Chapter - 4

Remarkable Optical and Photocatalytic Properties of Solar Light Active Nd Substituted Ni Ferrite Catalysts: For Environment Protection
4.1. Introduction

Catalysis is becoming a strategic field of science because it represents a new way to meet the challenges of energy and sustainability. These challenges are becoming the main concerns of the global vision of societal challenges, world economy and environmental safety. Environmental contaminants in water or air pose a serious threat to public health and safety. They have attracted considerable attention from a range of research groups. More than $7 \times 10^5$ tons of synthetic dyes was produced every year worldwide. About 10–15% of these dyes were lost as waste pollutants entering into the environment [1]. Synthetic dyes usually contain complex aromatic structures which were chemically stable and resistant to biodegradation in nature. Their toxicity and persistence in the environment are of a great concern to aquatic life and human health [2,3]. Treatment and cleaning of these pollutants from waste water thus becomes an essential issue of environmental and health protection. Due to the large degree of organics present in waste water and stability of modern textile dyes, conventional biological treatment methods were ineffective for their decolorization and degradation of waste water [4]. Consequently, novel technologies with more efficiency and less energy use have stimulated intensive research. An alternative to conventional method is photocatalytic degradation, i.e., advanced oxidation processes based on the generation of very reactive species such as hydroxyl radicals (OH') that oxidize a broad range of organic pollutants quickly and non-selectively [5]. The consumption of non-renewable energy sources such as fossil fuels for photodegradation is less favorable nowadays, not only because of current shortage and a final exhaustion of these sources, but also for serious environmental considerations [6,7]. Vast clean energy source that remains incompletely
exploited is solar energy. With an annual insolation level of 1000 W/m², solar energy is an attractive energy source that exceeds all current human needs [3,4]. The conversion of solar energy (electromagnetic radiation) into a practically applicable form can be achieved by a photocatalyst (i.e. semiconductor with an appropriate band gap and band edges) through a process which was similar to photosynthesis [7-12].

In recent years, semiconductor photocatalysis, as a "green" technology, has been widely used for the treatment of polluted water. Most of them suffer from their intrinsic limitations (band gap > 3.1 eV) that only ultraviolet radiation can be utilized [13,14]. However, it is well-known that, although the sun can provide an abundant source of photons, UV light accounts for only a small fraction (4%) of the solar energy compared with visible light (45%), indicating that low band gap catalysts were more desirable. In this respect, developing a photocatalyst that efficiently extends photocatalytic activity into visible region for environmental remediation has become a great challenge and one of the most active research topics in photocatalysis [14-16]. Usually, photodegradation reactions were carried out in heterogeneous systems. The ability to reuse the suspended ultrafine photocatalysts after degradation can result in substantial cost savings. The introduction of magnetic nanoparticles to a variety of solid matrixes allows the combination of well-known procedures for photocatalyst heterogenization with techniques for magnetic separation [17].

