



ISSN: 2350-0328

**International Journal of Advanced Research in Science,  
Engineering and Technology**

**Vol. 4, Issue 5, May 2017**

# **Synthesis, Characterization of $\text{Fe}_3\text{O}_4$ , $\text{CoFe}_2\text{O}_4$ Nanomaterials and Its Application in Photodegradation of Rhodamin B dye**

**Sandhya Singh, Gaurav Hitkari, Gajanan Pandey**

Research Scholar, Dept. of Applied Chemistry, Babasaheb Bhimrao Ambedkar University, Lucknow, U.P., India  
Research scholar Dept. of Applied Chemistry, Babasaheb Bhimrao Ambedkar University, Lucknow, U.P., India  
Asso. Prof., Department of Applied Chemistry, Sophisticated Instrumentation Laboratory,  
Babasaheb Bhimrao Ambedkar University, Lucknow, U.P., India

**ABSTRACT:** Cobalt ferrite has concerned more considerable attention in modern years because of its exceptional physical properties such as more Curie temperature, greater magneto crystalline anisotropic nature, reasonable saturation magnetization, large magnetostrictive coefficient, outstanding chemical stability and mechanical hardness. Magnetic materials were successfully synthesized by co-precipitation method using Fe (III) and Co (II) in the presence of  $\text{NH}_4\text{OH}$ , at  $90^\circ\text{C}$ . The structure, morphology and magnetic properties of as-prepared materials were characterized via X-ray diffraction (XRD), High resolution Scanning electron microscope (HRSEM), Energy dispersive x-ray spectroscopy (EDX), Fourier transform Infrared (FTIR) and UV-visible spectroscopy. XRD revealed the crystalline structure of the prepared materials. HRSEM images have shown that the nearly spherical morphology of cobalt ferrite nanoparticles. The EDS spectra have shown strong peaks of Fe, Co and O. These synthesized materials has shown the effective degradation of rhodamine b (Rh B) dye.

**KEYWORDS:** Cobalt ferrite, EDS, FTIR, HRSEM, Rh B.

## **I. INTRODUCTION**

In the ancient few centuries, magnetic nanoparticles of spinel ferrite fascinates great curiosity, due to their characteristic properties, such as, catalytic, optical, magnetic and electrical properties [1]. They have prospective applications in a number of area like electromagnetic absorbers, catalysis, microwave devices, sensors, antibacterial activity, water purification, nanoelectronics, high density storage media, drug delivery, and magnetic resonance imaging [2]. The universal formula of spinel ferrite is represented by the formula  $\text{AB}_2\text{O}_4$ , where A and B assume the role of divalent and trivalent cations correspondingly. In an unexceptional spinel structure, complete divalent cations take of the tetrahedral sites, although the trivalent cations supersede the octahedral interstices [3]. The universal formula of spinel ferrite nanoparticles are represented by a  $\text{A}^{2+}\text{Fe}_2^{3+}\text{O}_4$ , where  $\text{A}^{2+}$  has been switched by appropriate divalent metal ions such as Co, Cu, Mg, Zn, Mn and Ni etc. Cobalt ferrite  $\text{CoFe}_2\text{O}_4$  is one and only one of the greatest momentous magnetic materials which can be extensively used in electronic technologies, specifically on magnetic and magneto-optical recording media as a consequence of their extraordinary magneto crystalline anisotropy, temperate saturation magnetization, mechanical inflexibility, and high coercively and chemical stability [4-6]. Singh and co-workers reported zinc and nickel doped cobalt ferrite nanomaterial fabricated by reverse micelle technique and investigate the photocatalytic capability for removal of RhB under visible light irradiation [7, 8]. In the present work material consequently synthesized and investigated for the photocatalytic degradation of RhB using visible light. The prepared photocatalyst is characterized by using so many characterization techniques to study the structural, morphological and optical properties.

