Study of Application of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs prepared via Sol-gel Method for Dyestuff Industry in Waste water Purification

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Abstract
NPs of mixed metal oxides, pure ferrites, mixed ferrites and inverse spinels are popular in the field of photocatalysis, magnetic and optical because they exhibit significant oxidation, magnetic and optical properties compared to the bulk dimensions. By using nitrate salts of respective metal ions, $Zn_{0.5}Mn_{0.5}Fe_2O_4$ was prepared via Sol-gel auto-combustion method. The photocatalytic property of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs is investigated. The structural properties of the produced nano-particles were examined through X-ray diffraction (XRD) and Fourier transforms infrared spectroscopy (FT-IR). The XRD pattern revealed a single phase cubic spinel structure for the sample and the mean particle size of the sample was calculated by Scherer's formula using necessary corrections. Scanning electron microscope investigations showed that the particle size distribution was homogeneous and their size was in a good agreement with those obtained by Scherer's formula.

The objective of this study is to find a synthesized compound as photocatalyst for purification of waste water from dyestuff industry. Enhanced photocatalytic activity was demonstrated for the prepared NPs in photo degradation of tartrazine dyes at λ_{max} values 430 nm. $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs gave better photocatalytic activity under the UV light radiations. This study showed that dyes undergo fast degradation with UV light in presence of prepared compound.

Keywords: $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs, Photocatalyst, degradation, tartrazine dye.

Introduction
The synthesis of mixed metal oxides such as ferrite NPs is currently an intensive research area due to the verified size dependence of their functional properties and wide range of applications. Polycrystalline spinel ferrites are widely used in many electronic devices. They are preferred because of their high permeability in the radio- frequency (RF) region, high electrical resistivity, mechanical hardness and chemical stability[1]. Many efforts have been made to improve the basic properties of these ferrites by substituting or adding various cations of different valence states depending on the applications of interest. Among spinel ferrites, Zn^{2+} substituted $CoFe_2O_4$ nanoparticles exhibit improved properties such as excellent chemical stability, high corrosion resistivity, magnetocrystalline anisotropy, magnetostriction and magneto-optical properties[2,3].

It has been further reported that the catalytic activity of manganese ferrite ($MnFe_2O_4$) is 50-100 fold higher than the other spinel ferrites[4]. The substitution of cations (Mg^{2+}, Zn^{2+}, or Al^{3+}) into ferrites improves the stability of ferrites while substitution of transition metals (Ni^{2+}, Cu^{2+}, Mn^{2+} or Co^{2+}) into the spinel lattice strongly modified the redox properties of the ferrites[5]. Various preparation techniques such as sol–gel pyrolysis method[6,7], the microwave hydrothermal method[8], template-assisted hydrothermal method[9] and sol–gel auto combustion techniques are used to prepare ferrites nanoparticles.

Recently, photo catalytic oxidation of dyes using ferrites has gained enormous interest. Most of the dyes used in the pigmentation of leather, textiles, paper, ceramics, cosmetics, inks and food-processing products are derived from azo dyes which are characterized by the presence of one or more azo groups (-N=N-) in their structure. But during synthesis and processing of materials, much of the dyes goes waste within water. Because of toxic nature of azo dyes, this waste produces a great hazard to human and environmental health.

Therefore, it is a challenge to researchers for effective removal of dyes of wastewater from industries. Hence for degradation of polluted waste water containing both toxic and non-biodegradable compounds, the development of suitable process is needed[10,11].

The study on ferrospinels based Manganese doped Co-Zn Ferrite, Zinc-Cobalt Ferrite for their structural characterization and photocatalytic activity was recently reported[12-15]. It is reported that the spinel ferrite materials is efficiently utilized as a photocatalyst for degradation of methylene blue[16], methyl orange[17] and other dyes[18] etc.

This work is again extended to synthesize $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs by sol-gel auto combustion method from nitrate salts of respective metal ions. The focus was to utilize synthesized compound as photocatalyst for purification of waste water from dyestuff industry.

