

Synthesis, Size Characterization and Photocatalytic Activities of Zinc Ferrites and Cobalt Ferrites Nanoparticles Using Oxidative Degradations of Methylene Blue, Crystal Violet and Alizarin Red Dyes in Aqueous Medium at 25°C

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Abstract— Nanoparticles of ferrites exhibit significant magnetic, optical and oxidation properties compared to the bulk dimensions. Nanoparticles of zinc and cobalt ferrites possess band gap energies 3.1 eV and therefore are capable of performing as photocatalysts for irradiations lying in the range of solar and visible regions. Nanoparticles of pure ferrites, mixed ferrites and inverse spinels are popular in the field of photocatalysis. In the present work, using poly n-vinyl pyrrolidone (PVP) as capping agent nanoparticles of zinc ferrite and cobalt ferrite are prepared adapting wet chemical method. The samples are ultra-centrifuged, washed and dried to fine powder. The nanoparticles samples are size characterized using UV-DRS, PXRD, FESEM and EDAX measurements. After applying poisson distribution to the particle sizes, the mean sizes of the nanoparticles are found to be $27.7\pm 1\text{nm}$ and $27.4\pm 1\text{nm}$ for the Zinc and Cobalt ferrites respectively. FTIR measurements are used to ascertain PVP stabilization of the ferrite nanoparticles. The utilization of the ferrites nanoparticles for the environmental remediation on the dye polluted waters has been chosen. In this investigation, intensely colored and popularly used in exceeding levels the three dyes such as methylene blue (MB), crystal violet (CV) and alizarin red (AR) are chosen for the oxidative degradation studies. One pot batch type reactor was adopted. 1 mg/20ml catalyst loading was chosen. Under ambient and aerobic conditions UV-Actinide blue irradiation and solar irradiation are chosen. 1 mM dye solution was used. Absorbance versus time measurements are made at max values 664 nm, 570 nm and 420 nm correspondingly to methylene blue (MB), crystal violet (CV) and Alizarin red (AR) dyes. Pseudo first order kinetic conditions are maintained. The overall pseudo first order values are determined for three dye degradations using the two nano ferrite catalysts. Optimizations for the amount of catalysts and dye concentrations are found out. It was found that cobalt ferrite nanoparticles exhibited the photocatalytic activity more efficiently than the zinc ferrite nanoparticles. Crystal violet dye degraded more efficiently than methylene blue and alizarin red. The salient results are discussed.

Keywords- Zinc ferrite nanoparticles, Cobalt ferrite nanoparticles, Dye degradation.

I. INTRODUCTION

Nano sized particles of ferrite class of compounds exhibit enhanced photocatalytic activity, magnetic susceptibility and electrical properties compared to their bulk counter parts [1,2]. Among the spinel type ferrite materials, zinc ferrite and cobalt ferrite nanomaterials are widely used as potential photo catalysts, semiconductors and reaction catalysts particularly in the synthesis of organic substrates. Additionally, due to powerful oxidation capacity, they are used to catalyze degradation of organic dyes in water. Applications of nano materials in the advanced oxidation processes involving a greener method for the remediation of intensely colored polluted waters due to textile dyes from various industries are most prevalent in current research [3,4]. The photocatalytic activity of spinel ferrites depends on various experimental factors and can be tuned by the effects of nanoparticle size, morphology and stability of the nanoparticles [5]. There are many reports available in the literature on the usage of zinc ferrite and cobalt ferrite nano materials for the photo catalytic oxidation of various textile dyes [6,7]. In the present work zinc ferrite (ZFNps) and cobalt ferrite (CFNps) nanoparticles are prepared using the wet chemical method by treating the metal salt precursors with fresh solution of polymeric stabilizing agent poly n-vinyl pyrrolidone (PVP) which is a water soluble polymer and NaOH, which gelates the metal hydroxide. Here, the ferrite nanoparticles are prepared at 25°C by drying the hydrogel and size characterized using PXRD, FESEM and EDAX measurements. FTIR measurements are used to ascertain PVP stabilization of the ferrite nanoparticles. The effect of morphology on the photocatalytic activity has been tested for the oxidative degradation of methylene blue (MB), crystal violet (CV) and alizarin red (AR) dyes which act as the source of pollutants in many aqueous environments [8,9]. One pot batch type reactor was adapted with optimized catalyst loading under aerobic conditions separately using two different irradiation sources such as UV-Actinide blue and solar radiation. 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 three 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 ZFNps and CFNps. The role of hole/e- pairs formation on the catalyst surface in the presence of radiation was invoked, in the mechanism of dye degradation. The salient features are discussed.

