



DEGRADATION OF AZO DYE CONGO RED USING $\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$ AS PHOTOCATALYST

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ABSTRACT

Cobalt substituted nickel nanoferrite with compositional formula $\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$ was prepared via sol-gel auto combustion method at pH = 7 and annealed at 800°C. Structural characterization of prepared samples was done using XRD, FTIR techniques. The photocatalytic degradation efficiency of the synthesized sample against Congo Red dye in aqueous solution was investigated. The photocatalytic experiment was carried out in presence of natural sunlight for 0.100 g catalyst / 100ml dye solution (10mg/L) at pH=5 and the influence of these parameters on degradation was studied.

Keywords: Ni-Co nanoferrites, XRD, autocombustion, Congo Red, Photocatalytic degradation

INTRODUCTION

The effluent produced by dyeing industries is harmful to the living beings. The undesirable substances present in liquid effluents pose severe threat to the immediate recipients. Wastewaters from dyeing industries have caused a serious problem to the environment. The discharged wastes containing dyes are toxic to microorganisms, aquatic life and human beings [1]. The release of coloured waste waters in the environment causes pollution and eutrophication and can originate dangerous byproducts through oxidation, hydrolysis, or through other chemical reactions [2]. It is reported that textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger [3, 4]. The majority of these dyes are azo dyes, which are characterized by the presence of -N=N- group [5]. At the time of production and application about 10% of



these dyes are lost as waste effluents [6]. The degradation of azo dyes in industrial wastewater has therefore received increasing attention. Thus it is important to report that photocatalytic oxidation has been come up as an efficient water treatment technology, especially for organic dye contaminated water, since it is cost effective, highly efficient, low energy-consumption, moderate condition, extensive applicability and decreases secondary pollution. Photocatalysis has gained attention of the researchers in the field of environmental remediation since the discovery of photo-electrochemical splitting of water on titanium dioxide (TiO₂) electrodes. It is reported that semiconductors such as nanosized TiO₂ and ZnO are most promising and investigated photocatalysts for the degradation of organic dyes in aqueous media in presence of solar/ultraviolet (UV) illumination[7]. For the present study Congo Red, an azo dye is selected to investigate photocatalytic efficiencies of newly synthesized ferrite sample by sol gel auto combustion method [8,9].

EXPERIMENTAL

Synthesis of Ni_{0.6}Co_{0.4}Fe₂O₄ nanoparticles

Nanoparticles Ni_{0.6}Co_{0.4}Fe₂O₄ have been synthesized by sol gel autocombustion method. AR Grade Fe(NO₃)₃.9H₂O, Ni(NO₃)₂.6H₂O, Co(NO₃)₂.6H₂O and citric acid (SD fine-chem limited) were accurately weighed in desired stoichiometric proportions and dissolved separately in minimum amount of distilled water. The molar ratio of metal ion precursors to citric acid was kept 1:1. The individual solutions were then mixed together with constant stirring and the pH value of the solution was adjusted to 7 by adding aqueous ammonia solution. The solution was then slowly heated and stirred on a hot plate magnetic stirrer at 80°C till gel was formed which was ignited and burnt in a self-propagating combustion manner to obtain loose powder. The powders were annealed at 800°C in a muffle furnace for 2 hours.



Characterization of $\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$ nanoparticles

Structural characterization of the prepared samples were carried out by X-ray diffraction studies using Bruker AXS, D8 Advance spectrophotometer with Cu-K α radiation($\lambda=1.5418\text{\AA}$) in a wide range of Bragg's angle (20-80°) at room temperature. Infrared spectra of the powder samples were recorded using Fourier Transform Infra-Red Spectrophotometer (FTIR Nicolet, Avatar 370 model) by the KBr pellet method.

Photocatalytic degradation experiment

Photocatalytic degradation experiment was carried out in presence of direct sunlight in the month of April during 10.30A.M.to2.00P.M. 10mg/L Standard dye stock solution was prepared by dissolving commercially available Congo red (synonyms-Direct red28, Cotton red.C.I.22120) as received without further purification in double distilled water. 100 ml of this standard dye stock solution was taken in a borosil glass beaker. The pH of the dye solution was adjusted to 5 using 0.01N HCl. The initial absorbance was recorded (0.413) at 486 nm (λ_{max}) and 0.1g synthesized ferrite was added in it. The dye solution was stirred well and 5 ml samples were withdrawn at regular time interval of 15 minutes, centrifuged to remove photocatalyst and absorbance was measured using Shimadzu UV1800 spectrophotometer. The percentage of degradation was calculated by using the formula.