## **II. EXPERIMENTAL SECTION**

### **A. MATERIALS USED:**

All chemicals used in this work were analytical grade and used devoid of further purification. Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous sulphate hepta-hydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), Cobalt chloride ( $\text{CoCl}_2$ ) ammonium hydroxide

(NH<sub>4</sub>OH, 26 % of ammonia) and rhodamin B (RhB) were purchased from Merck India. Double distilled water was used as solvent. All the glasswares were washed by concentrated acid. The dried glasswares were used in all the experiments.

### B. SYNTHESIS PROCEDURE:

In this study Fe<sub>3</sub>O<sub>4</sub> nanostructures have been synthesized by the simple co-precipitation method using Fe<sup>2+</sup> and Fe<sup>3+</sup> ions. Aqueous solutions Fe<sup>2+</sup> and Fe<sup>3+</sup> were prepared by dissolving ferric chloride and ferrous sulphate in double distilled water. The solutions Fe<sup>2+</sup> and Fe<sup>3+</sup> ions were mixed in 2:1 molar ratio and heated at 80 °C for 10 minutes. Subsequently heating, the solution was precipitated by addition of ammonia solution with uninterrupted stirring on the magnetic stirrer at 80 °C until pH reached to 13. The reaction mixture was all over again heated at 80 °C for 2 h. Black colored nanoparticles of iron oxide were precipitated. These nanoparticles were separated from the solution by using a strong magnet and washed several times with double distilled water. The powder was then dried in oven at 100 °C for overnight. The overall reaction can be written as



The products were annealed at 400 °C for 3 h to get Fe<sub>3</sub>O<sub>4</sub> nanoparticles and the same procedure follow for the synthesis of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles.

### C. PHOTOCATALYTIC ACTIVITY:

The photocatalytic application of as prepared Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> materials was determined by photodegradation of rhodamin (Rh b) dye under visible light, exposure using Xe lamp (1000 W). 100 mg quantity of Fe<sub>3</sub>O<sub>4</sub> was first dispersed in 100 mL of 50 ppm Rhb solution and stirred for 30 minutes in the murky condition in order to achieve the adsorption equilibrium. The solution was irradiated by visible light in a photocatalytic compartment. Throughout irradiation, solution was agitated using a magnetic stirrer and air was bubbled into the reaction medium to be responsible for a constant resource of oxygen. After desired period interval, an aliquot of solution was isolated, centrifuged and its absorbance was measured on UV-Visible spectrophotometer to calculate the proportion degradation. The similar procedure was repeated for CoFe<sub>2</sub>O<sub>4</sub> nanoparticles also. The photocatalytic degradation efficiency was calculated using the following equation:

$$(\%) \text{ degradation} = ((A_0 - A)/A_0) \times 100$$

Where A<sub>0</sub> represents the original absorbance of the dye solution and A; the absorbance subsequently irradiation at particular time.

## III. CHARACTERIZATION TECHNIQUE

The XRD patterns of as prepared Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> nanoparticles were recorded on Pananalytical's X'Pert Pro X-ray diffractometer in the 2θ range 20 to 80° with step size of 0.025°. High resolution Scanning electron microscope (HRSEM) images of the prepared nanomaterial were observed on SUPRA 40, Ziess equipment. The HRSEM micrographs were achieved at an operating voltage of 3 kV. EDX (Quantax 200 with X-Flash e Bruker) clearly identified the elements present in the nanoparticles. FTIR spectra of as prepared Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> samples were characterized by the Perkin Elmer Spectrum RXI in the range 4000-400 cm<sup>-1</sup>. UV-Visible spectra were recorded in absorption mode on Cary 100 spectrophotometer in the wavelength region 200-800 nm.

## IV. RESULTS AND DISCUSSION

### A. STRUCTURAL STUDY:

Fig. 1 (a, b) shows the XRD patterns of Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> samples, prepared by chemical coprecipitation methods. The structural analysis of the samples were made with the aid of X'pert software and the crystal structure of the samples was found to be inverse cubic spinel type. Using Scherer's equation, the average sizes of the crystals were estimated to be 33 nm for Fe<sub>3</sub>O<sub>4</sub>, 38 nm for CoFe<sub>2</sub>O<sub>4</sub> sample. XRD pattern of Fe<sub>3</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub> is match with JCPDS standard cards no. 861358, 770426 with no extra phases and space group is fd-3m.