Use of ecofriendly ferrites [18-21] for efficient solar energy usage has been an important topic in the visible light photocatalysis research. Ferrites are well known for their tremendous applications in the field of magnetic and electronic materials [22,23], but there are few reports on their photocatalyst applications [24,25]. Unlike TiO₂, the
ferrites offer an advantage of displaying the desirable optical absorption for the low energy photons (hv~2 eV) and of exhibiting the well suited electronic structure desirable for photocatalytic applications. To make full use of solar energy, many attempts have been made to prepare the narrow band gap ferrite semiconducting material that utilizes much larger visible region. Some of the recent reports were important indicators with respect to the potential of visible light photocatalytic application of the spinel ferrites [25-27]. Among the ferrites, owing to unique properties of low price, environmental benignity, and the large abundance of Ni, NiFe$_2$O$_4$ has received great attention and one of the most important magnetic materials having high-electrical resistivity, high-Curie temperature and environmental stability. As an important class of magnetic materials, NiFe$_2$O$_4$ with an inverse spinel structure shows ferrimagnetism that originates from a magnetic moment of antiparallel spins between Fe$^{3+}$ ions at tetrahedral sites and Ni$^{2+}$ ions at octahedral sites [28]. The properties of nickel ferrite can be varied by changing the identity of the trivalent Fe$^{3+}$ and divalent M$^{2+}$ cations. Eventhough, NiFe$_2$O$_4$ has a band gap of 2.19 eV, [29] little research have been conducted on its photocatalytic activity. Although NiFe$_2$O$_4$ alone was photocatalytically inactive under visible light irradiation [30], it is possible to improve the efficiency of the photoinduced charge separation in NiFe$_2$O$_4$ by substituting metals, resulting in enhanced photocatalytic performance. It has been reported that, Kundu et al. [31] investigated the microstructure and dc resistivity of Ti$^{4+}$ ion doped nickel ferrites, Zhijian et al. [32] studied the Effect of Pr$^{3+}$ doping on magnetic and dielectric properties of Ni–Zn ferrites, Shihong et al. [33] reported the photocatalytic properties of magnetically separable TiO$_2$ supported on nickel ferrite, Jitendra et al. [34] demonstrated the multiferroism in gadolinium substituted nickel ferrite, Ishaque, et al. [35] investigated the electrical and dielectric properties of
yttrium substituted nickel ferrites. To the best of our knowledge, as per the literature no reports have been cited on the photocatalytic properties of magnetically recoverable neodymium substituted nickel ferrite nanoparticles under solar light irradiation.

It is of great interest to explore a novel approach for imparting multifunctional properties onto the neodymium substituted nickel ferrite system. If that can be accomplished, then it may be possible to obtain widely useful material with good recycling stability and also have high performance under solar light irradiation, as well as with great magnetic recycling property (as photocatalysts). In our previous work, we have shown that, the visible light activities of ZnFe$_2$O$_4$ photocatalysts could be markedly improved by substitution with a cadmium metal [36]. This work actually motivated us with further interest to design solar-light-driven ferrite photocatalysts substituted with a different metals. Herein, we have reported the synthesis of a neodymium substituted nickel ferrite system by a modified size-controlled coprecipitation method. Interestingly, when neodymium was substituted into nickel ferrite, the inactive NiFe$_2$O$_4$ dramatically converted into a solar light active photocatalyst. The photocatalytic activity of the pure and neodymium substituted nickel ferrite under natural solar light were investigated and reported for the first time.

4.2. Experimental Section

4.2.1. Materials

The starting materials such as ferric nitrate (Fe(NO)$_3$$\cdot$9H$_2$O), nickel nitrate (Ni(NO)$_3$$\cdot$6H$_2$O), neodymium chloride (NdCl$_3$$\cdot$6H$_2$O) and sodium hydroxide (NaOH) were used. Rose Bengal was used as target compound for degradation. All chemicals and solvents were of analytical grade purchased from Himedia laboratory. All the compounds were used as received without further purification.
4.2.2. Preparation of catalysts

Nanocrystalline neodymium substituted nickel ferrite nanoparticles were synthesized by the chemical co-precipitation method [37]. The starting materials were of high-purity Fe(NO)₃·9H₂O, Ni(NO₃)₂·6H₂O, NdCl₃·6H₂O. According to the formula of NiFe₂₋ₓNdₓO₄ (where \(x = 0.0, 1.0, 1.5, 2.0\)), each starting material were weighed and dissolved in double distilled de-ionized water and then mixed together. Sodium hydroxide (GR, 28–30%) of 3.0M (as the precipitating agent) was added to the above salt solution drop-wise. The pH of the solution was constantly monitored as the NaOH solution was added drop-wise. The reactants were constantly stirred using a magnetic stirrer until a pH level of 13 was achieved. A specified amount of oleic acid (2–3 drops for total reacting solution of 75ml) was added to the solution as a surfactant. The liquid precipitate was then brought to a reaction temperature of 80 °C and stirred for 60 min. The product was cooled to room temperature and then washed twice with double distilled water and ethanol to remove unwanted impurities and the excess surfactant from the prepared sample. The size and size distribution were controlled by controlling the nucleation and growth rates during the reaction. Smaller particles were obtained if the nucleation rate was higher than the growth rate. Large pH value (13) was used because it controls the process of nucleation (rate) and lowers the particle size [38]. Nd-concentration (\(x\)) in nickel ferrite has been controlled by the initial stoichiometric ratios of the reactants.