The percentage degradation = $\{(A_o - A_t) \div A_o\} \times 100$

Where, A_o is the initial absorbance of the dye solution, A_t is the absorbance at time interval 't'.

RESULT & DISCUSSION

Characterization of ferrite

X-ray diffraction patterns corresponding to $\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$ ferrite system confirms the formation of single phase cubic spinel structures. All the planes present in XRD pattern were indexed using Bragg's law. All the characteristics peaks corresponding to the characteristic planes at their respective 2θ values were matched with JCPDS standard powder diffraction card No. 742081 having space group $\text{Fd}3\text{m}$ (227). Most intense peak (311) was used to calculate crystallite size using Debye Scherrer's formula given by, $D_{\text{hkl}} = 0.9 \lambda / \beta \cos \theta$

where, D_{hkl} = crystallite size, λ is wavelength of the X-ray radiation, β is the full width at half maximum (FWHM) of the most intense diffraction peak and θ is Bragg's angle. The average crystallite size of the ferrite samples was found to be 57.12nm. FTIR spectrum shows a band at 576 cm^{-1} , a characteristic of ferrites.

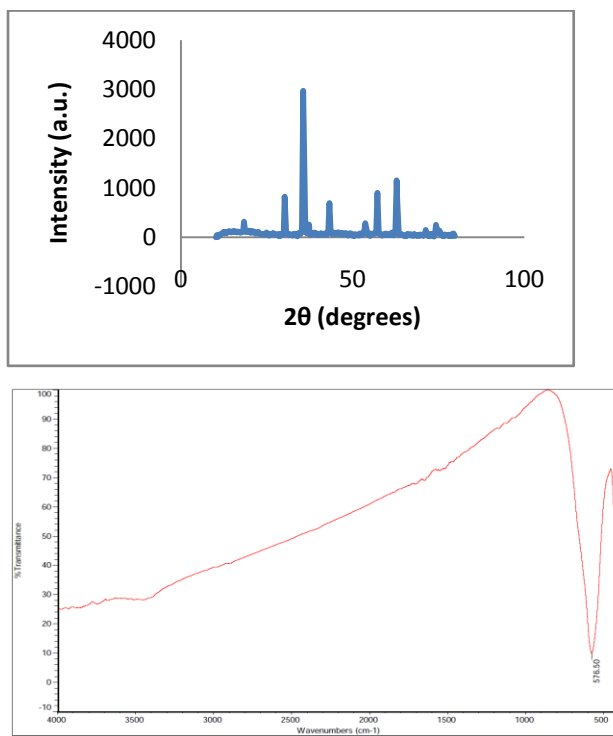


Fig.1&2:-XRD & FTIR spectrum of ferrite sample $\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$

UV-Visible Absorption spectroscopy

UV-Visible absorption spectra of Ferrite nanoparticles was recorded using Shimadzu UV1800 spectrophotometer over the wavelength range 200-800 nm. It has been analyzed to obtain the optical band gap value of the nanoferrite.

The optical band gap energy of the ferrite was calculated using the Planck's equ

$$e = hc/\lambda$$

$$h = \text{Planck's constant} = 4.135 \times 10^{-15} \text{ eV},$$

$$C = \text{Velocity of light} = 3 \times 10^8 \text{ ms}^{-1},$$

$$\lambda = \text{wavelength of absorption} = \text{---} \times 10^{-9} \text{ m},$$

$$\text{Band gap energy (eV)} = 4.135 \times 10^{-15} \times 3 \times 10^8 \times 10^9 / \lambda_{\text{max}}(\text{nm})$$

$$\text{Band gap energy} = 1240 / \text{wavelength (nm)}$$

From fig. 3, λ_{max} for the Ferrite sample was found 300nm

$$\begin{aligned} \text{Band gap energy} &= 1240.5 / 300 \\ &= 4.135 \text{ eV} \end{aligned}$$

Nanoparticle	$\lambda_{\text{max}}(\text{nm})$	Band gap Energy (eV)
$\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$	300	4.135

Table 1: Band gap energy of Ferrite nanoparticle

The band gap energy of Ferrite is found to be 4.135eV (Table 1) which depends upon partial size[10].

