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**PAPER**

Synthesis, characterization of Mg/Mn substituted Ni-Zn ferrites and mechanism of their visible light photo catalysis of Methylene Blue and Rhodamine B dyes under magnetic influence

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**Abstract**
Rare earth doped spinel ferrites belonging to the series \( \text{Ni}_{0.6}\text{Zn}_{0.2}\text{Me}_{0.2}\text{Gd}_{x}\text{Fe}_{2-x}\text{O}_4 \) (where \( \text{Me} = \text{Mg}/\text{Mn}, x = 0/0.06 \)) were synthesized by sol-gel method. The characterizations of the prepared samples were performed using X-ray Diffraction (XRD), High Resolution Transmission Electron (HRTEM) Microscopy, Vibrating Sample Magnetometry (VSM), X-ray Photoelectron Spectroscopy (XPS) and Open aperture z-scan technique. The XRD patterns confirm the crystallization of the ferrites in cubic form with spinel structure. The average crystallite size calculated using Debye–Scherrer’s equation is in 10–20 nm range. The HRTEM images reveal the formation of spherically shaped agglomerated nanoparticles. The magnetic parameters such as remanence magnetization \( (M_r) \), coercivity \( (H_c) \) and saturation magnetization \( (M_s) \) were obtained from the hysteresis curves. The samples show better optical limiting parameters than reported which make them promising materials for non-linear applications requiring low limiting thresholds. Owing to their low band gaps ferrites can be efficiently used for the photo catalysis of organic dyes with visible solar energy which constitutes a major portion of sunlight. Ferrites have an added advantage by virtue of their spinel lattice which makes available extra catalytic sites. In the present work, the photocatalytic activity under visible sunlight irradiation was explored from the degradation of Methylene Blue (MB) and Rhodamine B (RhB) dyes. Higher photocatalytic efficiency was exhibited by magnesium containing samples. Near total decolouration of dye solution subjected to magnetic separation has not been reported before. The improvement in photocatalytic degradation efficiency is due to the adsorption followed by effective separation and prevention of photo generated electron-hole pair recombination for a longer period by these ferrites. To further aid the degradation, \( \text{H}_2\text{O}_2 \) was added as precursor to the reactive mixture which increases the formation of hydroxyl radical \( (\text{OH}^-) \).

1. **Introduction**

Many industries extensively use organic dyes for colouring and dispose these directly into aqueous effluents which in turn pollute natural water bodies. The presence of even small concentration of these dyes in water prevents penetration of sunlight into water thus affecting the aquatic flora. Also, many dyes are carcinogenic, mutagenic and also toxic to microorganisms and aquatic species [1, 2]. Scarcity of potable water is a serious concern the world over. Therefore, the effective removal of these dye pollutants or their transformation into some harmless products before release into the environment is of utmost importance. Various methods for removal of dye have been developed which include adsorption [3, 4], chemical oxidation [5, 6], photocatalytic degradation [7, 8] and membrane filtration [9, 10]. Among these methods the adsorption process followed by photocatalytic degradation is an effective technique that has been successfully employed for purification of wastewater containing dyes. Research efforts are increasingly focused on the development of photocatalysts that can aid in the treatment of wastewater laden with these harmful contaminants. The recent progress in
nanoparticles contributes towards higher catalytic activity.

Photo catalysis is a highly efficient and cost effective advanced oxidation process which is based on the generation of highly reactive and oxidizing hydroxyl radicals (OH·) [11]. Eco-friendly and stable photocatalysts have found their way in the form of nano sized semiconductors. TiO₂, ZnO, Fe₂O₃, CdS, CdO, ZnS have proved to be suitable photocatalysts for the oxidation and hence the subsequent removal of organic dyes from aqueous systems [12–14]. The light absorbing ability is an imperative factor which influences the photocatalytic efficiency of any photocatalyst in a photocatalytic reaction.

The photocatalytic degradation using visible light of solar spectrum is desired over UV light because visible light constitutes about 50% of solar radiation whereas UV light forms only 4% [15]. Hence utilizing semiconducting materials which have strong absorption in the visible region is advantageous and can yield higher efficiency in photocatalytic applications.

Removal of contaminants by absorption is effective but a serious drawback of this method is the separation of the adsorbent. Use of magnetic adsorbents can help to overcome this limitation [16].

In these contexts, ferrites and transition metal doped mixed ferrites have been thoroughly investigated for their photocatalytic activities. The advantage of ferrites as photocatalysts is their capability to absorb visible range of the solar radiation owing to their small band gaps (<2.2eV) and availability of numerous catalytic sites for adsorption [17]. Doping with transition metals has significantly improved the photocatalytic ability of ferrites by increasing surface defects and production of surface oxygen vacancies and delaying recombination of electron hole pairs as reported in literature.

TiO₂ and ZnO are widely used photocatalysts, both of which are easily available, chemically stable and cost less. But the major drawback in using them is their large band gap (~3.2eV) due to which they can absorb only 4% of sunlight [18–21].

