Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2018, 7 (4): 779-784

(International Peer Reviewed Journal)

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

Manohar R. Patil[1]* and Annapurna Jha[2]

1. Nano-Chemistry Research Laboratory,G.T.P.College, Nandurbar-425412, **INDIA**
2. Jamshedpur women's college Bistupur Jamshedpur-831004, **INDIA**

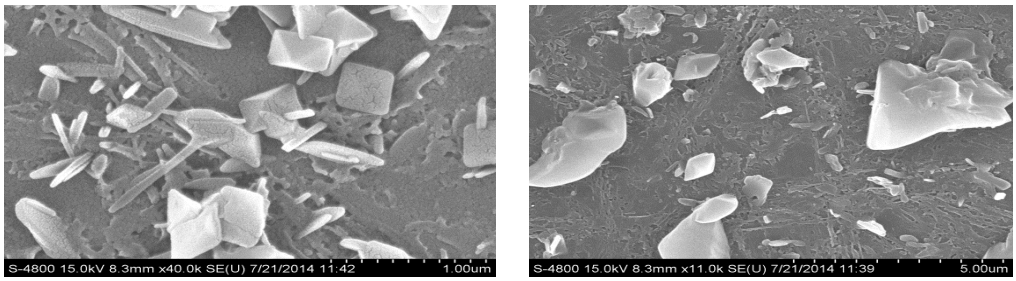
Email:profmanoharpatil@gmail.com

Accepted on 1st July, 2018

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 ($CoFe_2O_4$) 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 $CoFe_2O_4$ 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 $CoFe_2O_4$ 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 $CoCl_2$ $6H_2O$ and 0.2 M solution of $FeCl_3$ $6H_2O$. These salts were used as source of Co^{+2} and Fe^{+3}ions by adding NH_4OH 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.

$$CoCl_2 + 2FeCl_3 + 8\ NH_4OH \rightarrow CoFe_2O_4 + 8\ NH_4Cl + 4H_2O$$

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 35.58^0 and subsidiary peak at 43.73^0, 64.45^0. It shows match scan with **JCPDS card NO-221086** at radiation of 1.54 A^0.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.

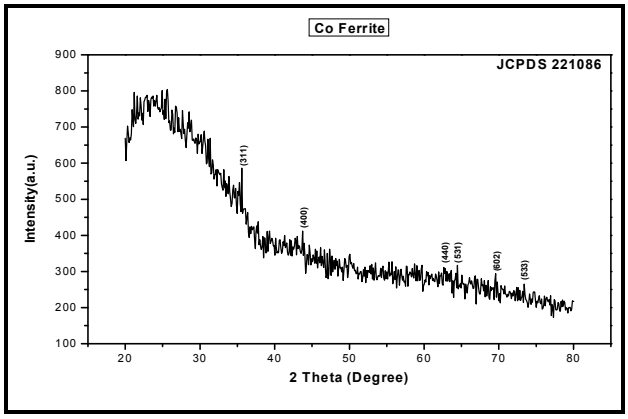


Figure 1. XRD analysis of prepared $CoFe_2O_4$ thin film.

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.

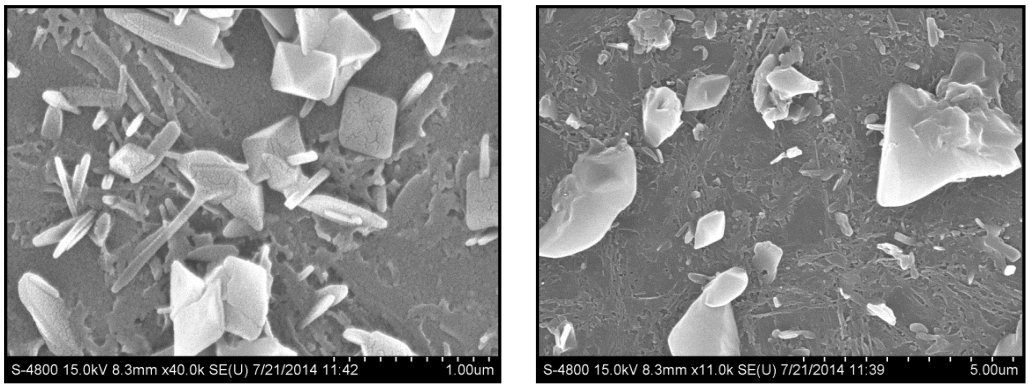


Figure 2. (a) and (b) SEM micrograph of prepared $CoFe_2O_4$ thin film

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).

