Microwave Combustion Synthesis, Structural and Morphological Properties of Mg-doped CoFe2O4 Nano-Magnetic Photocatalyst

P. Antony Lyla, E. Thirumal, D. Sahaya Lenin,

Abstract: ***In the present study, pure and Mg-doped $CoFe_2O_4$ nano-magnetic photocatalyst was rapidly prepared based on a microwave-assisted method. Magnetic nano-catalyst are potent heterogeneous photocatalysts for degradation of methylene blue (MB) and promising alternatives to conventional catalysts used in wastewater treatments. Powder XRD, FTIR, HRSEM, EDS, and VSM were performed to identify the structure of Mg-doped $CoFe_2O_4$. The optimal conditions for maximum degradation efficiency were confirmed. The degradation efficiency was also reported to be 87.85% under optimal conditions. Finally, nano-magnetic photocatalyst could be reused for six further runs without remarkable changes in catalytic efficiencies; after six runs, adequate reusability and chemical stability were observed.***

Keywords: ***Microwave combustion; Nano-magnetic photocatalyst; Methylene blue; Heterogeneous photocatalyst.***

I. INTRODUCTION

Recently, semiconductor magnetic nano-catalyst shows abundant interest, owing to their distinctive properties such as physical, electrical, magnetic and catalytic activity [1, 2]. Due to the above reasons, low cost, reusability nature of nano-catalyst, various eco-friendly magnetic nano-catalyst materials have been prepared and used as best catalysts [3, 4] or photocatalysts in removing aqueous pollutants [5, 6]. Among them, spinel ferrites with the formula, $(A^{2+}(B^{3+})_2O_4$: A^{2+} = Mn^{2+}, Co^{2+}, Cu^{2+}, etc. and B^{3+} = Fe^{3+}, Al^{3+}, etc.) have developed an vital electro-magnetic materials, due to their probable applications in various inter-disciplinary parts [7]. Rendering to the spreading of cations in tetrahedral (A-) and octahedral (B-) sites, spinel ferrites are secret into normal and inverse structure [8]. In normal spinel, the divalent (A^{2+}) cations on A-sites and the trivalent (B^{3+}) cations on B-sites, and is represented by the formula $^{IV}(A^{2+})^{VI}(B^{3+}B^{3+})O_4$. However, the inverse spinel, with the formula $^{IV}(B^{3+})^{VI}(A^{2+}B^{3+})O_4$, in which the divalent cations occupy the B-sites and the trivalent cations are equally divided among A- and B-sites, where, A and B represents the divalent (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, etc.) and trivalent (Fe^{3+}, Al^{3+}, etc.) cations occupying A- and B- sites, respectively, of a cubic crystal structure with a space group Fd-3m [9].

Cobalt ferrite ($CoFe_2O_4$) is a spinel metal oxide with advantages of low cost, simple preparation in nano-dimensions, simple separation by external magnet, reusability, high oxidization power, and high magnetic potential due to two magnetic oxidant metals, including iron and zinc in its structure [10]. These properties have made $CoFe_2O_4$ a good magnetically separable photocatalyst [11]. The more advantageous nano $CoFe_2O_4$, available by co-precipitation of cobalt and iron salts under alkali conditions, has low band gap energy.

Therefore, for realizing the practical application of photocatalytic reduction method, new high efficiency, easy recovery, and low cost visible-light photocatalysts need to be developed.

II. EXPERIMENTAL PROCEDURE

A. Methods and Materials

All chemicals were used of analytical grade acquired from Merck (India), were used as directly. $Co(NO_3)_2.6H_2O$, 98%, $Fe(NO_3)_3{\cdot}9H_2O$, 98% and $CO(NH_2)_2$ were used as the fuel. The compositions of Mg-doped $CoFe_2O_4$ were prepared with the accumulation of Mg cations of dissimilar molar ratios ($Mg_xCo_{1-x}Fe_2O_4$ with x = 0.0, 0.5) to $CoFe_2O_4$. Preparation of $CoFe_2O_4$ by this technique, the above precursor's mixture, was located into domestic microwave oven and uncovered to the microwave energy (2.45 GHz) multimode cavity at 850W for 15 min. The attained powders were labelled as $CoFe_2O_4$ and $Mg_{0.5}Co_{0.5}Fe_2O_4$.