Previously, Singh et al have reported the synthesis of nickel and zinc doped cobalt ferrites by reverse micelle technique and analysis of its photocatalytic activity on the degradation of RhB dye under visible light illumination [22]. Sundararajan et al have successfully synthesized zinc doped cobalt ferrite by microwave combustion method and examined its photocatalytic activity on the degradation of RhB under illumination of visible light [23].

Zhang and Kong have synthesized magnetic Fe₇O₈/C core–shell nanoparticles as adsorbents for removal of organic dyes from aqueous solutions [24]. Wang et al have prepared different MFe₂O₄(M=Mn, Fe, Co, Ni) spinel ferrite nanocrystals synthesized by hydrothermal method for the removal of Congo Red [25].

Wojciech Konicki et al synthesized magnetic ZnFe₂O₄ nanocomposite by a microwave assisted hydrothermal method and used it for the removal of Rhodamine B from aqueous solutions [26]. Tatarchuk et al have reported that the cobalt doped zinc ferrites can be utilized as potential candidate for the wastewater treatment [27]. Nevertheless, the intention of the present work is to synthesize various transition metal doped mixed ferrite catalysts by sol–gel method and to investigate their photocatalytic activity in the photo degradation of Methylene Blue (MB) and Rhodamine B(_RB) dye under illumination of sunlight. Magnetic nature of ferrites gives them the added advantage of easy recovery after photocatalytic reaction [28].

Moreover, the development of ferrite nanoparticles that have a uniform size distribution, high surface area, large porosity and enhanced photocatalytic ability is still a challenge. In this context, a systematic study on the complete properties of mixed ferrite nanoparticles has been undertaken.

Though reports on photocatalytic degradation of the dyes by ferrites are available in literature, studies on degradation activities exhibited by magnetically separated aliquots of solution containing dye and ferrite nanoparticles have not been reported. In this work, we discuss the probable reasons for this efficiency difference.

2. Experimental details

2.1. Synthesis

Mixed ferrites of the form Me₀.2Ni₀.6Zn₀.2GdₓFe₂₋ₓO₄ (where Me=Mg, x = 0 for MG1, Me=Mn, x = 0 for MN1, Me=Mg, x = 0.06 for MG4) and AG4 of the form Ag₀.02Mg₀.2Ni₀.88Zn₀.2Fe₂O₄ were synthesized by the sol–gel method. Nitrate salts of Mg, Mn, Ni, Zn, Fe, Ag and Gd used in the synthesis are of analar grade form and were used as such without any further purification. Required stoichiometric ratios of AR grade nitrates were added to minimum amount of ethylene glycol which was stirred on a magnetic stirrer at room temperature till the salts got completely dissolved and was heated at 60 °C to form a wet gel. This gel was dried at 120 °C which self ignites to form an ash like product. This product was then ground well till fine in an agate mortar. The finely ground powders were sintered at 400 degree Celsius for 4 h in muffle furnace. For optical nonlinear studies using z–scan technique the finely ground nanoparticles were dispersed in DMSO.
2.2. Characterization

Various characterization techniques such as X-ray diffraction, high resolution transmission electron microscopy, vibrating sample magnetometer and impedance analyzer were used for the structural, morphological and physical property analyses of the prepared samples. The valence states of elements on surface were examined by X-ray photoelectron spectroscopy (XPS). The open aperture z-scan technique employing linearly polarized Gaussian pulses of 5ns pulse width at 532nm was used to study the non-linear optical properties. The UV-visible spectroscopy was used to determine the change in concentration of the dyes in solution.

2.3. Photocatalytic dye degradation measurement

The photocatalytic activities of the samples MG1, MG4, MN1 and AG4 were investigated over the degradation of Methylene Blue (MB) and Rhodamine B (RhB) dyes under solar irradiation. The structures of the dyes are as shown in figures 1(a) and (b). The studies were carried out at room temperature and at neutral pH. Studies have shown that ferrites can be more effective at neutral pH [29].

Before irradiation, 50 ml of 5ppm dye solution containing 50 mg of the photocatalyst was sonicated for 10 min and left in the dark for 1 h to reach adsorption—desorption equilibrium. The adsorption of target molecules onto the nanoparticle photocatalyst should be a critical step towards efficient photo catalysis. Due to small size of nanoparticles, a high surface area and thus a large number of active sites will be available for the adsorption of dye on the catalyst surface. The initial concentration of dye in solution was kept at 5ppm. For higher concentrations of dye, the absorption of photons by dye itself may increase and the light photons may never reach the photocatalyst surface, thus limiting the production of hydroxyl and superoxide radicals and leading to decrease in photo degradation [30]. 50 mg of catalyst loading per 50 ml of dye solution was preferred after optimization. Increased catalyst amount in solution is reported to decrease the photo degradation rate due to light scattering and reduced penetration of light through the solution. The chances of the deactivation of activated molecules by collision with ground state molecules also increase with increase in photocatalyst loading [31]. 0.1ml of 30% of H2O2 was added to 50 ml of solution mixture and kept under sunlight between 12.00 p.m to 2.00 p.m. Solution aliquots of 2–3 ml each were taken at regular time intervals of 60 min, 90 min and 120 min and subjected to centrifugation at 3000 rpm for 10 min or magnetically separated using a supermagnet. Thereafter, the decanted solution was analyzed for absorbance using UV-visible spectrophotometer.