4.2.3. Characterization

Physical and chemical characterizations of NiFe₂₋ₓNdₓO₄ were carried out as described below. Light absorption properties of the NiFe₂₋ₓNdₓO₄ nanocrystals dispersed
in ethanol were studied by UV–Vis spectrophotometer (Shimadzu, UV-1650 PL model). The phase compositions and structures of the NiFe$_{2-x}$Nd$_x$O$_4$ samples were determined by powder X-ray diffraction (PXRD, PANalytical Xpert Pro X-ray Diffractometer) with Cu-Kα radiation ($k=0.15406$ nm) over the 2θ range of 10–80°. The structural characterization of the nanocrystalline NiFe$_{2-x}$Nd$_x$O$_4$ samples were examined by fourier transform infrared spectroscopy (FTIR) (using a Nicolet IR200 FT-IR spectrometer). The morphology of NiFe$_{2-x}$Nd$_x$O$_4$ ferrite samples were observed by scanning electronic microscopy (SEM) with a JSM-6700 LV electron microscope operating at 5.0 kV and the chemical compositions were examined by energy-dispersive X-ray spectroscopy (EDS).

4.2.4. Photocatalytic activity study

The reactions of the photocatalytic degradation of organic pollutants with synthesized NiFe$_{2-x}$Nd$_x$O$_4$ catalysts samples were measured under natural solar light irradiation in an aqueous solution at ambient temperature. Experiments conducted are as follows: In each experiment, 0.1g of NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticles were added into 100 ml of Rose Bengal solution with a concentration of 10 mg L$^{-1}$. The suspension were magnetically stirred in the dark for 30 min to establish the adsorption/desorption equilibrium at room temperature, then the solution was directly irradiated under natural solar light with similar conditions on sunny days of March-May between 10 A.M. and 3 P.M. where the solar intensity fluctuations were minimal. The sky was clear and the sunrays were very intense in this period in the city of Shivamogga (India). During irradiation, stirring was maintained to keep the mixture in suspension. At regular intervals, samples were taken from the suspension and then magnetically separated to remove NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticle catalysts and reused for additional runs. The color
removal of the dye solutions were monitored on a UV–Vis spectrophotometer (Shimadzu, UV-1650 PL model) by measuring the absorbance in the range of 200–800 nm wavelength. Distilled water was used as the reference sample. According to the calibration plot of the UV absorbance as a function of the remaining Rose Bengal concentration, the efficiency of the Rose Bengal decomposition was calculated. In addition we have investigated the recyclability of NiFe$_{2-x}$Nd$_x$O$_4$, after each catalytic run, the samples were washed and dried to permit subsequent photoreaction cycles.