II. EXPERIMENTAL

A. Materials and Methods

All the chemicals used in this study are commercial samples and belong to analytical grade obtained from Merck, India. They were used as received without further purification. Zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$, Cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$, Ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$ were used as a precursors and poly n-vinyl pyrrolidone $(C_6H_9NO)_n$ as a stabilizing agent. Alizarin Red $C_{14}H_7NaO_7S$, Crystal violet $C_{25}H_{30}N_3Cl$, Methylene blue $C_{16}H_{18}ClN_3S \cdot XH_2O$, Hydrogen peroxide H_2O_2 were also used for this study.

B. Synthesis of Zinc ferrite and Cobalt ferrite nanoparticles

In the preparation of ZFNps, 50 ml of 2wt% solution of poly n- vinyl pyrrolidone was taken in a beaker. To that 0.1 M of Ferric nitrate and 0.05 M Zinc nitrate were added separately drop wise under stirring condition. In order to maintain alkaline condition Sodium hydroxide (1 %) was added to the reaction mixture. The reaction mixture was stirred for 6 hrs at 25°C. The hydrogels were separated by ultra-centrifuge, washed repeatedly, collected, dried and subjected to size characterizations. This procedure was repeated fully by using 0.1 M ferric nitrate and 0.05 M Cobalt nitrate solution and thereby CFNps are obtained.

C. Size characterization of Zinc ferrite and Cobalt ferrite nanoparticles

The ferrite nanoparticles prepared are size characterized using FESEM with EDAX, using SU6600 HITACHI model operating at an accelerating voltage of 100 kV. Powder X-ray diffraction (XRD) patterns of the ZFNps and CFNps are measured using Bruker D8 advance diffractometer. The patterns are studied with JCPDS file cards and peaks are characterized. Applying the Scherer formula, the size values of the nanoparticles are calculated to be 27.7 ± 1 nm and 27.4 ± 1 nm for ZFNps and CFNps respectively. FTIR of ZFNps, CFNps and pure PVP are carried out using KBr pellets and TENSOR 27-FTIR Spectrometer.

D. Photocatalytic studies

The catalytic degradation of the three organic dyes was performed separately in open beakers loaded with 20 ml of dye solution and 15 cm distance separation from the irradiation lamp and the surface of the solution was maintained. The optimized catalyst feed loading was chosen for each dye to be 1mg/20 ml. The solution was irradiated separately with both UV-Actinide blue radiation and solar radiation. The progress of the reaction was monitored by measuring the absorbance values of the dyes at their wavelength maxima at regular intervals of time of irradiation using systronics UV-Visible spectrometer at regular intervals of time.

III. RESULTS AND DISCUSSIONS

A. Size Characterizations

The structure and phase purity of the samples were confirmed by analyzing X-ray powder diffraction patterns (Fig. 1). The average crystallite sizes of the samples are calculated using FWHM and Scherer formula $[10]. L = 0.89 \lambda / \cos \theta$, where L is the average particle size, λ is the X-ray wavelength (0.1542nm), θ is the full width at half maximum (FWHM) and θ is the diffraction angle. According to JCPDS file card it was found that nanocrystalline ZFNps and CFNps possess cubic crystal structure. This agrees well with the literature report. The mean size values are found to be 27.7 ± 1 nm and 27.4 ± 1 nm respectively for ZFNps and CFNps.

FESEM- EDAX of the two ferrite nano particles is given in Fig. 1. The mean size values are obtained to be 27 ± 1 nm and 26.5 ± 1 nm respectively for ZFNps and CFNps. These values agree well with those of PXRD data. For both ZFNps and CFNps spherical nano particles resulted in this work. The UV-DRS spectra are given in Fig.1 and the bandgap energies are found to be 1.5 eV and 1.3 eV for ZFNps and CFNps respectively. These values agree well with the literature report [11].