3. Results and discussion

3.1. XRD analysis

Figure 2 presents the X-ray diffraction images of the studied samples labelled as MG1, MG4, MN1, AG4. The XRD pattern indicates that the samples were crystallized in single phase cubic spinel structure with no peaks corresponding to secondary phases in any of the compositions. Structural parameters such as lattice
constant $a$, crystallite size $D$, theoretical X-ray density $\rho_x$ and apparent density $\rho_a$ are calculated using relevant equations and tabulated in table 1. The values of lattice parameter are in the reported range and it is noted that it is the least for the sample containing manganese and is maximum for the silver doped system. The lattice parameter depends on the ionic radius of the substituted cation and distribution of cations over the tetrahedral and octahedral sites. The Mg$^{2+}$ ions have a strong preference for octahedral site whereas Mn$^{2+}$ ions prefer to occupy tetrahedral site \cite{32}. The ionic radius of Mn$^{2+}$ (0.83 Å) is larger than that of Mg$^{2+}$ (0.72 Å) ions. A large value of lattice parameter for AG4 is expected because the ionic radius of Ag$^{2+}$ is very large (1.08 Å) compared to other ions in the system and the unit cell of the spinel ferrite expands to accommodate larger silver ions. Large ionic radius of an ion entering octahedral site replacing Fe$^{3+}$ ions causes internal stress making the lattice distorted and hence the expansion of unit cell. From Vegard’s law, if the radius of displacing ions is larger than the displaced ion, the lattice gets expanded and the lattice constant increases \cite{33}. The crystallite size also exhibits a similar decrease which could be attributed to a connection between lattice constant and crystallite size. The moderate porosity values in the studied samples indicate that the substituted cations have dissolved and entered the spinel lattice. The presence of pores is beneficial in applications like photocatalytic dye degradation that require porous nanoparticles.

### Table 1. Structural parameters of ferrite systems.

| Sample | Lattice constant $a$ (Å) | Crystallite size $D$ (nm) | X-ray density $\rho_x$ (g cm$^{-3}$) | Apparent density $\rho_a$ (g cm$^{-3}$) | Porosity $P$ (%) |
|--------|--------------------------|--------------------------|-------------------------------------|-------------------------------------|-----------------|
| MG1    | 8.3375                   | 14.43                    | 5.245                               | 2.906                               | 44.59           |
| MG4    | 8.3357                   | 13.57                    | 5.387                               | 2.785                               | 48.30           |
| MN1    | 8.3095                   | 13.47                    | 5.44                                | 2.944                               | 45.88           |
| AG4    | 8.3648                   | 17.73                    | 5.216                               | 2.807                               | 46.19           |

Figure 2. X-ray diffraction images of the photocatalysts.

3.2. Magnetic properties analysis

The magnetic measurements of the samples were done at room temperature using a vibrating sample magnetometer and the applied field was varied from $-15$ kOe to $+15$ kOe. Figure 3 depicts the hysteresis loops of the systems and it can be inferred that the samples are ferrimagnetic materials. The magnetic parameters of the photocatalysts are given in table 2.

The net magnetic moment in a ferrimagnetic material is the difference between the magnetic moments of B and A sublattices. A high value of saturation magnetization $M_s$ for the sample labelled MG1 is because Mg ions entering the octahedral (B) site push Fe$^{3+}$ ions to tetrahedral (A) site thereby strengthening A-B interaction which increases $M_s$. Exchange interaction between ions on A and B-site depends on magnetic moments of ions at the sites and distance between the ions. If the distance increases A-B exchange interaction weakens and vice versa. Even though Ag is non-magnetic and prefers to enter B-site, the sample AG4 doped with Ag ions exhibits large $M_s$ which could be attributed to its large crystallite size. $M_s$ increases with crystallite size due to decreased domain walls displacement. For the sample MG4 which contains Gd ions the low $M_s$ value is due to...
the fact that incorporation of Gd$^{3+}$ ions replacing magnetic Fe$^{3+}$ ions at the octahedral B-site decreases A-B interactions and reduces net magnetic moment of the B sublattice. The difference between the net magnetic moment of the octahedral B and tetrahedral A sublattices becomes lesser leading to the observed decrease in $M_s$.

