution was evaluated using a UV-Vis spectrophotometer.

2.4 Catalytic Activity Test

Initially, 0.1 g of $CoFe_2O_4$ nanoparticles were introduced into 200 ml of a methyl orange solution at a concentration of 30 mg/L. The resulting aqueous suspension was subjected to stirring for a duration of 30 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). Following 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.

3. Results and Discussion

Figure 1 illustrates the powder X-ray diffraction (XRD) pattern of $CoFe_2O_4$ spinel ferrite synthesized via the sol-gel ignition method. The diffraction peaks observed in the patterns are consistently indexed to a monophasic cubic spinel structure characterized by the space group Fd-3m (JCPDS Card No. #80-2377), with no evidence of any contaminating phases [11]. The Bragg reflections for this sample exhibit a slight broadening, which indicates the presence of a nanocrystalline structure. The identified planes, including (220), (311), (222), (400), (422), (511), (440), and (533), approved the cubic spinel configuration. Furthermore, the reflection peaks are notably sharp and intense, reinforcing the conclusion that the samples are of a single-phase nature.

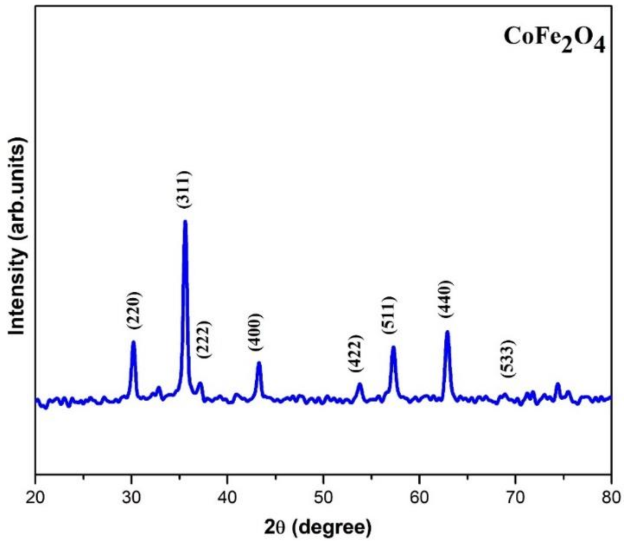

Figure 1: XRD pattern of cobalt ferrite nanoparticles

The lattice constant (a) was determined by means of the typical relation and their values are tabulated in Table 1,

$$a = d\sqrt{(h^2 + k^2 + l^2)} \quad (2)$$

where, d is interplanar spacing; (hkl) is Miller Indices.

The unit cell volume (V) was assessed by using lattice constant.

The estimation of the X-ray density (d_x) value was conducted utilizing relation (3), with the results compiled in Table 1;

$$d_x = \frac{Z \times M}{V \times N_A} \quad (3)$$

where, Z is the number of molecules per formula unit (Z = 8 for spinels), M is molecular mass of the sample, V is the unit cell volume, N_A is the Avogadro's number.

Table 1: 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 cobalt spinel ferrite nanoparticles

Sample	*a* (*Å*)	*V* (*Å*³)	*dₓ* (*g/cm³*)	*t* *nm*	*D* (*nm*)
$CoFe_2O_4$	8.3449	581.11	5.41	35.5	33.54

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. The average crystallite size (D) of the synthesized nanoparticles, as determined by TEM, was measured to be 33.54 nm, as detailed in Table 1.

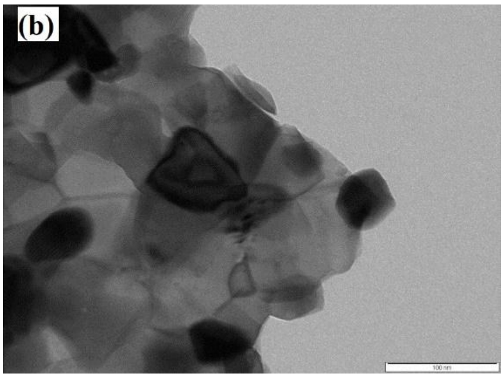

Figure 2: TEM micrograph of cobalt ferrite nanoparticles

Magnetic characteristics

To investigate the magnetic properties of the synthesized sample in response to an external magnetic field, the field-dependent magnetization at room temperature was assessed using a Vibrating Sample Magnetometer (VSM). Figure 3 illustrates the M-H curve for the synthesized cobalt ferrite sample, which displays a well-defined hysteresis loop characteristic of ideal soft ferrimagnetic materials. Cobalt ferrite sample shows magnetic values of including saturation magnetization Ms = 31.44 emu/g, remanent magnetization Mr = 19.18 emu/g, and coercivity Hc = 830.5 Oe.