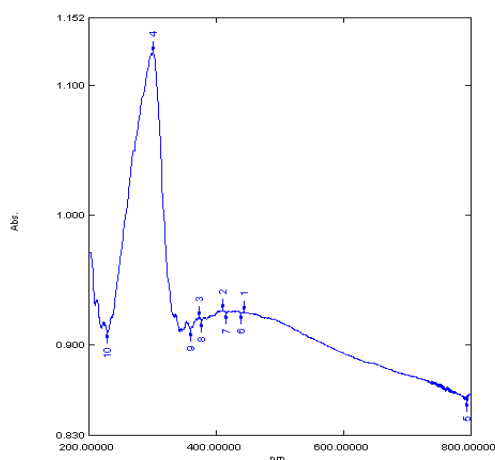


Fig.3:-UV-VIS spectrum of ferrite sample $\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$

Photo degradation of dye

The above experiment indicates that both sunlight and photocatalyst is needed for the effective degradation of azo dye. The variation in absorbance and the efficiency of ferrite sample in degradation of aqueous solution of Congo Red with respect to time and kinetics for 0.1g ferrite/100ml dye solution (10mg/L) at pH 5 is shown in fig 4, 5 & 6 respectively. It is observed that 42.37% degradation of dye solution occurs in 90 minutes for 0.1g/100ml photocatalyst concentration against 10mg/L dye concentration.

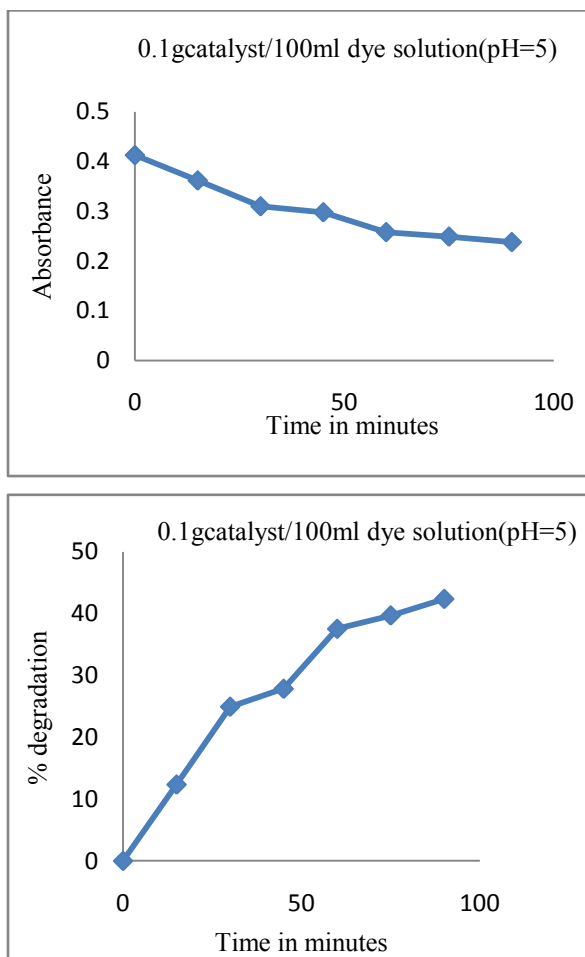


Fig.4&5:- Variation in absorbance and % degradation of dye solution w.r.t. time of irradiation