The magnetic moment per ion of Gd$^{3+}$ ions is $7.94 \mu_B$ where $\mu_B$ is Bohr magneton. The source of magnetic moments of rare earth ions is the spin magnetic moment of the localized 4f electrons and these are characterized by magnetic ordering only at lower temperatures\cite{34}. Therefore, their magnetic dipoles are randomly oriented exhibiting disordered form at room temperature and hence substitution of Gd$^{3+}$ ions makes no contribution to the net magnetization of doped ferrites at room temperature\cite{35}. The saturation magnetization is less for MN1 than MG1 as the magnetic Mn ions show a site preference for A-site. Moreover, the magnetization values not only depend on cation distribution but also on several other factors such as lattice defects, random orientation of magnetic spins, magnetic super-exchange interactions among others\cite{36}. The remanent magnetization $M_r$ is independent of grain size. It is not an extrinsic effect rather it is an intrinsic effect. It originates from spin canting state of the sample. The finite-size effects of the nanoparticles lead to non-collinearity of spins on their surface\cite{37}. Coercivity, $H_c$ values are in the reported range for spinel ferrites. There is no consistent relationship between $H_c$ and crystallite size. The remanent ratio $R$ is found to be low suggesting isotropic nature of the samples\cite{38}. The variation of $R$ is as reflected in case of $H_c$.

3.3. Electric properties analysis

3.3.1. Relative permittivity $\varepsilon'$

The dielectric properties of the samples have been studied in the frequency range from 100 Hz to 10 MHz at room temperature. Figure 4(a) shows the variation of relative permittivity, $\varepsilon'$ with frequency at room temperature. In general, nanocrystalline spinel ferrites are good dielectric materials with high permittivity and low dielectric losses. It is noted from the figure that $\varepsilon'$ decreases rapidly with increase in frequency in the low frequency range and later the decrease becomes sluggish at higher frequencies and attains almost a constant value with further increase in frequency. This is absolutely the normal dielectric behaviour which can be explained by the Koop’s theory which considers the dielectric ferrites as inhomogeneous medium of two layers of the Maxwell-Wagner type\cite{39, 40}. This model suggests that the ferrites consist of highly conducting grains surrounded by poorly conducting grain boundaries which leads to space charge polarization produced by a local accumulation of charges under the influence of an external applied electric field. The grain boundaries are more effective at low frequencies whereas the grains dominate at high frequencies. In ferrite systems, conduction...
mechanism and dielectric polarization are related [41]. The hopping of electrons between metal ions of different oxidation states present at octahedral sites is responsible for dielectric polarization. During hopping of electrons between Fe$^{3+}$ and Fe$^{2+}$, owing to the high resistance of grain boundaries the electrons accumulate on the boundaries resulting in space charge polarization which is the reason for comparatively high value of permittivity at low frequencies. At higher frequencies, the decrease in $\varepsilon'$ is due to decrease in space charge polarization due to the dominance of the conducting grains. At still higher frequencies, the hopping cannot

![Figure 4](image-url)
follow the applied field variations, thereby $\varepsilon'$ becomes independent of frequency. In the samples studied, the magnesium substituted samples MG1 and MG4 have higher values of $\varepsilon'$. The conduction mechanism is largely influenced by the concentration of Fe$^{2+}$ ions. A low concentration of Fe$^{2+}$ causes a low resistivity and hence a high value of dielectric constant. It is known that, for ferrite systems, the relative permittivity, $\varepsilon'$ is inversely proportional to the square root of resistivity. For the MG4 system, the entry of Gd ions at octahedral site forces more of Fe$^{3+}$ ions to move to tetrahedral site which decreases hopping leading to the decrease in $\varepsilon'$. Increase in hopping length between cations is responsible for the decline in hopping rate. Gadolinium ions do not participate in the conduction process due to their stable valencies. The sample MN1 exhibits the least relative permittivity value which may be due to a decrease in hopping rate probably because of the tetrahedral site preference of Mn ions. The exchange of electrons between A-B sites is more pronounced in determining the electrical properties than the B-B exchange.

3.3.2. Dielectric loss $\varepsilon''$

The dielectric loss tangent (tan $\delta$) gives the energy loss within a dielectric medium. Dielectric loss, $\varepsilon''$, as shown in figure 4(b), exhibits a similar trend as is the case with ferrites which again is due to the fact that at low frequencies due to the high resistance of grain boundaries more energy is required for electron to hop and as a consequence the loss is high. At high frequencies where the high conductivity grains dominate, energy required for the electron hopping is less and hence $\varepsilon''$ decreases. Loss peaks that appear when the hopping frequency of electrons become equal to the frequency of the applied electric field are not seen in any of the samples for the investigated range of frequencies.

3.3.3. AC conductivity $\sigma_{ac}$

The AC conductivity $\sigma_{ac}$ values are determined using the dielectric data. The variation of AC conductivity with frequency at room temperature for the studied ferrite samples is given in figure 4(c). It is observed to increase with frequency for all the samples and the plots are almost linear over a wide frequency range which confirms that the conduction is due to small polaron hopping. AC conductivity decreases with frequency in the case of large polaron hopping, whereas in small polaron hopping, it increases with frequency. The frequency dependence of $\sigma_{ac}$ can also be explained with the help of Maxwell-Wagner two-layer model of polycrystalline ferrites. The linear increase in AC conductivity is related to the conduction by electron exchange between ions of same element but in different valence states. On applying the ac field the electron exchange increases thereby increasing the AC conductivity. The observed decrease in AC conductivity at high frequencies can be explained in terms of the decrease in hopping rate.

