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Preparation, Characterisations and Photocatalytic Studies of Nano Cobalt (II) Ferrite and Zirconia (ZrO_2) Doped Nanoparticles for Aqueous Dye Degradations

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A B S T R A C T

Transition metal ferrites (MFe_2O_4) are magnetic materials with inverse spinel structure and possess potential technological applications such as inductor core, transformer circuits, magnetic sensors, recording equipment, telecommunications, magnetic fluids, microwave absorbers and other high frequency appliances. Cobalt ferrite is one of the important ferrites because it has various properties like semi conducting, magnetic and electrical properties etc. It is used extensively in colour imaging, gas sensing, catalytic applications, ferrofluids and Photocatalysis. In the present work using wet chemical method involving poly N-vinyl pyrrolidone (PVP) as the stabilising agent, nano Cobalt ferrite and Zirconia doped Cobalt ferrite particles are prepared. The samples are ultra-centrifuged, washed and dried to fine powder and are subjected to size characterisations using PXRD and FESEM. The most widely used dyes such as crystal violet (CV) and methylene blue (MB) are chosen for the oxidative degradation assisted by photo irradiation and catalysed by nano Cobalt Ferrite and Zirconia doped Cobalt ferrite. Adopting one pot batch type reactor assembly into which 1mg/20 ml of catalyst loading for 1 mM aqueous dye solution under irradiations are maintained. Pseudo first order kinetic conditions are maintained. The overall pseudo first order rate coefficient values are determined for the two dye degradations using nano Cobalt ferrite and ZrO_2 doped Cobalt ferrite catalyst for three different irradiations (UVA, Solar, IR). For complete degradation of dyes, H_2O_2 addition was tried and similar measurements are made in presence of H_2O_2 separately. In presence of H_2O_2 both catalysts produced higher yields of degradations. The trend observed for dye degradation is CV>MB. The salient results are discussed.

Keywords: Cobalt ferrite nanoparticles, Zirconia doped nanoparticles, Photo catalysis dye degradation.

A R T I C L E I N F O

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1. Introduction

Enhanced photo catalytic activity, magnetic susceptibility, electrical and optical properties are exhibited by nano sized particles of inverse spinel class of mixed metal ferrite compounds. Among the nano ferrite materials, cobalt ferrite nanoparticles with and without dopant show potential and significant applications in magnetic sensors, recording equipment, photo catalysis, semiconductors and other high frequency applications [1-3]. Photo catalysis is useful in many fields like odour control, bacterial inactivation, removal of contaminants from water etc.,

The photo catalytic activity of inverse spinel ferrites depends on various experimental factors and can be tuned by the effects of nanoparticle size, morphology and stability of the nanoparticles [4]. There are many reports available in the literature on the usage of Cobalt ferrite nano materials for the photo catalytic oxidation of various textile dyes [5-11]. The present study evaluates the effectiveness of $CoFe_2O_4$ and ZrO_2 doped $CoFe_2O_4$ for the degradation of harmful dyes such as Crystal violet and Methylene blue. Cobalt ferrite ($CoFe_2O_4$) and ZrO_2 doped cobalt ferrite nanoparticles are prepared by wet chemical method.

The prepared ferrite nanoparticles are size characterized using PXRD and FESEM. FTIR measurements are used to ascertain PVP stabilization of the ferrite nanoparticles. The photo catalytic activity of Cobalt ferrite ($CoFe_2O_4$) and ZrO_2 doped cobalt ferrite nanoparticles was evaluated by degradation of aqueous solution of Methylene blue(MB) and Crystal violet (CV) under three different irradiations. One pot batch type reactor was adapted with optimized catalyst loading under aerobic conditions separately using three different irradiation sources such as UV-Actinide blue, solar and IR irradiation. The absorbance values of the dyes at various intervals of time are measured adapting pseudo first order conditions. The overall pseudo first order rate coefficient values are determined for two dye degradations. Based on the kinetic parameters the catalytic efficiency of ferrite nanoparticles systems is evaluated. Using hydrogen peroxide the kinetics of complete dye degradations are studied under the same irradiations with cobalt ferrite and ZrO_2 doped cobalt ferrite nanoparticles.