4.3. Results and Discussion

4.3.1. Structure and morphology of NiFe$_{2-x}$Nd$_x$O$_4$ photocatalysts

The X-ray diffractograms of NiFe$_{2-x}$Nd$_x$O$_4$ ($x = 0$, 1.0, 1.5, 2.0) system were presented in Figure 4.1. Experimentally observed d-spacing values, 2θ values and relative intensities were in good agreement with the standard XRD pattern. When the ferrite doped with a relative amount of rare-earth ions, besides the spinel phase, a foreign phase in a small amount was formed [39]. Accordingly, NiFe$_2$O$_4$ ($x=0.0$) particles exhibited the cubic phase with space group Fd3m (SG No. 227, JCPDS Card No. 86-2267) and in addition, peak designated by * may be due to the formation of small amount of α-Fe$_2$O$_3$ phase. As it can be seen in Figure 4.1, the substitution of Fe$^{3+}$ ($r = 0.78$ Å) by Nd$^{3+}$ ions ($r = 1.16$Å) determines a gradual change in the crystalline structure from cubic to orthorhombic one. Thus in the Nd substituted ferrites (NiFe$_{1}$Nd$_{1}$O$_4$ and NiFe$_{0.5}$Nd$_{1.5}$O$_4$) the initial cubic phase of the nickel ferrite co-existed with the newly formed orthorhombic phase of NdFeO$_3$ (peak designated by $\$, see Figure 4.1). The formation of NdFeO$_3$ secondary phase can be explained by the limited solubility of voluminous Nd$^{3+}$ ions in the host spinel lattice [58]. An oxide having a distorted tetragonal structure
was obtained for a substitution of $x=2$ (NiNd$_2$O$_4$) and in addition peak designated by # may be due to the formation of small amount of Nd$_2$O$_3$ phase exists. In NiNd$_2$O$_4$ structure the Nd$^{3+}$ and Ni$^{2+}$ ions were surrounded by 8 and 4 O$^{2-}$, respectively [40].

The XRD results were used to determine the average crystallite sizes of the NiFe$_{2-x}$Nd$_x$O$_4$ nanocrystals based on the FWHM values. The Debye–Scherrer formalism was applied (crystallite size = $0.89\lambda/\beta \cos \theta$, where $\lambda$ = wavelength of X-ray, $\beta$ = full width at half-maxima, and $\theta$ = diffraction angle), which results in an average crystal size of 22, 23, 24 and 19 nm with respect to $x=0.0$, 1.0, 1.5 and 2.0. The value of the lattice constant for NiFe$_{2-x}$Nd$_x$O$_4$ were found to be $a=8.34$, 8.78, 8.92 and 9.3 Å for the samples $x=0.0$, 1.0, 1.5 and 2.0 respectively. It was observed that the lattice parameter increases linearly with Nd$^{3+}$concentration obeying Vegard's law. This can be explained on the basis of relative ionic radii of Fe$^{3+}$ and Nd$^{3+}$ ions. Since Fe$^{3+}$ ions have smaller ionic radius (0.78 Å) than those of Nd$^{3+}$ ions (1.16 Å), a partial replacement of the former by the later causes the increase in ionic radii on B-site. Shinde et al. [41] reported similar behavior for Nd$^{3+}$ substituted nickel ferrites, increase in lattice constant with increase in Nd$^{3+}$content in nickel ferrites were also reported by Vermenko et al. [42]. The obtained value of the lattice parameter for nickel ferrite was in good agreement with that reported values [43].
4.3.2. SEM and EDS analysis

The SEM micrographs of the as-synthesized samples $x=0.0$, 1.0, 1.5 and $x=2.0$ were shown in Figure 4.2. The results illustrate that the morphology of the samples changes significantly with the change in the Nd concentration. Surface morphology of the sample at $x=1.5$ show a fine structured morphology. However, the sample at $x=0.0$ shows, some small particles get aggregated together to form bigger particles. The EDS spectra of synthesized photocatalysts were illustrated in Figure 4.3 (a) and 4.3 (b) indicates the presence of Ni, Fe, Nd and O atoms were the major chemical components present in the samples. The photocatalysts having majority of 26.78 wt.% of Ni, 48.99 wt% of Fe and 24.23 wt.% of O, for the sample $x=0.0$ and 14.76 wt.% of Ni, 8.47 wt% of Fe, 57.90 wt.% of Nd and 18.87 wt.% of O, for the sample $x=1.5$. 