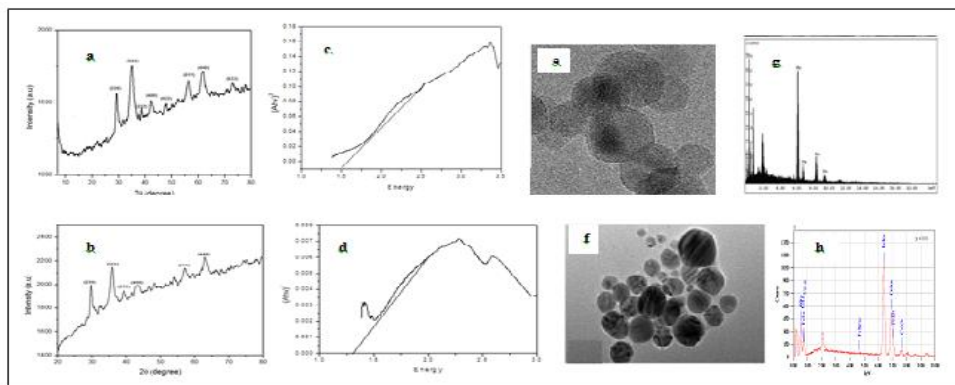


Fig.1 (a-b) XRD pattern of ZFNPs and CFNPs. (C-d) UV-DRS of ZFNPs and CFNPs. (e-f) FESEM images of ZFNPs and CFNPs.(g-h) EDAX images of ZFNPs and CFNPs respectively

B. FTIR studies

In Fig. 2, the FTIR of ZFNPs, CFNPs and pure PVP are given. In pure PVP there is broad and strong band at 3444.80 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 $-\text{CH}_2-$ stretching, carbonyl stretching, CN asymmetric stretching and $-\text{CH}_2-$ bending respectively. In case of ZFNPs and CFNPs each stabilized with PVP, show the FTIR spectra with peaks of PVP being red shifted, ascertaining the binding interactions and stabilization by PVP on the nanoparticle surfaces. The C=O stretching vibration peak at 1661 cm^{-1} for pure PVP is red shifted to 1655 cm^{-1} , 1652 cm^{-1} for ZFNPs and CFNPs respectively.

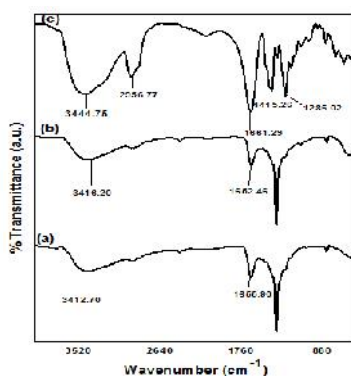


Fig.2 FTIR spectra of a) ZFNPs b) CFNPs c) Pure PVP

C. Kinetic studies

In all the dye systems subjected to degradation studies under irradiation conditions without the catalyst slow rates of degradation resulted and less than 10% degradation was recorded for 24 hrs reaction. When the same are repeated with the inclusion of ferrite nanoparticles the degradation preceded immediately. In Fig.3 the absorbance variation with time for the dyes CV and MB are given for two catalyst system separately. When the effect of nature of irradiations are considered UV-actinide blue and solar sources it was found that for both the ferrite nanoparticle catalyze solar irradiations produced higher rate coefficient values than UV-actinide blue irradiation. Therefore the effects of composition of the dye and catalyst are studied under solar irradiations only. When the catalyst feed loading is increased from $1\text{ mg}/20\text{ ml}$ and $2\text{ mg}/20\text{ ml}$ it was found that overall rate values increased with further increase in the catalyst feed there is no significant increase in the rate degradation and hence all the kinetic evaluation are made with $1\text{ mg}/20\text{ ml}$ feed loading.

The role of composition of dyes for constant catalyst feed and irradiations, under pseudo first order conditions directly proportional existed between the dye concentration and observed rate constant values. All the pseudo first order rate coefficient values determined for the two ferrite catalyst systems and for the three dye substrates. The values are tabulated in the Table 1. In Fig. 3, as represent case CV and MB dye degradation with the catalyst under solar irradiation has been presented.