3.4. Transmission electron microscopy analysis

Figures 5(a) and (b) show TEM images of MG1 and MN1 samples respectively. Most of the nanoparticles appear to be almost spherical in shape and a few are agglomerated. Agglomeration has been observed in ferrites due to their magnetic nature.

The Selected Area Electron Diffraction (SAED) patterns of the samples MG1 and MN1 are depicted in figures 6(a) and (b) respectively. The continuous and diffused rings observed in the micrographs indicate the polycrystalline nature of these samples. A diffraction ring corresponds to a group of lattice planes with the same Miller indices. The appearance of spots indicates the crystallinity of the sample, brighter the spot, the more crystalline is the particle. Small spots that make up the ring arise from Bragg reflection from an individual crystallite.

3.5. X-ray photoelectron spectroscopy analysis

The binding energy values recorded using XPS system is used to identify the elements and their valence states in a mixed valence compound. The binding energy value of a peak in XPS spectra depends both on the chemical state and the molecular environment of an atom in a molecule. Figures 7(a)–(d) respectively give the BE versus intensity plots of Fe 2p, Ni 2p, Mg 2p, Mn2p as obtained for the samples MG1, MG4, MN1. The photoelectron peak positions noted from the plots are presented in table 3. The obtained values are in good agreement with the reported data.

When cations get distributed in two different lattice sites in a spinel ferrite, two XPS peaks or a peak broadening is expected. The difference in binding energy is attributed to the difference in the stabilization between the two sites due to difference in their co-ordination. The Fe 2$p_{3/2}$ main peak, shouldering with the characteristic satellite peak of Fe$^{3+}$ at 720.25 eV, is fitted into signals positioned at around 711 eV and 713 eV indicating the existence of Fe ions in two different lattice sites. The peak around 711 eV is ascribed to the Fe$^{3+}$ ions at octahedral site while the peak near 713 eV is due to Fe$^{3+}$ ions in tetrahedral site. The changes in binding energy values of Fe 2p peak position is due to cation redistribution due to different site preferences of the
incorporated cations. In the case of Ni$^{2+}$ ion in the samples, the binding energy of Ni 2p$_{3/2}$ is seen around 854 eV [55]. The BE of Ni 2p$_{3/2}$ in NiO is reported to be at 854.0 eV and in Ni ferrites, it is at 855.1 eV. This shows that Ni$^{2+}$ ions have entered the spinel structure at octahedral site only. For Mg 2p, the higher energy peak near 55.6 eV corresponds to Mg ions at octahedral site and the lower energy peak near 49 eV is due to Mg ions at the tetrahedral site. The observed values for Mg ions are close to Mg 2p peak value (49.7 eV) in MgO indicating that Mg ions enter as Mg$^{2+}$ in the spinel ferrite [56]. A decrease in binding energy in the case of tetrahedral Mg$^{2+}$ ions was due to lower no. of oxygen ions surrounding the tetrahedral site. The increase in width of Fe and Mg XPS peaks in the sample MG4 is attributed to the redistribution of these ions in octahedral and tetrahedral sites on doping with Gd ions which tends to occupy only octahedral site. Fe$^{3+}$ and Mg$^{2+}$ can enter both sites with almost 90% of Mg$^{2+}$ ions showing a tendency for octahedral site [32]. The Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ core level emission peaks were observed near 642 and 653 eV. The Mn 2p peak was observed close to those of MnO (641 eV) and Mn$_2$O$_3$ (641.6 eV). It can be inferred from the peak positions that Mn existed as Mn$^{2+}$ and Mn$^{3+}$ states in the

Figure 5. (a) TEM image of nanoparticles of MG1. (b) TEM image of nanoparticles of MN1.
studied Mn1 sample. Mn$^{2+}$ ions may get oxidized to Mn$^{3+}$ during synthesis if oxygen impurities are present in the atmosphere.

3.6. Open aperture Z-scan analysis

The z-scan plots obtained at a linear transmission of 70% for the investigated samples are as shown in figures 8(a)–(d). The observed data points were fitted using the non-linear transmission equation given below [57].

$$T(z) = \frac{C}{q'\sqrt{\pi}} \int_{-\infty}^{\infty} \ln(1 + q'e^{-t^2}) dt$$

![Figure 6. (a) SAED pattern of MG1. (b) SAED pattern of MN1.](image)
Figure 7. (a) Fe 2p photoelectron peaks in XPS spectra. (b) Ni 2p photoelectron peaks in XPS spectra. (c) Mg 2p photoelectron peaks in XPS spectra. (d) Mn 2p photoelectron peak in XPS spectra.
where $q'(z,r,t) = \beta I_0(t) L_{\text{eff}}$ and $L_{\text{eff}} = \frac{1}{1 - e^{-\alpha z}}$. $I_0$ is the irradiance at the focus, $z$ is the sample position, $L_{\text{eff}}$ is the effective thickness, $\alpha$ and $\beta$ are the linear and non-linear absorption coefficients respectively.