2. Experimental

Pure Cobalt nitrate $Co(NO_3)_2.6H_2O$, Ferric nitrate $Fe(NO_3)_3$. $9H_2O$, Zirconium dioxide (ZrO_2), poly n-vinyl pyrrolidone $(C_6H_9NO)_n$ from Merck, India were used as a starting material without further purification. The mixed metal ferrites were prepared by co precipitation method, using PVP as the stabilizing agent. Crystal violet $C_{25}H_{30}N_3Cl$,Methylene blue $C_{16}H_{18}ClN_3S.XH_2O$, Hydrogen peroxide H_2O_2 were also used as received. For the preparation of Cobalt ferrite nanoparticles, 0.1 M of ferric nitrate and 0.05 M of Cobalt nitrate were added drop wise to 50 ml of 2% PVP solution under stirring 1 M of NaOH was added drop wised to maintain the basic condition. The formed precipitate was thoroughly washed with deionized water and then ultra-centrifuged. The resulting precipitate was dried and was characterized by FESEM, PXRD and FT-IR. 5% wt of ZrO_2 and 10 %wt of ZrO_2 was added for the doped Cobalt ferrite nanoparticles.

Instruments

Powder X-ray diffraction (PXRD) patterns of the cobalt ferrite and ZrO_2 doped cobalt ferrite nanoparticles are measured using Bruker D8 advance diffractometer. The patterns are studied with JCPDS file cards and peaks are characterized. Field emission scanning electron microscope (FESEM) was carried out using SU6600 HITACHI model operating at an accelerating voltage of 100 kV. FTIR of Cobalt ferrite and ZrO_2 doped Cobalt ferrite nanoparticles and pure PVP are carried out using KBr pellets and TENSOR 27-FTIR Spectrometer.

Photo catalytic studies

1mM aqueous solutions of Crystal Violet (CV) and Methylene Blue (MB) dye were prepared. 1mg/20 ml of catalyst loading was fixed for photo catalytic studies. Irradiations were carried out using tungsten lamp for UV-Actinide Blue, IR lamp for IR and natural solar irradiation. The lamp was separated with 15 cm distance from the surface of the solution. The kinetics of dye degradation was studied by measuring the absorbance values at their wavelength maxima at various time intervals. At given irradiation time intervals, 2 ml of dye solution were collected and absorbance values are noted using UV-Visible spectro photometer.

3. Results and Discussion

Size Characterization of the synthesized Photo catalyst

$CoFe_2O_4$ and ZrO_2 doped $CoFe_2O_4$ nanoparticles were prepared by co precipitation method. The crystallinity and phase purity of the samples were confirmed by analyzing X-ray powder diffraction method. The X-ray diffraction patterns of $CoFe_2O_4$ and ZrO_2 doped $CoFe_2O_4$ nanoparticles agree closely with the standard values given in the JCPDS data card (22-1086) [12]. (Figure 1).

The average crystallite sizes of the samples are calculated using FWHM and Scherer formula. $L = 0.89\ \lambda/\beta\ \cos\theta$, where L is the average particle size, λ is the X-ray wavelength (0.1542nm), β is the full width at half maximum (FWHM) and θ is the diffraction angle.[13] The well-defined peaks at (220), (311), (222), (400), (422), (511) ,(440) indicate that the $CoFe_2O_4$ material in the inverse spinel phase. The strongest reflection comes from the (311) plane which corresponds to cubic crystal structure. The relative intensity of main peaks of $CoFe_2O_4$ increases with doping of zirconium. The mean size values are found to be 28.5 ± 1 nm, 27 ±1 nm and 26 ±1 nm respectively for $CoFe_2O_4$ and 5 %wt ZrO_2 doped and 10 %wt ZrO_2 doped nanoparticles respectively.

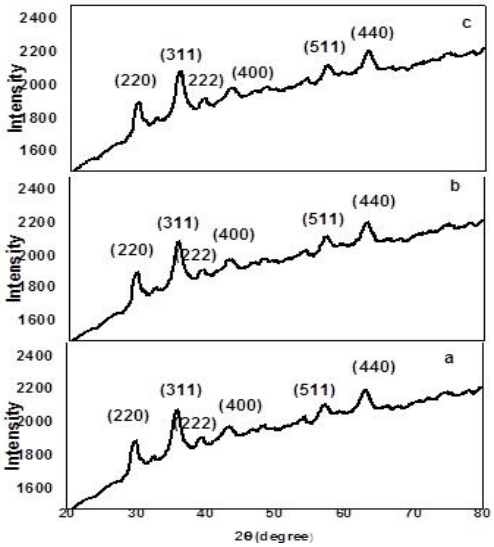

Figure 1: PXRD of a) $CoFe_2O_4$ b) 5 %wt ZrO_2 doped c) 10 %wt ZrO_2 doped nanoparticles