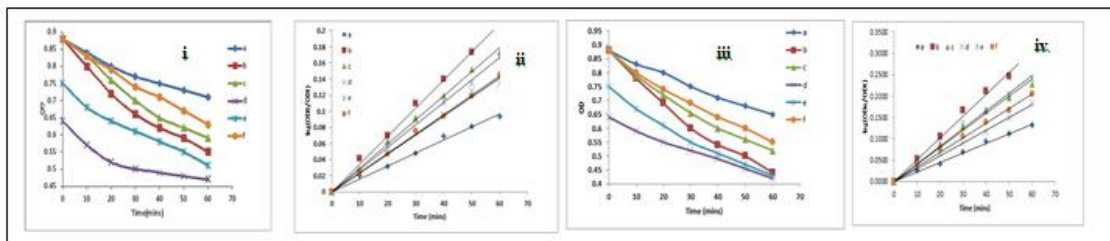


Fig. 3(i and iii) OD versus time plots of ZFNPs,CFNPs .(ii and iv) kinetic plots of $\log(OD_o/OD_t)$ versus time for ZFNPs,CFNPs . (i ,ii) and (iii,iv)'a' represents the degradation of CV dye (0.02mM) in UV-Actinide blue irradiation of ZFNPs and CFNPs particles respectively. (i ,ii) and (iii,iv)'b-c' represents the degradation of CV in the presence of catalyst amount 1mg/20ml and 0.5 mg/20ml in solar irradiation for ZFNPs,CFNPs respectively. (i ,ii) and (iii,iv)'d-e' represents concentration variation of CV (d-0.01mM,e-0.005mM) in solar irradiation for ZFNPs,CFNPs respectively. (i ,ii) and (iii,iv)'f' represents the degradation of MB dye (0.02 mM) in solar irradiation of ZFNPs,CFNPs respectively

TABLE I. THE OVERALL RATE COEFFICIENT VALUES OF THE DEGRADATIONS OF CV AND MB DYES IN PRESENCE OF ZFNPs AND CFNPs UNDER UV-ACTINIDE BLUE AND SOLAR IRRADIATIONS AT 25°C

Dye system	Dye concentration (mM)	Irradiation type	Catalyst amount (mg/20ml)	ZFNPs k ($\times 10^{-4} s^{-1}$)	CFNPs k ($\times 10^{-4} s^{-1}$)
CV	0.02	UV-Actinide blue	1.0	0.6141	0.8444
CV	0.02	Solar	1.0	1.3434	1.9576
CV	0.02	Solar	0.5	1.1515	1.5353
CV	0.01	Solar	1.0	0.9212	1.1515
CV	0.005	Solar	1.0	0.1075	1.5737
MB	0.02	Solar	1.0	0.9212	1.3050

When AR dye solution was irradiated with either UV-actinide blue or solar irradiation, unlike CV and MB dyes the absorbance values increased steadily at regular interval of time. This is a unique behavior exhibited by AR. In the absence of ferrite catalyst only 5% increase in the absorbance values are noted for irradiation up to 24 hrs. The absorbance versus time plots is shown in Fig. 4. And the corresponding OD versus time plots for rate coefficient determination is presented in Fig. 4. The rate constant values are listed in Table-2. This increase in the absorbance values may be attributed to the incitu complexation of the dye with surfacial Fe_2O_3 molecules. The formation of this is catalyzed by irradiation which causes substantial increase in absorbance with time upon addition of the catalyst.

