



**Synthesis of Magnetic Nano Sized Cobalt Ferrite Thin Film by
Chemical Bath Deposition Method and their Photocatalytic
Application for Removal of Congo red Dye**

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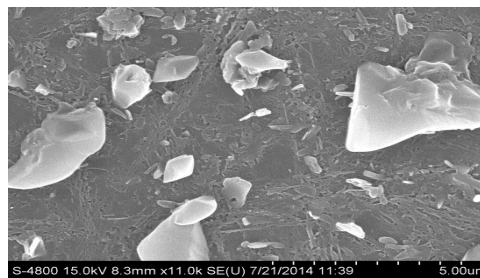
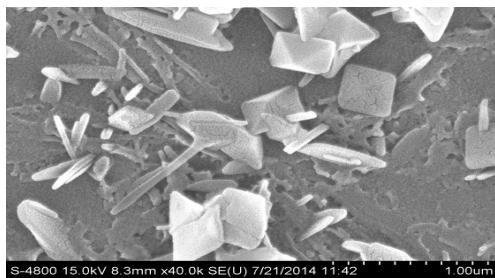
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ABSTRACT

The present investigation report is a novel method for the removal of Congo red (CR) dye from an aqueous solution. In present investigation cobalt ferrite (CoFe₂O₄) thin film was deposited on glass substrate by using chemical bath deposition method. It was successfully prepared while nanostructure of thin film was confirmed by SEM and XRD characterization method. The magnetic property of the film was confirmed by VSM (Vibrating sample magnetometer). The average crystal size calculated by Scherrer formula from XRD analysis is 28 nm. Prepared thin film was then applied for photocatalytic degradation of Congo red dye by dipping it in aqueous solution. Different parameters like contact time, different initial conc. and pH have been studied to optimize reaction condition. The optimum conditions for the removal of the dye are initial concentration 30 mg L⁻¹, contact time 120 min and pH 7.

Graphical Abstract



SEM micrograph of prepared CoFe₂O₄ thin film

Keywords: Congo red dye, cobalt ferrite, SEM and XRD, VSM.

INTRODUCTION

Azo dyes are synthetic dyes, having an azo group (-N=N-) in the structure. Azo dyes are commonly utilized for dyeing textiles and leather. Some azo dyes may engender carcinogenic aromatic amines under certain conditions [1]. Most of those colored dyes are synthetic in nature and are conventionally composed of aromatic rings in their molecular structure, which makes them carcinogenic, mutagenic, inert, and non-biodegradable when discharged into aqueous streams without felicitous treatment. Therefore, the abstraction of such colored agents from the polluted aqueous stream is very exigent predicated on the point of human health and environmental resource auspice [2, 3].

Chemical bath deposition (CBD) is a very simple method has been used for preparation of Nano thin films. In this method only important thing is to maintain proper condition for the preparation of thin films. Several researchers have been using this method for the preparation of Nano thin films [4-10].

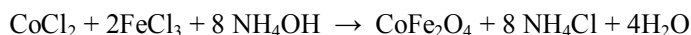
Photocatalytic degradation of organic pollutants especially dyes are carried out using catalyst in powder form. But during the recovery of this catalyst after experiment loss takes place. To overcome this shortcoming best alternative is use of thin film for the degradation of dyes. By using thin films several researchers have carried photocatalytic removal of pollutants [11-16]. But in this report we have used magnetic nano thin film which is very different from other researcher work.

MATERIALS AND METHODS

All chemicals used were analytical grade. The stock solution 1000 mgL⁻¹ of dye was prepared in distilled water. 100 mL of dye solution of the desired concentration was prepared from stock solution. In 100 mL of Congo red dye solution of a different concentration prepared thin film is dipped. Then dipped thin film, dye solution was irradiated with mercury lamp to provide energy to excite CoFe₂O₄ thin film molecule in the reactor. At specific time intervals suitable aliquot of the sample is withdrawn and analyzed after centrifugation. The changes of dye concentration are determined by UV-Visible double beam spectrophotometer (Systronics model-2203) at λ max 510 nm in our laboratory.