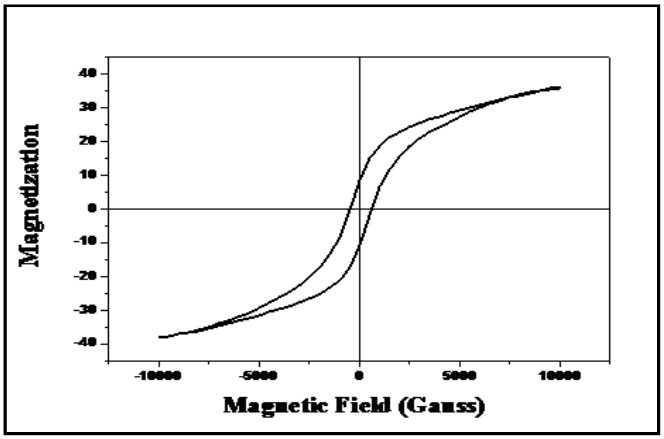


Figure 3. VSM analysis of $CoFe_2O_4$ Nano thin films (Hysteresis loop).

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.

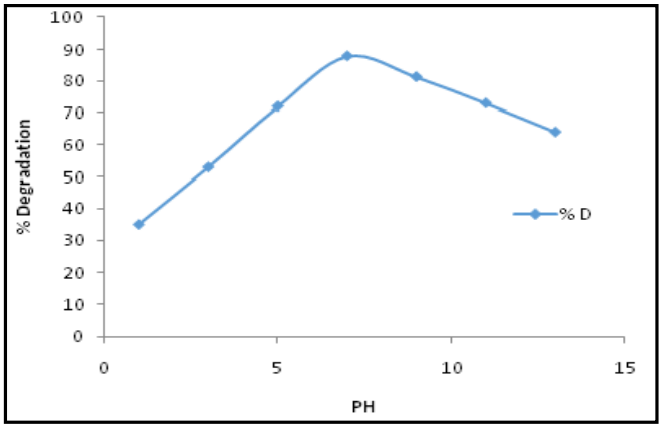


Figure 4. Effect of pH on removal of Congo red dye by $CoFe_2O_4$ thin film.

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).

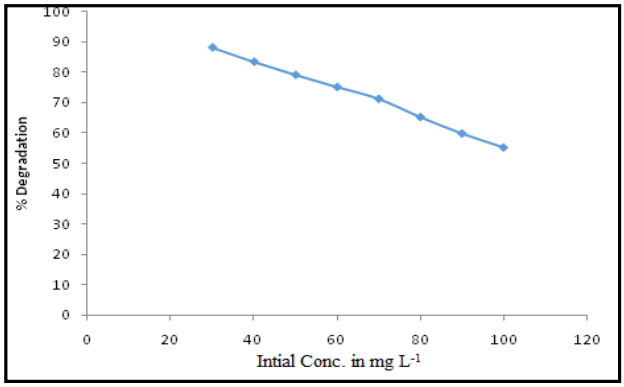


Figure 5. Effect of initial concentration of Congo red dye on % degradation at pH 7.

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.

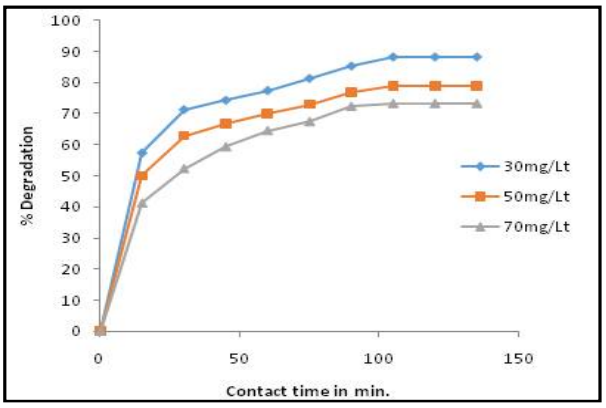


Figure 6. Effect of contact time on % degradation of Congo red at pH 7.

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.