B. Photocatalytic experiments

Photocatalytic degradation of methylene blue was used to examine the photocatalytic potential of Mg-doped $CoFe_2O_4$ nano-photocatalysts. The UV lamp was located at a 5-cm distance from the solution surface. After adding the pure and Mg-doped $CoFe_2O_4$ nano-photocatalysts to an MB solution, it was stirred mechanically for 20 minutes in the dark for adsorption equilibrium reaction. Other UV lamps were used to irradiate the solution, and the reactor contents were mixed in a mechanical stirrer. It should be noted that all experiments were carried out at ambient temperature.

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For keeping a constant temperature, we placed the reactor in a cooling chamber. During irradiation, the samples were collected at specific intervals and examined by HPLC after photocatalyst separation by an external magnet.

III. RESULTS AND DISCUSSION

A. Powder XRD analysis

The XRD pattern and crystal phase structure of Mg doped $CoFe_2O_4$ with diffraction peaks at 2θ = 30.09°, 35.35°, 42.93°, 53.22°, 56.81°, 62.32°, 70.68°, 73.70°, and 78.43° shown in Fig. 6 were conclude the cubic spinel phase of $CoFe_2O_4$ according to JCPDS 22-1086. These data revealed that, both crystal structure of pure and Mg doped $CoFe_2O_4$ was well preserved (Table 1). Manikandan *et al*. determined the XRD pattern of synthesized $CoFe_2O_4$ using the plant extract assisted microwave combustion method, which confirmed the XRD results of this study [15].

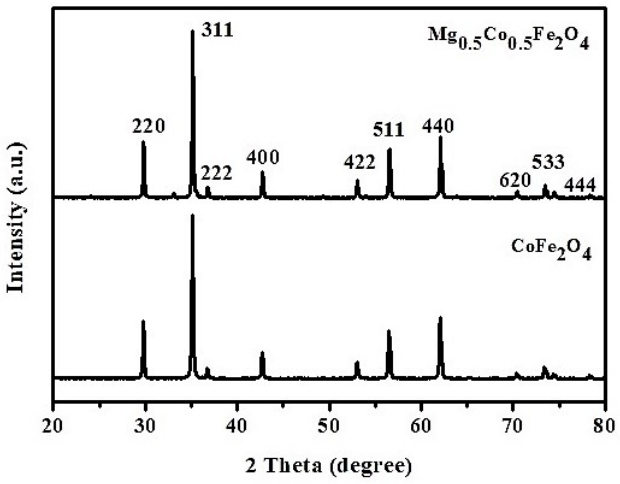

Fig. 1. Powder XRD pattern of pure and Mg-doped $CoFe_2O_4$ NPs.

Table 1. Crystallite size (D), and lattice parameter, (a) values of Mg-doped $CoFe_2O_4$

Sl. No.	Samples	Crystallite size (nm)	Lattice parameter (Å)
1	$CoFe_2O_4$	32.64	8.348
2	$Mg_{0.5}Co_{0.5}Fe_2O_4$	27.15	8.336

B. *FT-IR analysis*

Fig. 2 presents a FTIR spectra of Mg-doped $CoFe_2O_4$ NPs. The adsorbed water stretching at 1646 cm^{-1}, C-O stretching at 1100- 1150 cm^{-1}, and C-H bending 1, respectively. In the spectra of pure and Mg-doped $CoFe_2O_4$ NPs, the peak at 3420 cm^{-1} corresponded to the overlapped OH stretching with aliphatic C-H stretching, and the peak at 1636 cm^{-1} resembled to surface water. In the FTIR spectrum of pure and Mg-doped $CoFe_2O_4$ NPs, tetra-O stretching vibrations in the tetrahedral position could explain the frequency bands observed at 594 cm^{-1}. Also, the band at 588 cm^{-1} represents the Fe octa-O bond in the octahedral position; therefore, the M-O stretching band was present in ferrites. In a study by Manikandan *et al*., similar results were reported regarding the FTIR of cobalt ferrite spinel structure [16].