Solid lines represent the theoretical fit and the measured data points are represented by the circular dots. A transmission dip in all the plots point to reverse saturable absorption (RSA) [58]. The non-linear absorption coefficients ($\beta$) for the samples are presented in table 4. The sample MG1 has the maximum value of $\beta$ and the least for MG4 which is the sample containing Gd ions. This behaviour could be related to the porosities of the samples (table 1). Z-scan measurements were carried out for three different input pulse energies for a linear transmission of 70%. However, it is seen that the $\beta$ value does not show a systematic variation with increase in input laser pulse energy. Non-linearity is exhibited by virtue of processes like Excited State Absorption (ESA), Two Photon Absorption (TPA), Non-linear Scattering, Free Carrier Absorption, RSA etc [59]. In RSA, $\beta$ values increase with input pulse energy whereas in ESA it decreases with input pulse energy and in TPA, $\beta$ does not vary much with input intensity. Hence, it can be concluded that the non-linear behaviour exhibited by the studied samples may be due to the involvement of more than one process depending on the input pulse energy and available states in the samples or due to a higher order process like free carrier absorption, which needs to be confirmed through further study.

The choice of an optical limiting material depends on another important non-linear parameter called the optical limiting threshold (OLT). It is the input fluence at which the transmittance reduces to half the linear

### Table 3. Binding energy values of photoelectron peaks in XPS spectra.

| Sample name | BE of Fe 2p$_{3/2}$ (eV) | BE of Mg 2p$_{3/2}$ (eV) | BE of Ni 2p (eV) | BE of Mn 2p$_{3/2}$ (eV) |
|-------------|--------------------------|--------------------------|----------------|--------------------------|
| MG1         | 710.55 (octahedral)     | 55.55 (octahedral)       | 854.75 (octahedral) | —                        |
| MG4         | 711.25 (octahedral)     | 55.65 (octahedral)       | 854.55 (octahedral) | —                        |
| MN1         | 710.00 (octahedral)     | —                        | 854.95 (octahedral) | 642.05                   |
transmittance. Lower the OLT better is the optical limiting performance \[60\]. The plots between non-linear transmittance and input fluence calculated using the standard equation for the Gaussian beam are shown in figures 9(a)–(d). The limiting threshold values noted from these plots are found to be low indicating that the studied samples possess better optical limiting characteristics.

### 3.7. Photocatalytic activity

The photo degradation efficiency percentage of the investigated samples is listed in table 5. The photocatalytic degradation efficiency was calculated using the following equation:

\[
(\% \text{ degradation}) = \left( \frac{A_0 - A_t}{A_0} \right) \times 100,
\]

where \(A_0\) and \(A_t\) are the absorbance of the solution before and after irradiation respectively \[61\].

Figures 10(a)–(f) show the UV-visible spectra of the photocatalytic degradation of the dyes using the investigated spinel nanoparticles. The characteristic absorption peaks of MB and RhB dyes are obtained at 664

| Sample Name | Input laser energy (\(\mu J\)) | \(\beta\) \((10^{-11} \text{ m W}^{-1})\) |
|-------------|-----------------------------|-------------------------------|
| MG1         | 10                          | 18.5                          |
|             | 20                          | 16                            |
|             | 40                          | 19.5                          |
| MG4         | 10                          | 13                            |
|             | 20                          | 11                            |
|             | 40                          | 7.5                           |
| MN1         | 40                          | 13                            |
| AG4         | 40                          | 17.5                          |
and 554 nm respectively. It is seen that the ferrites containing magnesium exhibit better degradation efficiency than the samples containing manganese and silver. The same result is observed in case of both MB and RhB dyes. The percentage degradation achieved with H$_2$O$_2$ alone in dye solution is less than that achieved with the solution mixture containing ferrites as photocatalyst. The presence of nanoparticle ferrites speeds up degradation rate; the possible reasons for which could be

1. adsorption of dye molecules to the surface of the photocatalyst.
2. the delayed recombination of photo generated electron-hole pairs in ferrites.

### 3.8. Mechanism of photo degradation

When the solution mixture containing the photocatalyst and dye is kept under sunlight, the electrons in the valence band get excited to the conduction band and thus electron–hole (e-h) pairs are generated on the photocatalyst surface. In normal cases, the electrons immediately de-excite and recombine with the holes in the valence band. But in the ferrite systems the photo generated e-h pair recombination is much delayed due to the increase in band gap value. Due to the effective separation and delayed recombination of e-h pairs, the charge carriers are made available for the oxidation of the dye molecules in solution.