Material and Methods

Metal nitrates and chelating agents used for synthesis were of A.R. grade. They were used as received without further purification. Iron nitrate nonahydrate $Fe(NO_3)_3.9H_2O$, zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$, manganese nitrate and citric acid used were of purity 98-99%. The chemicals were used without further purification. For purification of waste water from dyestuff industry, tartrazine dye solution was used for photoctalytic study.

Synthesis of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs: $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs were synthesized by sol-gel auto combustion method using starting material of high purity AR grade metal nitrate and lemon juice. The metal nitrate solutions were mixed in the required stoichiometric ratios in minimum quantity of distilled water. The solutions will be mixed on a magnetic stirrer at 353K. In order to maintain alkaline condition, ammonia solution was added to the reaction mixture (pH 9 - 9.5). The solution mixture was slowly heated around 373K with constant stirring to obtain a fluppy mass. On further heating, colored powder will be obtained. The powder will be cooled for some time. The obtained powder nanoparticles were annealed at temperature of 973K for 4 hours.

Size characterization of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs: The formation of mixed metal ferrite nanoparticles was confirmed by Fourier transform infrared (FT-IR) studies. The ferrite nanoparticle prepared was analyzed by X-ray diffraction technique (XRD) for structure and crystallinity. X-ray diffraction (XRD) data was collected at room temperature. Crystallographic properties e.g. phase of the material and crystal structure were determined using the same data. FT-IR analysis was carried out in the range of 4000-400 cm^{-1}. The samples were pelleted with KBr. The particle surface morphology was studied using Scanning Electron Microscopy technique (JEOL-JSM 5360 Microscope).

Photocatalytic studies: The catalytic degradation of the dye was performed in open beakers loaded with 50 cm^3 of dye solution and 10 cm distance separation from the irradiation lamp and the surface of the solution was maintained. Photolysis was also carried for dye solution using UV radiations without photocatalyst. The optimized catalyst feed loading was chosen for dye to be 1mg/1cm^3. The solution was irradiated with UV lamp of 11 W powers. About 2-3 ml of sample was taken at 1 hrs intervals of time up to 7 hrs. The course of degradation reaction and concentration of dye in samples were monitored by measuring the absorbance values of the dye at their wavelength maxima at regular intervals of time of irradiation using UV-Visible spectrometer at regular intervals of time.

Results and Discussion

X-ray diffraction (XRD) analysis: X-ray diffraction (XRD) patterns for the as prepared and annealed $Zn_{0.5}Mn_{0.5}Fe_2O_4$ powders are presented in fig. 1. The XRD spectra showed all the characteristics peaks corresponding to the characteristic planes (311), (511) and (440) appearing at 35°, 57° and 64° on comparing with the patterns of all the investigated samples with that of standard JCPDS card, a single phase $Zn_{0.5}Mn_{0.5}Fe_2O_4$ was formed with no extra peaks. At 973K fully crystallized $Zn_{0.5}Mn_{0.5}Fe_2O_4$ was formed with sharp peaks indexed as (220), (311), (400), (422), (511) planes of spinel structure.

In the present work, fig. 1 reveals the presence of the spinel structure for the as prepared $Zn_{0.5}Mn_{0.5}Fe_2O_4$ and the broadening in the peaks of the as prepared sample could be attributed to the formation of ferrite particles in nano range.