Synthesis: Alkaline bath for cobalt ferrite thin films was prepared by A.R. grade chemicals using double distilled water. Bath consist of 0.1 M solution of CoCl₂ 6H₂O and 0.2 M solution of FeCl₃ 6H₂O. These salts were used as source of Co⁺² and Fe⁺³ ions by adding NH₄OH solution made the bath alkaline up to pH-11. The deposition of film was carried out on glass substrate. The glass substrate etched with 2 % dilutes HCl for approximately 20 Sec and ultrasonically cleaned with double distilled water. Finally substrate was dried in air.

The washed and dried glass substrate was immersed in combined alkaline cobalt (II) chloride and iron (III) chloride solution bath. When bath attains the temp of 70°C the precipitate of mixed solution was settled. During the precipitation heterogeneous reaction occurred on the substrate and deposition of cobalt ferrite takes place on the substrate. The film formation started after about 10 min and completed in 120 min at 70°C. Cobalt and iron hydroxides adsorbed onto the substrate during the process.



Then this film is dried in hot air and annealed at 500° C for 4 h to form pure cobalt ferrite with cubic Spinel phase, removing any hydroxide content and complete crystallization of the film takes place.

RESULTS AND DISCUSSION

X-ray Diffractometry (XRD): The XRD diagram of CoFe_2O_4 is as shown in fig-1. It shows main peak at 35.58° and subsidiary peak at 43.73° , 64.45° . It shows match scan with JCPDS card NO-221086 at radiation of 1.54 \AA . The intensity of peaks indicates the crystallinity of CoFe_2O_4 . The average particle size of CoFe_2O_4 is estimated by Scherer formula is 28 nm.

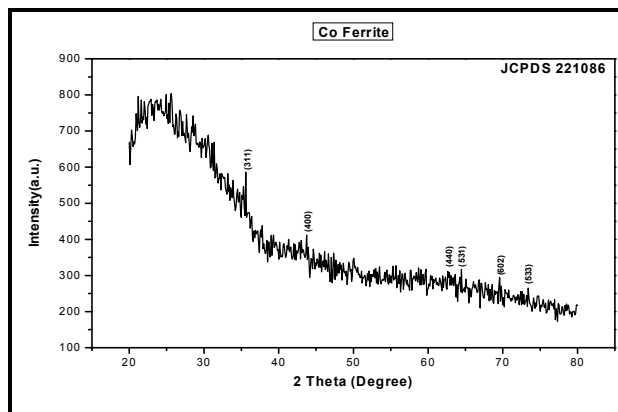


Figure 1. XRD analysis of prepared CoFe_2O_4 thin film.

Scanning electron microscopy (SEM): The CoFe_2O_4 Nano thin film is analyzed by SEM before fig 2(a) and after photocatalytic degradation of CR dye is shown in the fig 2(b). It shows SEM micrographs of CoFe_2O_4 . Fig-2(a) shows surface texture and whitish cluster on CoFe_2O_4 thin film. It has homogeneous surfaced, some microspores as seen from its surface micrographs. It is black-whitish in color, Fig-2 (b) shows after photo degradation of CR on CoFe_2O_4 surface. The thin film surface is similar to before photocatalytic degradation.