The primary oxidant in dye degradation is OH$^·$ radicals. There are several mechanisms which lead to the formation of OH$^·$ radicals and other responsible photo species such as O$_2^·$ depending on the redox potentials of the radicals and valence band and conduction band edges of the photocatalyst. In order to enhance the formation of reactive oxygen species, oxidants such as H$_2$O$_2$ are added to the reaction mixture. The redox potential of O$_2^·$/O$_2$ is at 0.33V and that of OH$^·$/OH is at 1.99V. The OH$^·$ radical has higher oxidation potential than hydrogen peroxide and ozone. The properties of ferrites strongly depend on the size, nature and amount of metals incorporated in the spinel structure. Substitution of Mg$^{2+}$, Mn$^{2+}$, Ni$^{2+}$ etc modify the redox properties of the ferrites. The holes in the valence band oxidises water by reacting with OH$^·$(hydroxide ion) to form OH$^·$ radical. The electrons in the conduction band react with the added H$_2$O$_2$ to produce more OH$^·$ radicals which then leads to the oxidation of more dye molecules. Fe$^{3+}$ ions on the catalyst surface can also capture the photo generated electrons to form more OH$^·$ radicals. These OH$^·$ radicals can oxidise the dye molecules adsorbed to the surface of the photocatalyst, thus resulting in higher photocatalytic degradation efficiency. The OH$^·$ radicals have a very short life time and can react where they are formed. Porous substances are better adsorbents as an increased surface area promotes adsorption.

A remarkable result achieved is the near total degradation overnight of RhB dye in solution which was decanted after magnetic separation of the ferrites from the reaction mixture. In spite of using a strong magnet to magnetically separate the ferrite, trace amounts of it does remain in solution as is seen in figure 11(a). A pink tinge (figure 11(b)) on the photocatalyst settled in the decanted solution indicates adsorption. Adsorption is a surface phenomenon and it is of two types—physisorption and chemisorption. Chemisorption involves chemical bond formation between the adsorbent and adsorbate. It is characteristic of covalent bonding and may occur due to electrostatic attraction.

The existence of adsorbate in solution as well as the charge on the adsorbent surface greatly depends on the solution pH. The point of zero charge of ferrites falls in the basic region. So at neutral pH the ferrite surface is positively charged which favours adsorption of anionic dyes. RhB dye exists in two structural forms—cationic and zwitterionic structures.

A zwitterion is a dipolar ion which is a molecule with two or more functional groups, of which atleast one has a positive and the other has a negative electrical charge and the net charge of the entire molecule is zero. At pH values less than 4, the RhB ions are of cationic and monomeric molecular form. At pH values more than

### Table 5. Photo degradation efficiency percentage of the studied photocatalysts.

| System (reaction mixture containing dye, photocatalyst and H$_2$O$_2$) | 120 min with H$_2$O$_2$ only | 60 min | 90 min | 120 min | Magnetic separation |
|---------------------------------------------------------------|-----------------------------|--------|--------|---------|---------------------|
| MB + MG1                                                      | 71                          | 60     | 69     | 74      | No change           |
| MB + MG4                                                      | 71                          | 61     | 71     | 80      | No change           |
| MB + MN1                                                      | 71                          | 25     | 32     | 38      | No change           |
| MB + AG4                                                      | 71                          | 63     | 66     | 72      | No change           |
| RhB + MG1                                                     | 21                          | -      | 30     | —       | 94                  |
| RhB + MG4                                                     | 21                          | -      | 28     | -       | 50                  |
4.4, the carboxyl group gets ionized and the zwitterionic form of RhB is formed. At 7.0 pH more molecules of RhB exist mainly in anionic form which can get adsorbed to the positively charged sites on the catalyst due to the electrostatic attraction. The deprotonated carboxylic acid function of RhB makes it negatively charged ion. The zwitterionic form of RhB may increase the agglomeration of RhB molecules to form larger molecular forms dimer and become unable to enter the porous sites. The aggregation is due to the attractive electrostatic interaction between the carboxyl and xanthene groups of the monomers. On adding H₂O₂, the excessive OH⁻ ions compete with carboxyl group (R-COO⁻) in binding with xanthene (R- N⁺) and thus aggregation of RhB decreases leading to increased adsorption [63, 64].