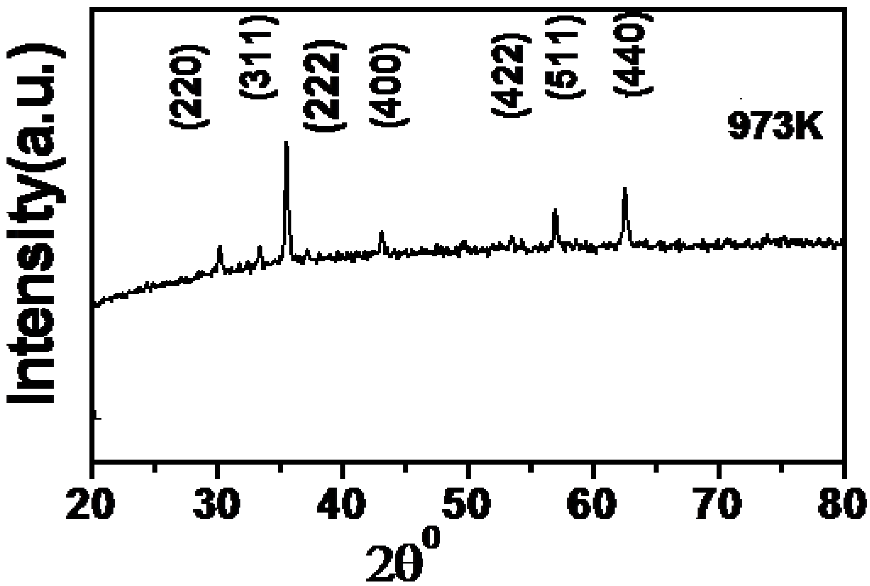

Figure 1: The X-ray diffraction (XRD) patterns of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NP's as prepared and that was annealed at 973K temperature

Particle size calculation of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs by Scherer formula: The size of the nanoparticle has been determined using Scherer equation from the full width at Half Maximum (FWHM) value of [311] diffraction peak.

$$D = 0.9\lambda/\beta \cos\theta$$

where D is the particle size, λ is the X-ray wavelength (1.5418), θ is the Bragg angle and β is the half maximum width. The size of nanoparticles was obtained as 25.7 nm for 973K annealing temperature for 4 hours.

Fourier transforms infrared (FT-IR) studies: IR spectrum is considered an important tool to get information about the structure and the positions of ions in the crystal through the crystal's vibration modes[19]. The formation of spinel $Zn_{0.5}Mn_{0.5}Fe_2O_4$ structure in the calcined zinc ferrite nanoparticles is further supported by FT-IR spectra shown in fig. 2. The peaks at 551.56 cm^{-1} correspond to the metal–oxygen (Fe–O) stretching vibrations and it is the characteristic peak of the spinel structure of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ nanoparticles. The strong absorption band at 400 cm^{-1} is described as the stretching modes of Zn–O [20].

Scanning electron microscopy: The microstructure of the samples depends on the sintering temperature. The scanning electron micrograph of sintered sample at temperature 973 K is shown in fig. 3. It can be seen that the average grain size and crystallinity are significant and also the particle size becomes more uniform at 973K temperature. At the sintering temperature of 973K, substantial grain growth occurs in which the ferrite grains are cubic and well crystalline in nature.

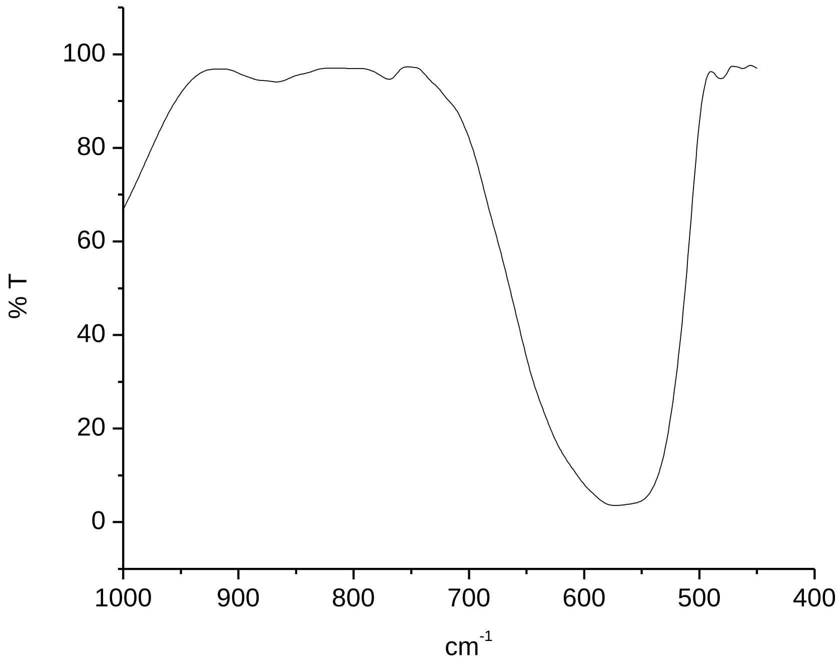

Figure 2: FTIR spectra of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NP's sintered at 973K