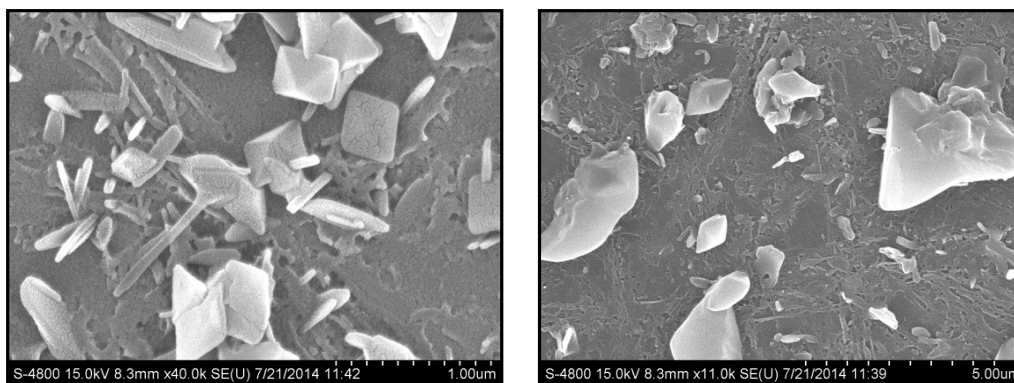


Figure 2. (a) and (b) SEM micrograph of prepared CoFe_2O_4 thin film

Vibrating sample magnetometer (VSM) Analysis: The magnetic property of CoFe_2O_4 Nano thin film was analyzed at R.T by VSM (Vibrating sample magnetometer) at an applied field of 10,000 Gauss. The value of saturation magnetization is 36.5 emu g^{-1} . It is shown in the curve of the fig 3. So this magnetization curve of the sample shows a ferromagnetic behavior, with hysteresis. The magnetic property of nanocomposite is dependent on the sample shape, crystallinity; therefore it can be adjusted to obtain optimum property.

Parametric Studies: The photocatalytic degradation of Congo red dye was studied at λ max 510 nm. The utmost condition for removal of dyes is 30 mg L^{-1} , pH 7 and prepared CoFe_2O_4 thin film. The results obtained during this study are represented in (Fig 4-6).

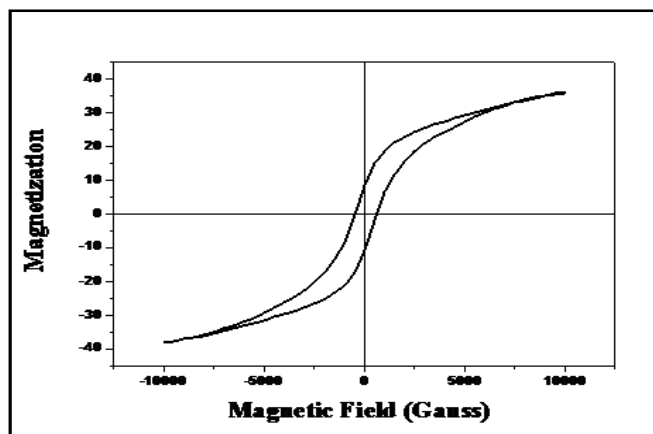


Figure 3. VSM analysis of CoFe_2O_4 Nano thin films (Hysteresis loop).

Effect of pH: The photocatalytic degradation of Congo red dye was studied at different pH values as it is an important parameter for reaction taking place on the particular surface. The role of pH in photocatalytic degradation of dye was studied in the pH range 0-11 at dye concentration 30 mg L^{-1} . It is observed that the rate of photocatalytic degradation enhanced with an increase in pH up to 7 as shown in the (Fig-4). As the pH increases, dye surface becomes basic. In this basic form it forms a bond with CoFe_2O_4 thin film. When the pH increases onwards 7 the repulsion of the dye molecules by CoFe_2O_4 surface would result in reduction in efficiency of degradation of CR.

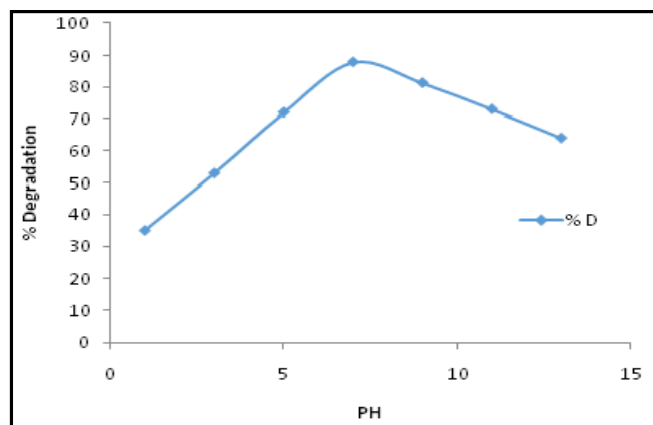


Figure 4. Effect of pH on removal of Congo red dye by CoFe_2O_4 thin film.