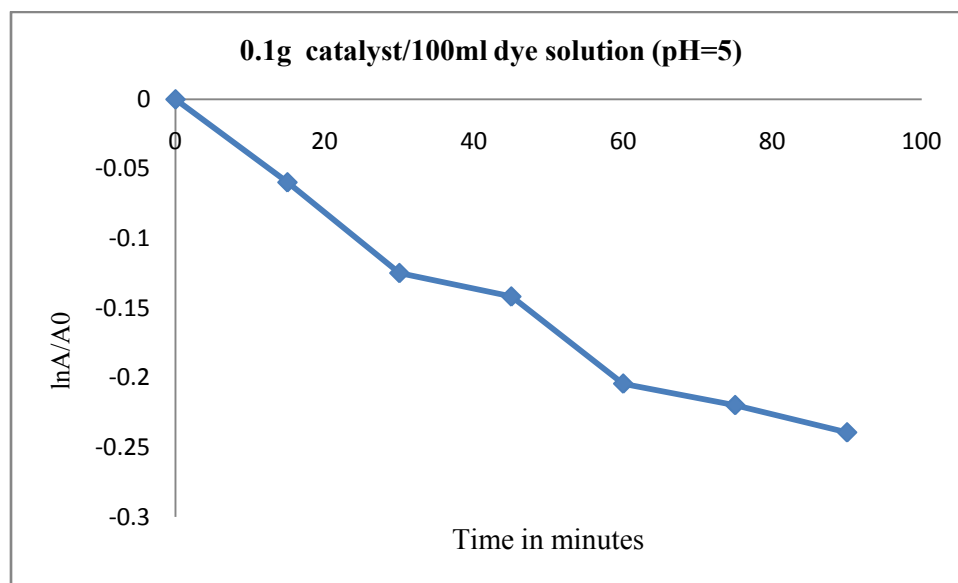
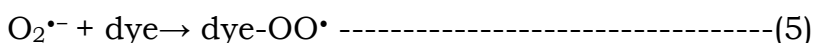
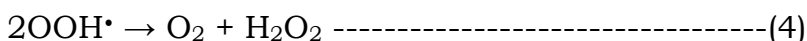
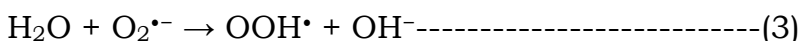
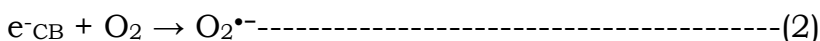
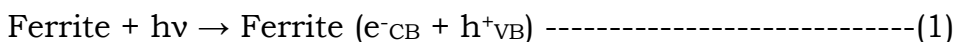
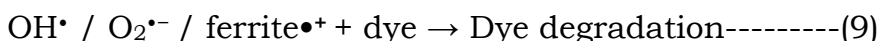
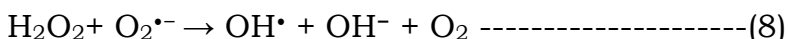
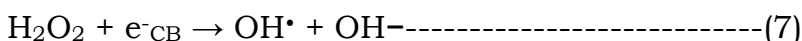
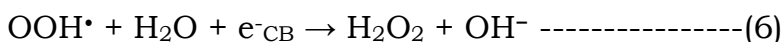


Fig.6:- Kinetics of photodegradation of dye solution

Mechanism of the photocatalytic degradation

The photocatalysed degradation of azo dye in solution is initiated by the photo excitation of the semiconductor (photocatalyst), followed by the formation of electron hole pair on the surface of the catalyst. The colour of azo dye is due to azo bonds and their associated chromophores and auxochromes. During photocatalytic degradation of azo dye nitrogen to nitrogen double bonds (N =N) are cleaved. Azo bonds are the most active bonds in azo dye molecules and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band. The cleavage of -N=N- leads to the decoloration of dyes [11]. Mechanism of the photocatalytic degradation can be explained by following equations:





In the presence of sunlight irradiation ferrite molecules get excited and transfer electron to the conduction band (Eq 1). Electron in the conduction band of ferrite can reduce molecular oxygen and produce the super oxide radical (Eq 2). Molecular oxygen, adsorbed on the surface of the photocatalyst prevents the hole-electron pair recombination process. Recombination of hole-electron pair decreases the rate of photocatalytic degradation. This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule (Eq 3, 4, 5). Hydrogen peroxide can be generated in another path (Eq 6). Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents (Eq 7, 8). The radicals produced are capable of attacking dye molecules and degrade them (Eq 9)[12].

CONCLUSION

In the present study photocatalytic degradation of Congo Red was carried out using ferrite sample $\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$ synthesized by sol gel auto combustion method. The photocatalyst is easily synthesized and is found effective for degradation of the dye.

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