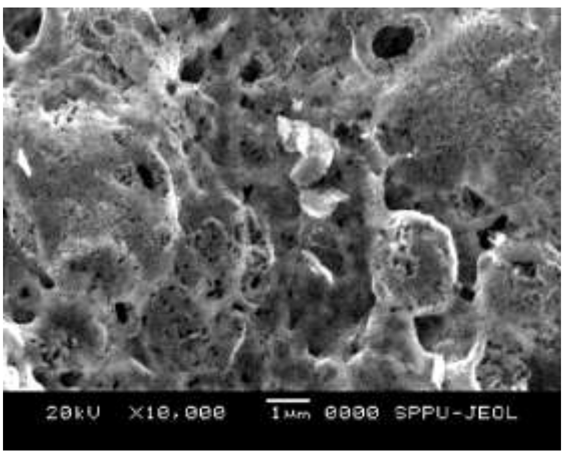

Figure 3: SEM analysis at sintering temperature 973K

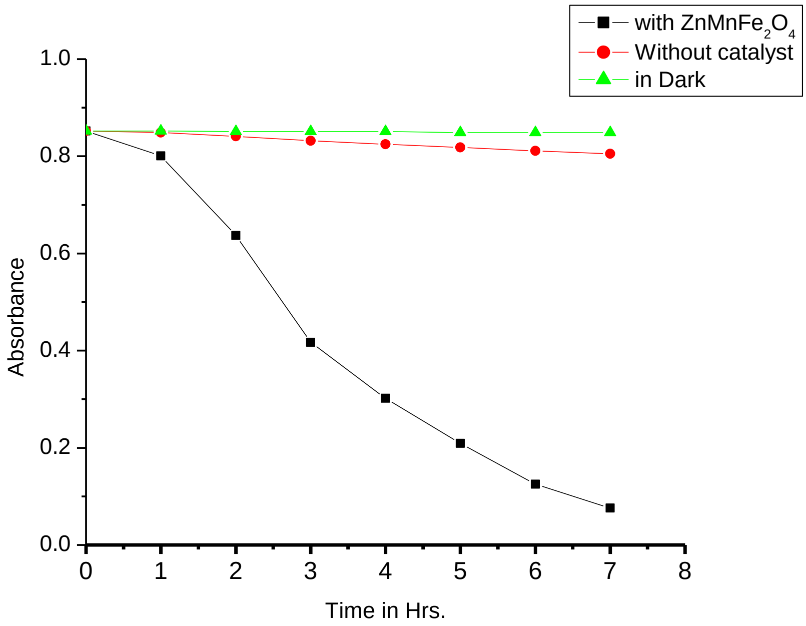

Figure 4: The time varying decrease in absorbance for used photocatalyst

Photocatalytic activity: The photocatalytic activity of synthesized samples under UV light was evaluated by performing experiments on the degradation of tartrazine dye in aqueous solution. Fig. 4 illustrates the degradation of the dye by photocatalysis in the presence of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ nanoparticles for 7 hours. The results showed that the concentration of dye solution barely changed after a solution had been directly illuminated. The absorption peaks of dyes became weaker along with the irradiation time and hence azo groups as well as aromatic part of the dyes molecule were destructed under UV light. It was found that dye degraded by catalyst $Zn_{0.5}Mn_{0.5}Fe_2O_4$.

Conclusion

The mixed metal oxides such as $Zn_{0.5}Mn_{0.5}Fe_2O_4$ NPs are successfully prepared by using sol-gel auto combustion method. XRD confirmed formation of $Zn_{0.5}Mn_{0.5}Fe_2O_4$ with cubic spinnel structure. The FT-IR and SEM analysis supported the formation of NP's at nanoscale. The progress of photocatalytic study of dye shows that the facile sol-gel synthesized $Zn_{0.5}Co_{0.5}Fe_2O_4$ is the effective catalyst in decolorisation and degradation of tartrazine dye.

The photocatalyst is reusable as there is no more major change in their structure after photocatalysis. Finally, it is concluded that the synthesized NPs will be helpful in purification of waste water from dyestuff industry.

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