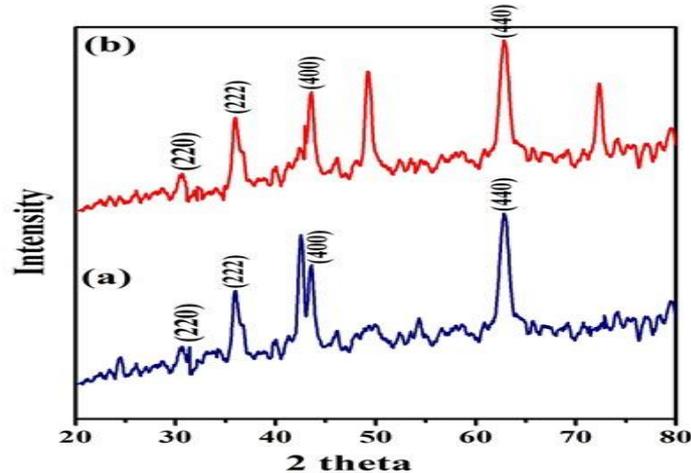


Figure: 1 XRD patterns of (a)  $\text{Fe}_3\text{O}_4$  and (b)  $\text{CoFe}_2\text{O}_4$

## B. MORPHOLOGICAL AND ELEMENTAL STUDY:

The morphology structure of the prepared ferrite nanoparticles is investigated by using HRSEM technique. Surface morphology of the prepared sample  $\text{Fe}_3\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  and are as revealed in Fig. 2 (a, b). HRSEM image of sample (a) demonstrate the formation of porous, microstructure, spongy and similar to network like structure and (b) confirmations that the sample has an insignificant, sphere-shaped in shape and homogeneous crystallites structure which are homogeneously distributed. It can be observed that sample exhibit entirely interannular network with homogenous cavities and pores. The pores structure is accredited to the release of considerable amount of gases during calcination process. Fig. 2 (c, d) exhibit the EDX investigation of  $\text{Fe}_3\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  nanoparticles carried out at room temperature for the elemental corroboration and purity of the sample. The EDX spectrum confirms the homogeneity and gradient of the elements Fe, O, Co are present in the sample.

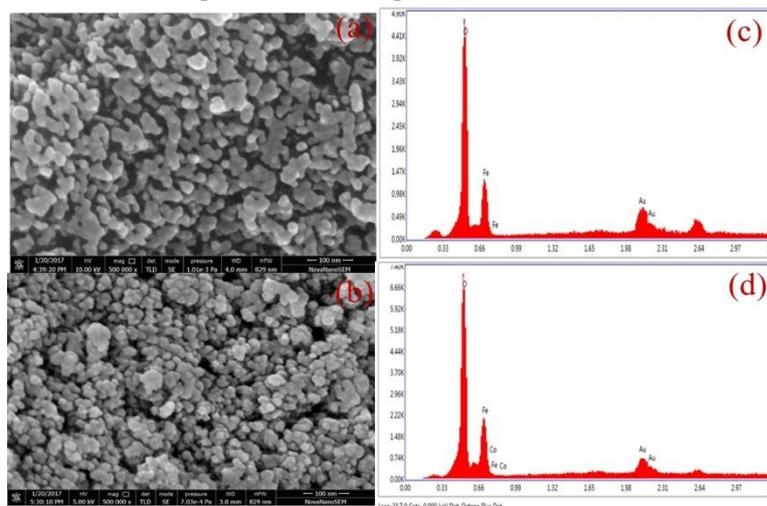


Figure: 2 HRSEM image of (a)  $\text{Fe}_3\text{O}_4$  (b)  $\text{CoFe}_2\text{O}_4$

C. FUNCTIONAL STUDY:

FTIR spectra of Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> nanoparticles is recorded in range 4000-400 cm<sup>-1</sup>. In Fig. 3 (a, b) shows the metal oxygen bond in 400-600 cm<sup>-1</sup> range.