REFERENCES

[1]. C. C.Yun, J. C. Chang, A. H. Chen, Competitive biosorption of azo dyes from aqueous solution on the template crosslinked-chitosan nanoparticles, *Journal of Hazardous Materials*, **2011,** 185,430-441.

[2]. G. Hongxu, YingchangKe, D. Wang, K. Lin, R. Shen, J. Chen, W. Weng, Efficient adsorption and photocatalytic degradation of Congo red onto hydrothermally synthesized NiSnanoparticles, *J.Nanopart. Research*, **2013,** 15, 1475.

[3]. N. V. Cuong, Bifunctional core–shell nanocomposite Mn doped ZnO/Fe_3O_4 for photo degradation of reactive blue 198 dye, *Nanosci. Nanotechnol*, **2014,** 5, 035014-19.

[4]. J. L. Lopez, W. A. Pacheco Serrano, H.D. Pfannes, magnetic properties of crystalline cobalt ferrite films, *Revista Colombiana De Fisica*, **2006,** 38 (3), 1074

[5]. S. M. Chavan,M. K. Babrekar, S. S. More, K. M. Jadhav, Structural and optical properties of nanocrystalline Ni–Zn ferrite thin films, Journal of Alloys and Compounds, **2010**, 507, 21–25.

[6]. Oladiran, A. Ayodeji, A. Oluwaseun, S. Y. Kolawole, study of optical and crystallographic properties of CBD grown CdS thin films, *Int. J. of Res. and Review in Applied Sciences*, **2012,** 12,(3).

[7]. Ozutoka .,F, K. Erturkb, V. Bilgina, Growth, electrical, and optical study of ZnS: Mn thin films, *Acta Physica Polonica A*, **2012,** 121, (1), 221-223.

[8]. Nabiyouni ,G, R. Sahraei, M.Toghiany, M. H. Majles Ara ,K. Hedayat, Preparation and characterization of nano-structured ZnS thin films grown on glass and n-type Si substrates using a new chemical bath deposition technique, *Rev. Adv. Mater. Science*, **2011,** 27, 52-57.

[9]. Raksa,Phathaitep, SanpetNilphai, Atcharawon Gardchareon, SupabChoopun, Copper oxide thin film and nanowire as a barrier in ZnO dye-sensitized solar cells, Thin *Solid Films*, **2009,** 517**,** 4741–4744.

[10]. Y. C. Wang, J. Ding, J. B. Yi, B. H. Liu, High-coercivity Co-ferrite thin films on 100.-SiO_2 substrate, *Applied Physics Letters*, **2004**, 84, (14). 2596-2598.

[11]. D. Zhao, C. C .Chen,Yifeng Wang, M .A .Wanhong, Jincai Zhao, Enhanced photocatalytic degradation of dye pollutants under visible irradiation on Al(III)-ModifiedTiO_2: structure, interaction, and interfacial electron transfer, *Environ. Sci. Technology, 2008***,** 42, 308–314.

[12]. K. Vinodgopal, P. V. Kamat, Enhanced rates of photocatalytic degradation of an azo dye using SnO_2/TiO_2 coupled semiconductor thin films, *Environ. Sci. Technology*, **(1995)**, 29 (3), 841-845**.**

[13]. W. W. Zhang, J. Y. Zhang, Z. Y. Chen, T. M. Wang, Photocatalytic degradation of methylene blue by $ZnGa_2O_4$ thin films, *Catalytic Communication*, **2009,** 10, 1781-1785.

[14]. M. E. Hajji, A. Hallaoui, L. Bazzi1, A. Benlhachemi, O. Jbara, A. Tara, B. Bakiz, Nano structured ZnO, ZnO-CeO_2, ZnO-Cu_2O thin films electrodes prepared by electrode position for electrochemical degradation of dye, Int. *J. Electrochemical Science,* **2014,** 9, 4297-4314.

[15]. K. E. Suryavanshi, A. M. Patil, R. B. Dhake, XRD and SEM Characterization of Chemically Deposited PbxCd1-xS Thin Films, *J. Applicable Chem*., **2015**, 4(4), 1227-1236.

[16]. H. P. Sachin, B M Praveen Treatment of Industrial Azo Dye Effluents by Electrochemical Technique and Its COD Measurement *J. Applicable Chem*., **2017**, 6(6), 1149-1157.