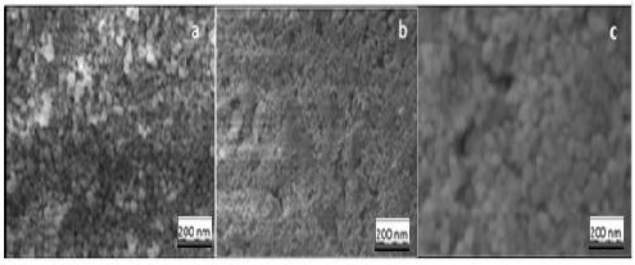

Figure 2: FESEM images of a) $CoFe_2O_4$ b) 5%wt ZrO_2 doped c) 10%wt ZrO_2 doped nanoparticles

FT-IR Studies

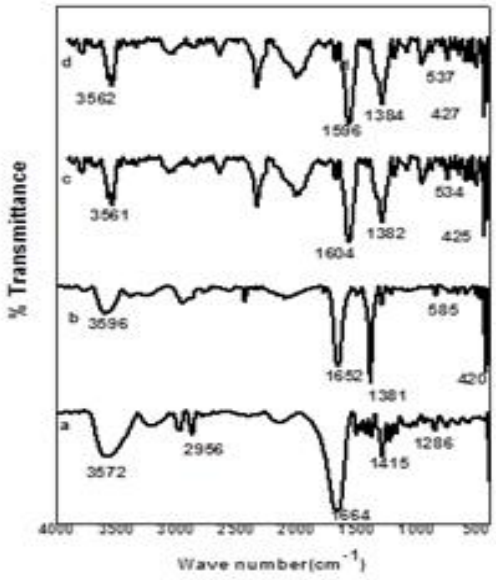

Figure 3: FTIR spectra of a) Pure PVP b) $CoFe_2O_4$ b) 5%wt ZrO_2 doped c) 10%wt ZrO_2 doped nanoparticles.

In Figure 3, FT-IR of $CoFe_2O_4$, 5%wt ZrO_2, 10 %wt ZrO_2 doped nanoparticles and pure PVP are given. . In pure PVP there is broad and strong band at 3444 cm^{-1} corresponds to OH of the coordinated water, 2956 cm^{-1},1661 cm^{-1}, 1415 cm^{-1} and 1286 cm^{-1} each corresponds to that of $–CH_2–$ stretching, carbonyl stretching, CN asymmetric stretching and $–CH_2–$ bending respectively.[14] In $CoFe_2O_4$ the following absorption bands are appeared 420, 585, 1382, 1652, and 3596. Two main broad Metal-Oxygen bands are seen in both doped and undoped ferrites. The peaks observed in the range of 550-600 cm^{-1} and 385-450 cm^{-1} corresponds to intrinsic stretching vibrations at the metal in the tetrahedral site and octahedral site respectively. The change in the wavelength region 1500 cm^{-1} to 2000 cm^{-1} indicates the doping of ZrO_2 into $CoFe_2O_4$. The C=O stretching vibration peak at 1664 cm^{-1} for pure PVP is shifted to 1652 cm^{-1},1604 cm^{-1} , 1596 cm^{-1} for $CoFe_2O_4$, 5%wt ZrO_2, 10 %wt ZrO_2 doped nanoparticles respectively [15]. This ascertaining the binding interactions and stabilization by PVP on the nanoparticle surfaces.