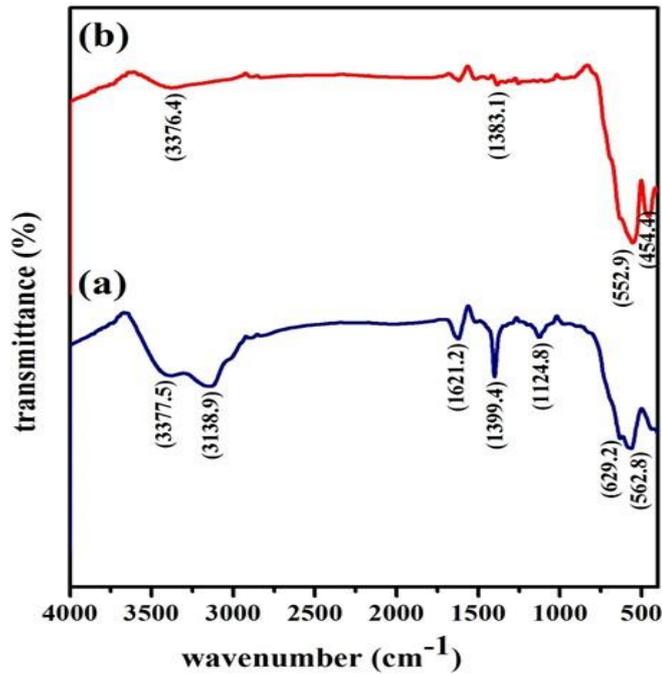


Figure: 3 FTIR spectra of (a) Fe<sub>3</sub>O<sub>4</sub> and (b) CoFe<sub>2</sub>O<sub>4</sub>

D. UV-VISIBLE SPECTROPHOTOMETER

The optical properties were investigated by using UV-vis spectrophotometer for pure Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> ferrite nanostructures as presented in Fig. 4 (a, b). Uninterrupted band gap energy of materials was calculated from the Tauc relation:

$$(\epsilon h\nu)^2 = P (E_g - h\nu) \tag{Eq. 1}$$

Where  $\epsilon$  is the molar extinction coefficient,  $h$  is plank constant,  $\nu$  is frequency of light,  $E_g$  is the band gap energy and  $P$  is the arbitrary constant. The linear part of the  $(\epsilon h\nu)^2$  verses  $h\nu$  graph was used to calculate the band gap values. The intercept of tangent at the x axis gives  $E_g$  value. The  $E_g$  values for the Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> materials 2.8, 2.9 eV using above relation (Fig. 4 c, d).

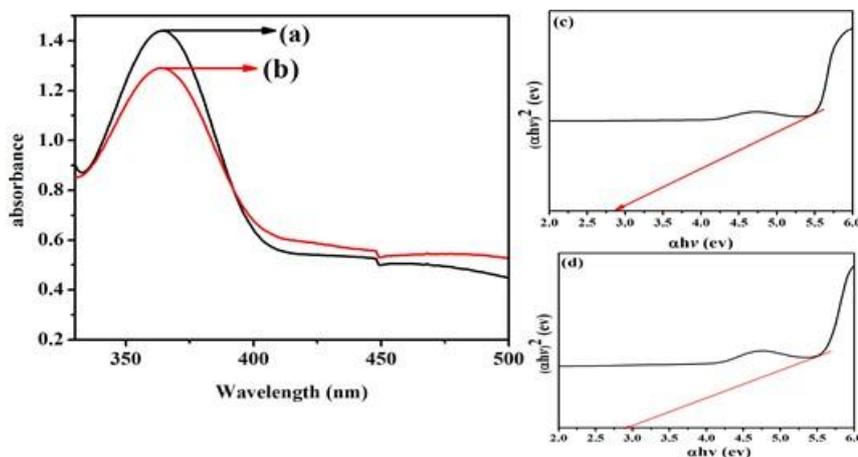


Figure: 4 Uv-spectra of (a) Fe<sub>3</sub>O<sub>4</sub> (b) CoFe<sub>2</sub>O<sub>4</sub> and band gap energy of (c) Fe<sub>3</sub>O<sub>4</sub> and (d) CoFe<sub>2</sub>O<sub>4</sub>