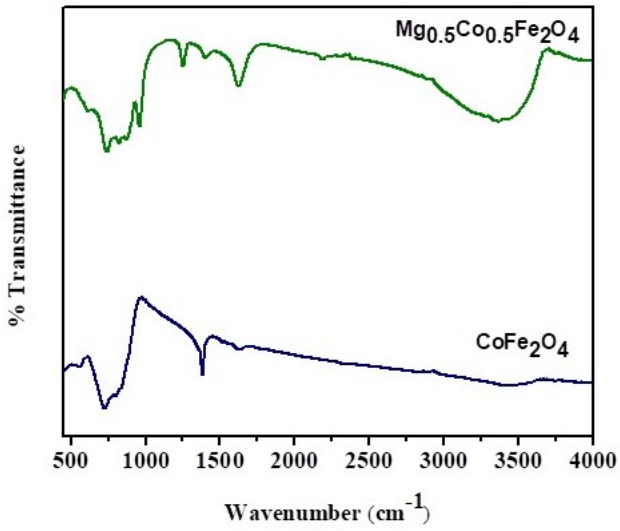

Fig. 2. FT-IR spectra of pure and Mg-doped $CoFe_2O_4$ NPs.

C. HR-SEM analysis

HRSEM images of Mg-doped $CoFe_2O_4$ NPs are shown in Figs. 3a,b represent the formation of spherical-shaped nanoparticles (particle size: ~20 nm). The surface morphologies of these spherical particles in pure and Mg-doped $CoFe_2O_4$ NPs were smooth, uniform, and compact, while the particles were loosely aggregated. The spherical particles had a uniform size distribution.

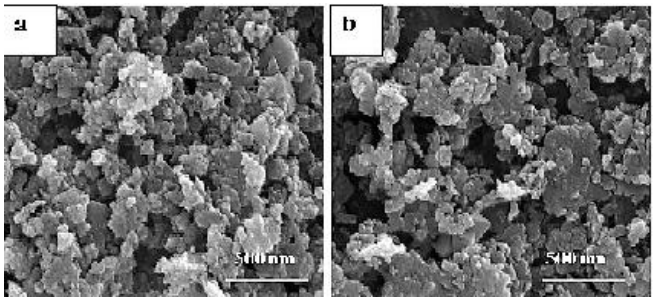

Fig. 3. HR-SEM images of (a) CoFe2O4 and (b) Mg-doped CoFe2O4 NPs.

D. EDX analysis

In Figure 4, the elemental composition analytical spectra of $CoFe_2O_4$ NPs are described. The colours depict areas enriched with Fe, Co, O, in the nanomagnetic photocatalyst. The elements showed a uniform distribution in the

nano-magnetic photocatalyst, and identification of Co, O and Fe confirmed the presence of $CoFe_2O_4$ NPs

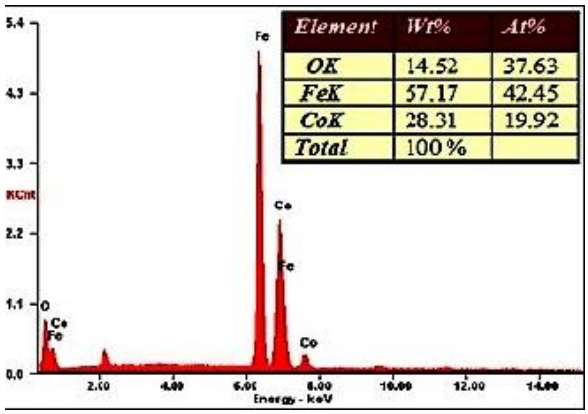

Fig. 4. The EDX spectrum of $CoFe_2O_4$ NPs.