Kinetic studies

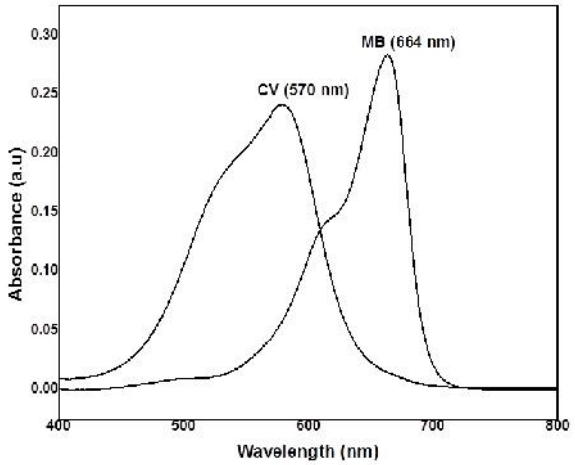

Figure 4: Typical UV-Visible Spectra of a) Crystal violet b) Methylene Blue

In Figure 4, the typical UV-Visible spectra of CV and MB are given. In both the dye systems without the photocatalyst under irradiation conditions less than 10 % degradation was observed for 24hrs reaction. In presence of $CoFe_2O_4$, 5%wt ZrO_2, 10 %wt ZrO_2 doped nanoparticles the degradation proceed immediately. The absorbance values of the dye decreases at constant λ max when degradation is progressing. The degradation studies of CV and MB dyes can be analyzed based on the rate coefficient values. In Figure 5, the OD vs time plot and the corresponding kinetic plots of CV dye were given. The slopes were multiplied with 2.303 constant and rate coefficient values are calculated. When the effect of nature of irradiations are considered UV-actinide blue, solar and IR sources it was found that for all ferrite nanoparticle catalyze solar irradiations produced higher rate coefficient values than IR and UV-actinide blue irradiation. Rate coefficient values versus catalysts weight under three different irradiations are given in Figure 7. In order to ensure the complete degradation of dyes H_2O_2 was incorporated into the dye solution containing nano ferrite catalyst. Both the dyes are separately decolorized completely in presence of $CoFe_2O_4$, 5%wt ZrO_2, 10 %wt ZrO_2 doped nanoparticles.

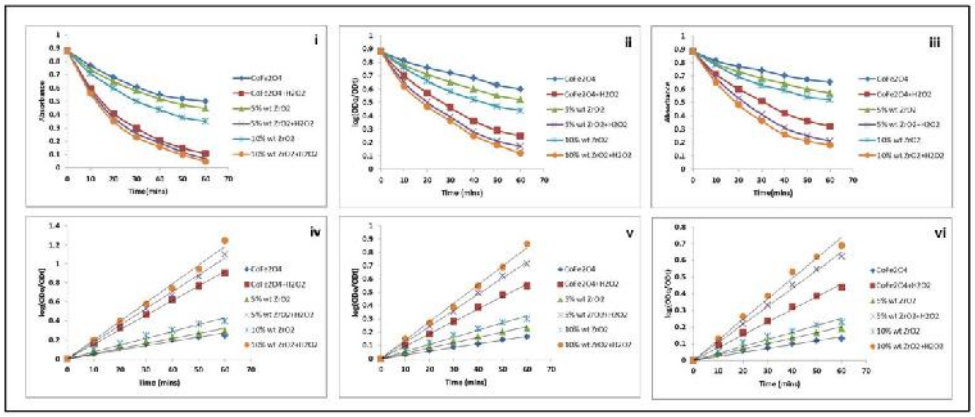

Figure 5 (i-iii): represents a OD Vs Time plots of Crystal violet dye under Solar, IR, UV- Actinide Blue irradiations respectively. (iv-vi) represents kinetic plots of Crystal violet dye under Solar, IR, UV- Actinide Blue irradiations respectively.

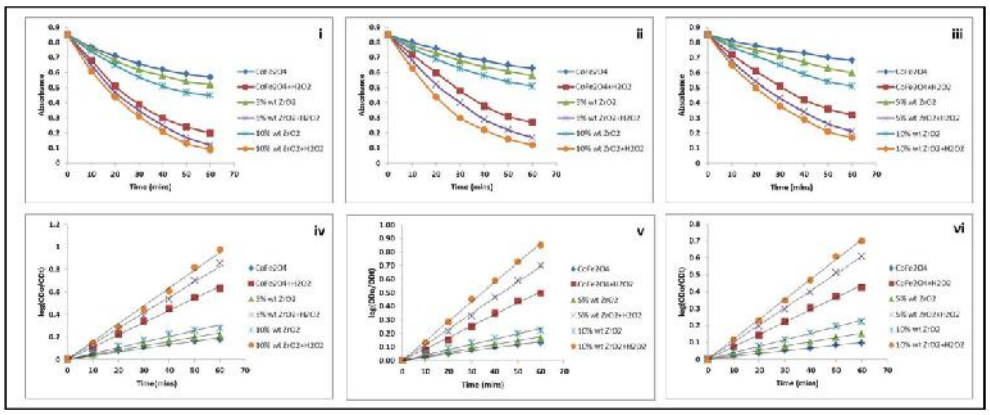

Figure 6 (i-iii): represents a OD Vs Time plots of Methylene blue dye under Solar, IR, UV-Actinide Blue irradiations respectively. (iv-vi) represents kinetic plots of Methylene blue dye under Solar, IR, UV- Actinide Blue irradiations respectively