Effect of initial dye concentration: The rate of degradation of Congo red dye was studied by varying the dye concentration from 10 to 100 mg L^{-1} because of fixed catalyst concentration active sites remains the same. With the increase of the initial Congo red concentrations, the Congo red molecules get accumulated on the surface of CoFe_2O_4 thin film. However, quenching between these excited Congo red molecules irradiated by visible light will takes place. The quenching probability could also increase with the increase of the initial Congo red concentrations. Consequently, the photocatalytic efficiency of the Congo red dye solution was decreased with the increase of the initial Congo red concentrations is shown in the (Fig 5).

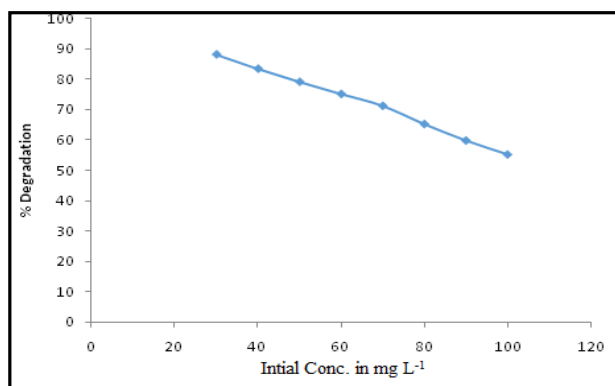


Figure 5. Effect of initial concentration of Congo red dye on % degradation at pH 7.

Effect of contact time: The effect of contact time for the photocatalytic degradation of CR dye by CoFe_2O_4 thin film as shown in the (Fig 6). The dye is slowly degraded in first 30 min and then degradation rate increases rapidly and reaches equilibrium in about 130 min. The rate of degradation of dye is initially slow because the surface of CoFe_2O_4 thin film is not efficiently activated, as the thin film surface get activated rate of degradation of dye increases rapidly.

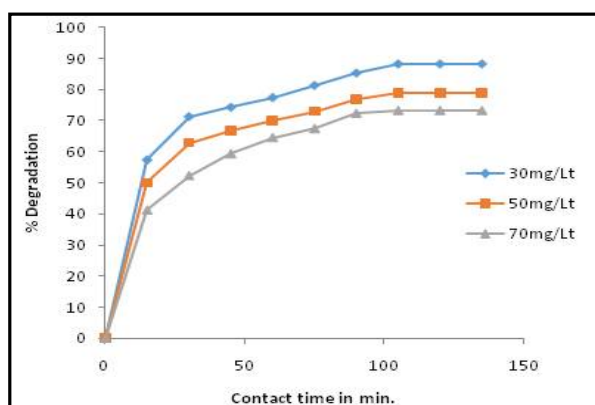


Figure 6. Effect of contact time on % degradation of Congo red at pH 7.

APPLICATION

The results indicate that this magnetic nano thin film has great potentials to be used as water purification media, where the potential of this material can be further modified to increase its degradation capacity towards targeted compounds. So this magnetic nano thin film can be successfully applied for the removal carcinogenic Congo red dye from an aqueous solution.

CONCLUSIONS

Azo dyes are one of the major contaminants present in industrial wastewater. It enters the environment when released through waste water and exerts detrimental effects on flora and fauna. The proposed nanomaterial found to be useful for the waste water purification. The prepared magnetic nano thin film was successfully applied for the removal carcinogenic Congo red dye from an aqueous solution. This magnetic nano thin film has great potentials to be used as water purification media, where the potential of this material can be further modified to increase its degradation capacity towards targeted compounds.

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