## VI. PHOTODEGRADATION STUDY

The photocatalytic degradation of rhodamine B (RhB) in contradiction of the irradiation time with catalyst  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  are shown in the UV-visible spectra in Fig. 5 (a, b). In case of Rhodamine B dye show two absorption peaks at 503 and 558 nm owing to characteristics absorption of completely de-ethylated and tetraethylated rhodamine B molecule correspondingly [9]. Then Fig. 5 (c, d) shows the  $\text{Fe}_3\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  follow first order kinetics. The value of  $R^2$  is 0.91 for both sample.

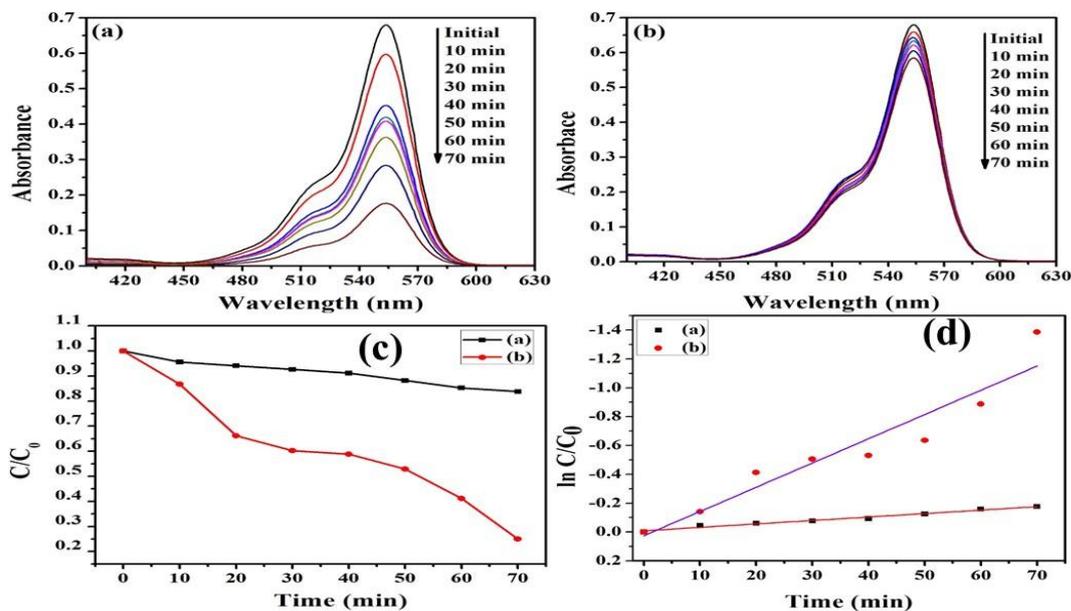


Figure: 5 photocatalytic degradation of rhodamine B by (a)  $\text{Fe}_3\text{O}_4$  and (b)  $\text{CoFe}_2\text{O}_4$  and (c and d) are kinetics graph

## VII. CONCLUSION

Pure  $\text{Fe}_3\text{O}_4$  and cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) has been synthesized by chemical coprecipitation method using ammonia solution as a precipitating agent. The diffraction pattern obtained for pure  $\text{Fe}_3\text{O}_4$  and cobalt ferrite system matched well with the JCPDS card number 86-1358, 77-0426. The effective crystallite size calculated by Scherer's method were found to be in the range, 33, 38 nm. Photocatalytic activity of pure  $\text{Fe}_3\text{O}_4$  is more effective as compared to  $\text{CoFe}_2\text{O}_4$  due to photoluminescence intensity of cobalt ferrite nanoparticles is increase.

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ISSN: 2350-0328

**International Journal of Advanced Research in Science,  
Engineering and Technology**

**Vol. 4, Issue 5 , May 2017**

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