The nanoparticle ferrites are ferromagnetic in nature. The magnetic moment of a ferrite molecule is due to the spin of the unpaired 3d electron. On subjecting the solution to a magnetic field, the magnetic moments of ferrites align in the direction of applied magnetic field. Due to relatively large coercivity Hc, the dipoles continue to remain aligned if left undisturbed. An RhB dye molecule being organic is diamagnetic and in the presence of a

Figure 10. Variation of photocatalytic degradation of MB dye with time (a) using photocatalyst AG4 = 50 mg in 50 ml of 5ppm of MB, pH = 7.0, (b) using photocatalyst MG1 = 50 mg in 50 ml of 5ppm of MB, pH = 7.0, (c) using photocatalyst MG4 = 50 mg in 50 ml of 5ppm of MB, pH = 7.0, (d) using photocatalyst MG4 = 50 mg in 50 ml of 5ppm of MB, pH = 7.0, (e) using photocatalyst MG1 = 50 mg in 50 ml of 5ppm of RhB, pH = 7.0, (f) using photocatalyst MG4 = 50 mg in 50 ml of 5ppm of RhB, pH = 7.0.
magnetic field the orbital magnetic moments of the dye molecules get aligned in the direction opposite to that of the magnetic field. Protons and electrons can be thought of as tiny magnets whose electromagnetic fields interact through space. This interaction is called a dipole-dipole interaction. Four factors that determine the strength of the dipolar interaction are-

(i) type of magnetic dipole moment
(ii) the distance between them
(iii) the angle between them
(iv) their relative motion.

The dipole-dipole interaction may be either proton-proton or proton-electron. Since the gyromagnetic ratio of an electron is much larger than a proton, the proton electron dipolar interaction is much stronger than a proton proton interaction. In the present case of ferrites in dye solution at neutral pH, the ferrites are positively charged and the RhB dye exists in the anionic form. Therefore, the proton electron interaction may be dominating. The strength of dipolar interaction depends on the distance between the dipoles. The effect is inversely proportional to the sixth power of distance. Due to nanoparticle size of the ferrite crystallites, more number of proton electron interactions between ferrites and RhB molecules are possible. The strength of the interaction also depends on the quantity $(3\cos^2 \theta - 1)$ where $\theta$ is the angle between the two dipole moments. As $\theta$ decreases the interaction increases. Subjecting the solution mixture to a magnetic field reduces the angle $\theta$ due to alignment of dipoles. The interaction is strong if the dipoles are aligned in opposite direction which is the situation with ferromagnetic ferrites and diamagnetic RhB dye molecules. Thus, it can be concluded that strong proton electron interaction leads to greater adsorption. Also in the nano regime, a quantum size effect could be the possible reason for the observed photo activity exhibited by nanoparticle ferrites.

The same photocatalytic behaviour was not exhibited by magnetically separated solution containing MB dye. Atoms and ions will only be diamagnetic if the resultant spin and orbital momentum of the electrons is zero or in general, if they are in an s-state. In diamagnetic materials, magnetic moments of each of the individual electrons in the material get cancelled. In solutions there are deviations which may be attributed to the effect of hydration of the ions or to the effect of the solute ions on the degree of association of the solvent. The main contribution to the diamagnetic susceptibility of an ion comes from the outer electrons and the effective charge acting on these is much less than the nuclear charge density owing to screening by inner electrons. The different boundary conditions for an ion in solution or crystal will necessarily result in some modifications in the charge distribution. In a non-monatomic molecule, however, even when the resultant angular momentum of the electrons and nuclei vanishes, there will be a continual transfer of momentum between the electrons and the nuclei. The average electronic angular momentum will still vanish but not its square. This leads to a small paramagnetic effect. There is no simple general relation between susceptibilities and number of electrons and number of atoms in the molecule [65].
4. Conclusion

Mg/Mn substituted Ni-Zn ferrites nanoparticles with size ranging from 10–20 nm have been synthesized using the sol-gel technique. The XRD analysis indicates that the samples were crystallized in single phase cubic spinel structure with no peaks corresponding to secondary phases in any of the compositions. The moderate porosity values in the studied samples indicate that the substituted cations have dissolved and entered the spinel lattice. The presence of pores is crucial for photocatalytic degradation of dyes. Magnetic property analysis using VSM reveals that the sample labelled MG1 has a high value of \( M_r \) as Mg has a strong preference for octahedral (B) site and Mg entering the B site pushes Fe\(^{3+}\) ions to A site thereby strengthening A-B interaction which increases \( M_r \). From the observed dielectric dispersion with frequency it is evident that all the samples exhibit normal dielectric behaviour. The sample MN1 exhibits the least relative permittivity value which may be due to a decrease in hopping rate probably because of the tetrahedral site preference of Mn ions. The linear increase of AC conductivity with frequency substantiates small polaron type hopping conduction in the samples. XPS spectral analysis points to the fact that cation redistribution has taken place based on different site preferences of the incorporated cations. The investigated samples also exhibit better optical limiting parameters. Photocatalytic degradation studies affirm that ferrites are good photocatalysts for organic dye degradation. Due to the effective separation and delayed recombination of e-h pairs in ferrites, the charge carriers are made available for the oxidation of the dye molecules in solution. It is seen that the ferrites containing magnesium exhibit better degradation efficiency than the samples containing manganese and silver. A near total dye degradation of RhB dye achieved with magnetic separation is remarkable and the outcome is the result of increased adsorption due to the enhanced structural, electrical and magnetic properties of the synthesized samples.

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