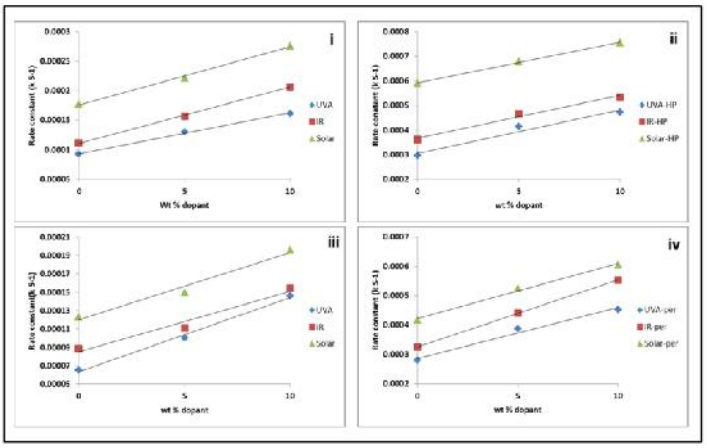

Figure 7: Plot of Rate coefficient values versus catalysts weight under three different irradiations.

Table 1: The overall Rate coefficient values of the degradations of CV dye in presence of $CoFe_2O_4$, 5%wt ZrO_2 and 10%wt ZrO_2 doped under Solar, IR and UV-Actinide blue at 25°C

Photocatalyst type	Rate coefficient k ($x10^{-4}s^{-1}$)					
	Solar		IR		UV-Actinide blue	
	With Catalyst	With H_2O_2	With Catalyst	With H_2O_2	With Catalyst	With H_2O_2
$CoFe_2O_4$	1.77	5.91	1.11	3.61	0.92	2.96
5 %wt ZrO_2 doped	2.22	6.79	1.57	4.68	1.31	4.15
10 %wt ZrO_2 doped	2.76	7.56	2.07	5.34	1.61	4.72

Table 2: The overall Rate coefficient values of the degradations of MB dye in presence of $CoFe_2O_4$, 5%wt ZrO_2 and 10%wt ZrO_2 doped under Solar ,IR and UV-Actinide blue at 25°C

Photocatalyst type	Rate coefficient k ($x10^{-4}s^{-1}$)					
	Solar		IR		UV-Actinide blue	
	With Catalyst	With H_2O_2	With Catalyst	With H_2O_2	With Catalyst	With H_2O_2
$CoFe_2O_4$	1.23	4.18	0.88	3.26	0.65	2.88
5 %wt ZrO_2 doped	1.50	5.26	1.11	4.41	0.99	3.88
10 %wt ZrO_2 doped	1.96	6.06	1.54	5.53	1.46	4.53

The calculated values of CV and MB dyes the rate constant is presented in Table-1 and Table-2 respectively. On comparing the rate constant values, the trend on the degradability observed among the two dyes for three ferrite nano catalyst systems is CV>MB. In presence of H_2O_2 also similar trend is observed. Regarding the dopant effect for all irradiations, 10%wt ZrO_2 doped nanoparticles produced higher rate coefficient values. This may be attributed to the nano size effect of 10%wt ZrO_2 doped possess lesser size than the others.

4. Conclusion

$CoFe_2O_4$, 5%wt ZrO_2, 10 %wt ZrO2 doped nanoparticles are synthesized using PVP as a stabilizer. The nanoparticles are size characterized PXRD and FESEM measurements. FTIR spectra of samples are carried out. Involving the three nano catalyst popularly used two dyes CV, MB degradations in the presence of Solar, UV-Actinide blue and IR irradiation are studied. The overall pseudo first order rate coefficient is determined. For the complete dye degradation, the photo catalytic degradations are repeated in the presence of H_2O_2. The trend in the photo degradability of the dyes is CV>MB. Similar trend was observed for all three catalysts and in presence of H_2O_2 as well. Regarding the photo catalytic efficiency 10 %wt ZrO_2 doped nanoparticles produced higher rate constant values than the others.

5. Acknowledgement

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