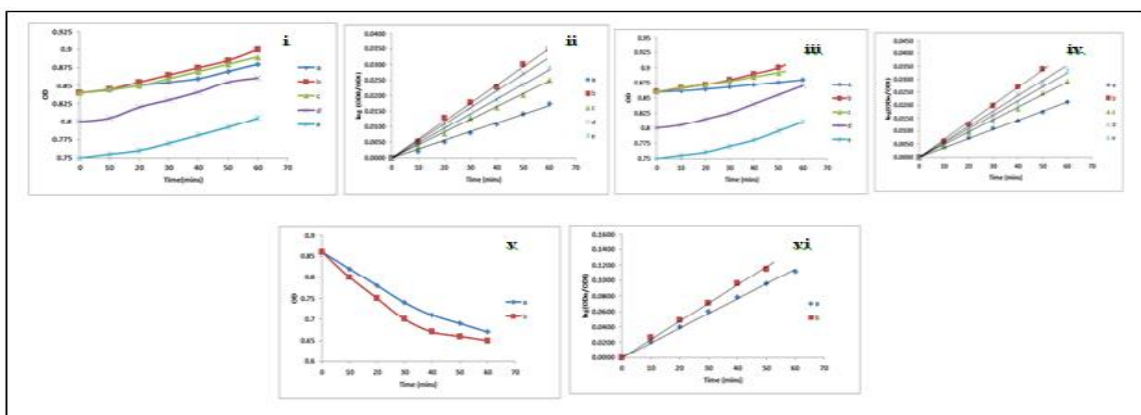


Fig. 4. (i and iii) OD versus time plots of ZFNPs,CFNPs for AR dye degradation. .(ii and iv) kinetic plots of $\log(OD_o/OD_t)$ versus time for ZFNPs,CFNPs for AR dye degradation. (i ,ii) and (iii,iv)'a' represents the degradation of AR dye (0.28mM) in UV-Actinide blue irradiation of ZFNPs and CFNPs particles respectively. (i ,ii) and (iii,iv)'b-c' represents the degradation of CV in the presence of catalyst amount 1mg/20ml and 0.5 mg/20ml in solar irradiation for ZFNPs,CFNPs respectively. (i ,ii) and (iii,iv)'d-e' represents concentration variation of AR (d-0.01mM,e-0.005mM) in solar irradiation for ZFNPs,CFNPs respectively.(v) OD versus time plots for AR dye degradation in the presence of H_2O_2 for the catalyst a)ZFNPs,b)CFNPs.

TABLE II. THE OVERALL RATE COEFFICIENT VALUES OF THE DEGRADATIONS OF AR DYE IN PRESENCE OF ZFNps AND CFNps UNDER UV-ACTINIDE BLUE AND SOLAR IRRADIATIONS AT 25°C

Dye concentration (mM)	Irradiation type	Catalyst amount (mg/20ml)	ZFNps k ($\times 10^{-4} \text{s}^{-1}$)	CFNps k ($\times 10^{-4} \text{s}^{-1}$)
0.28	UV-Actinide blue	1.0	0.1152	0.1535
0.28	Solar	1.0	0.2303	0.2687
0.28	Solar	0.5	0.1535	0.1919
0.1	Solar	1.0	0.1919	0.2303
0.05	Solar	1.0	0.1919	0.1919
H ₂ O ₂				
0.28	Solar	1.0	7.2928	9.212

In order to ensure the complete degradation of dyes H₂O₂ was incorporated into the dye solution containing nano ferrite catalyst. All the three dyes separately decolorized completely both in presence of ZFNps and CFNps.

Similar procedure has been adapted for rate coefficient determination. The calculated values of the rate constant are presented in Table-2. On comparing the rate constant values, the trend on the degradability observed among the three dyes for both the ferrite nano catalyst systems is CV>MB>AR. In presence of H₂O₂ also similar trend is observed. However AR dye exhibited a decrease in the absorbance value with time in presence of H₂O₂. Keeping the experimental condition constant CFNps exhibited higher catalytic efficiency than ZFNps which may be attributed to the nano size effect and CFNps possess lesser size than ZFNps. For constant composition of the catalyst smaller nanoparticles produce larger surface area, and therefore higher catalytic efficiency.

IV. Conclusion

Zinc ferrite and cobalt ferrite nanoparticles are synthesized using PVP as a stabilizer. The nanoparticles are size characterized PXRD and FESEM-EDAX measurements. UV-DRS and FTIR spectra of samples are carried out. Involving the two nano catalyst popularly used three dyes CV,MB,AR degradations in the presence of UV-Actinide blue and solar irradiation are studied. Adapting pseudo first order experimental conditions and the absorbance variation with time data. The overall pseudo first order rate coefficient is determined. For the complete dye degradation, the photocatalytic degradations are repeated in the presence of H₂O₂. The trend in the photo degradability of the dyes is CV>MB>AR. Similar trend was observed for both the catalyst and in presence of H₂O₂ as well. Regarding the photo catalytic efficiency CFNps produced higher rate constant values than ZFNps which may be due to role of nano size of the nanoparticles. 27.7±1 nm and 27.4±1 nm was observed for ZFNps and CFNps respectively. For constant catalyst compositions smaller sized particles produced larger surface area and therefore higher catalytic activity.

V. ACKNOWLEDGMENT

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