E. VSM analysis

Fig. 5 shows the magnetization curves of pure and Mg-doped $CoFe_2O_4$ NPs. The saturation magnetization of Mg-doped $CoFe_2O_4$ NPs was determined to be 45.68 emu/g and 37.25 emu/g respectively, which is slightly smaller than that (55.42 emu/g) of pure $CoFe_2O_4$. From the result (Table 2), it was observed that, the magnetization degreased with increasing the doping concentration of magnesium cations, due to the additional of magnetic cations Co^{2+} by the non-magnetic cations of Mg^{2+}.

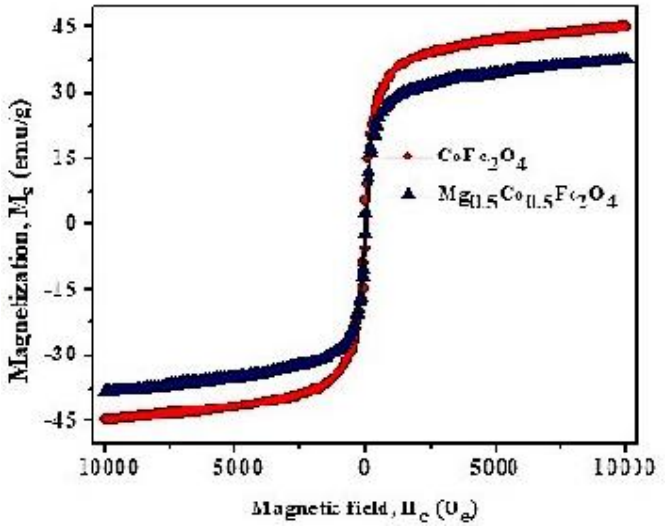

Fig. 5. VSM results of pure and Mg-doped $CoFe_2O_4$ NPs.

Table 2. Magnetic properties (H_c, M_r and M_s) of pure and Mg-doped $CoFe_2O_4$

Sl. No.	Samples	H_c (O_e)	M_r (emu/g)	M_s (emu/g)
1.	$CoFe_2O_4$	9.45	0.856	45.68
2.	$Mg_{0.5}Co_{0.5}Fe_2O_4$	9.12	0.732	37.25

F. Photocatalytic activity

It is essential to degrade the contaminations with the effects of adsorption and photolysis in the analysis of photocatalysis processes. Accordingly, photocatalysis experiment was carried out without photocatalysts and also, the photocatalyst was used for an adsorption experiment in the dark. Finally, comparisons were made regarding the photocatalytic degradation of MB and degradation efficiency is shown in Table 3. There is no major MB degradation was observed in the adsorption and photolysis processes without catalyst [17,18]. The efficiency of photolysis was low in degradation due to the limited production of hydroxyl radicals. Also, increased formation of active radicals, due to the presence of nanophotocatalysts, was observed during photocatalysis. The MB dye removal efficiency improved by increasing the level of active radicals in the photodegradation process. Therefore, with 87.85% degradation efficiency, the photocatalytic process with Mg-doped $CoFe_2O_4$ showed the greatest efficiency than pure cobalt ferrite (76.48 %) for MB dye degradation.

IV. CONCLUSIONS

Mg-doped $CoFe_2O_4$ nano-photocatalyst was obtained by a simple and easy step microwave combustion method. Powder XRD pattern was confirmed the crystal phase structure of Mg doped $CoFe_2O_4$ with cubic structure. FTIR spectrum confirms the pure and Mg-doped $CoFe_2O_4$ NPs, tetra-O stretching vibrations in the tetrahedral position could explain the frequency bands observed at 594 cm-1. The surface morphologies of these spherical particles in pure and Mg-doped $CoFe_2O_4$ NPs were smooth, uniform, and compact, while the particles were loosely aggregated. The spherical particles had a uniform size distribution. The elements showed a uniform distribution in the nano-magnetic photocatalyst, and identification of Co, O and Fe confirmed the presence of pure and Mg-doped $CoFe_2O_4$ NPs. The obtained pure and Mg-doped $CoFe_2O_4$ nano-photocatalyst had outstanding advantages such as much improved PCD activity, good photocatalytic reusability.

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