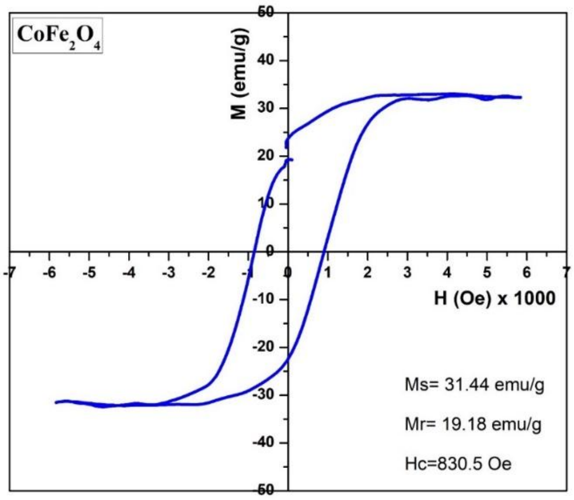

Figure 3: *M-H* hysteresis loop for cobalt ferrite nanocrystals

Photocatalytic Activity Studies

Figure 4 (a) illustrates the progression of UV-Vis spectra and the degradation efficiency of methyl orange with the existence $CoFe_2O_4$ nanocrystalline as a catalyst (as well as H_2O_2). During the catalytic reaction, the intensity of the characteristic absorption peak of methyl orange progressively decreased. After approximately four hours, this peak nearly disappeared, with no emergence of additional or new adsorption peaks, nor any significant shift in the primary peak, indicating that nearly 90% of methyl orange was effectively degraded (as shown in Fig. 4 b). The remarkable catalytic performance can be attributed to the high specific surface area and the presence of active absorbed oxygen species. Furthermore, the transfer of ions among various valence states of A and B site ions within the nanoparticles facilitated the degradation process. Therefore, it can be concluded that cobalt ferrite nanoparticles exhibited outstanding oxidative degradation activity towards methyl orange.

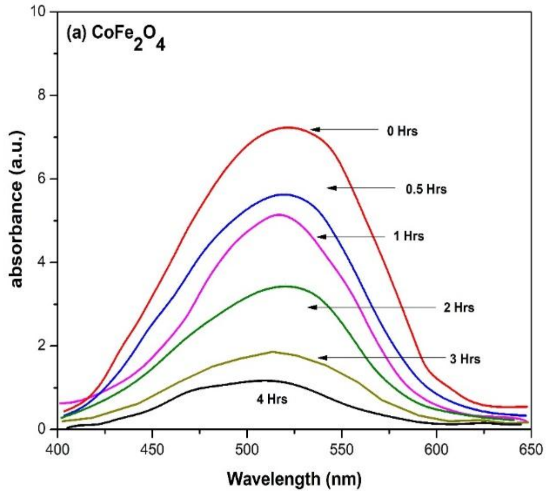

Figure 4 (a): UV- Vis absorbance spectra of methyl orange solution with reaction time (with cobalt ferrite)

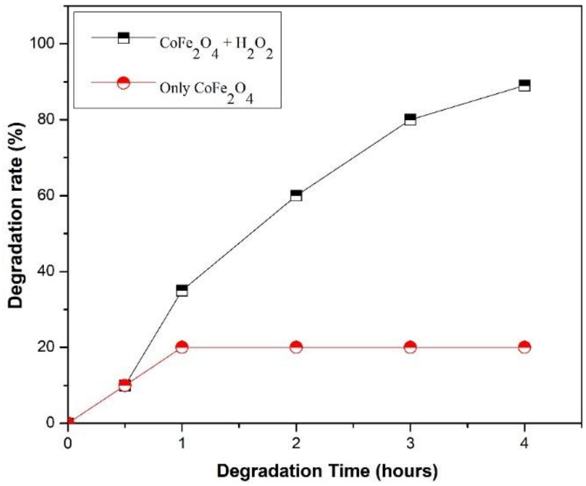

Figure 4 (b): Degradation efficiency of methyl orange for $CoFe_2O_4$ catalyst

4. Conclusions

In this study, $CoFe_2O_4$ nanoparticles were successfully synthesized using the ecofriendly sol-gel auto-ignition method, employing l-ascorbic acid as a combustion agent. A comprehensive examination of the structural, microstructural, magnetic, and photocatalytic characteristics of the synthesized nano-ferrite was conducted. XRD analysis confirmed the successful formation of fine nanoparticles exhibiting a cubic spinel geometry with the space group *Fd-3m*, devoid of any impurity phases. The average crystallite size of the synthesized nanoparticles was calculated using the Debye-Scherrer equation, yielding an estimate of 35 nm. TEM analysis revealed the successful synthesis of spherical, uniform nanocrystalline powder. The TEM findings corroborated the approximate nanoparticle sizes ~35 nm initially determined from the XRD data. M-H plot indicated the properties of a soft ferrimagnetic material. Consequently, it can be inferred that the cobalt ferrite nanoparticles exhibited remarkable oxidative degradation activity towards methyl orange, achieving a degradation efficiency of approximately ~90%.

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