Figure 4.1. Comparative XRD patterns of NiFe$_{2-x}$Nd$_x$O$_4$ photocatalysts
respectively. The EDS results were consistent within experimental stoichiometric ratio with small experimental error, confirming the compositional uniformity and formation of the NiFe$_{2-x}$Nd$_x$O$_4$ nanocatalysts synthesized by co-precipitation method. Large amount of Nd in sample $x=1.5$ indicates the correct method of preparation and high photocatalytic efficiency. Meanwhile the significant amount of Fe encourages the photocatalyst for better recovery with strong magnetic property.

Figure 4.2. SEM micrographs of $x = 0.0$ (a), $x = 1.0$ (b), $x = 1.5.$ (c) and $x = 2.0$ (d) samples
Figure 4.3. EDS spectra’s of x = 0.0 (a) and x = 1.5 (b) samples

4.3.3. FTIR analysis

The FTIR spectrum of NiFe$_{2-x}$Nd$_x$O$_4$ nanocatalysts were presented in Figure 4.4. In the normal ferrites, there are two high frequency infrared lattice vibrations. The bands $v_1$ and $v_2$ are sensitive to changes in interaction between oxygen and cations in octahedral and tetrahedral positions, the highest one, $v_1$ was generally observed in the range of...
600–500 cm⁻¹ corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site (T₄) M₄₄→O [A site], whereas the ν₂ lowest band were observed in the range 450–385 cm⁻¹ was assigned to octahedral-metal stretching (O₆) M₆₆→O [B site] [44]. The absorption bands observed at ~3450 and ~1630 cm⁻¹ prove the presence of adsorbed water on the surface of the ferrite nanocrystals. The bands occurring at ~2925–2854 cm⁻¹ were assigned to antisymmetric and symmetric CH₂-vibrations of the carbon chains, respectively. The positions corresponding to higher (ν₁) and lower (ν₂) frequency absorption bands of the samples prepared under investigation were given in Table 4.1. It was observed that the absorption band ν₂ shifts slightly to higher wave number side and ν₁ shifts to lower wave number side with increase in Nd³⁺ content (upto x=1.5), respectively. The shifts in the bands ν₁ and ν₂ were due to the perturbation occurring in the Fe³⁺–O²⁻ bond by substituting Nd³⁺ ions and also it was attributed to increase in bond length on B-site. This suggests that, the Nd³⁺ ion occupies B-site. Similar type of variation in band positions was reported by Shinde et al. [41] for Nd³⁺ substituted nickel ferrites. Hemeda et al. [45] discussed the similar results for rare earth substituted orthoferrites. From Figure 4.4, it was also observed that the width of absorption bands of Nd³⁺ substituted nickel ferrites were smaller as compared to nickel ferrite suggesting the occupancy of Nd³⁺ ions on octahedral B-sites. For the sample at x=2.0 complete replacement of Fe³⁺ by large amount of Nd³⁺ gives rise to a complete disappearance of the ν₁ and ν₂ bands, which assures the dominance of the Nd³⁺ in the nickel ferrite [46].
Table 4.1. Values of absorption bands ($v_1$ and $v_2$) for NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticles

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Absorption Band</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.0$</td>
<td>$v_1$ (cm$^{-1}$)</td>
<td>578</td>
<td>409</td>
</tr>
<tr>
<td>$x = 1.0$</td>
<td>$v_2$ (cm$^{-1}$)</td>
<td>569</td>
<td>418</td>
</tr>
<tr>
<td>$x = 1.5$</td>
<td></td>
<td>561</td>
<td>427</td>
</tr>
</tbody>
</table>

Figure 4.4. FTIR analysis of the NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticles
4.3.4. Optical absorption studies

Optical absorption properties of photocatalysts are very important in the photocatalysis process. Figure 4.5 shows a comparison of the photon absorbance of incident light as a function of the wavelength for the NiFe$_2$O$_4$ and Nd substituted NiFe$_2$O$_4$ photocatalysts. Which were helpful to distinguish theoretically whether the nanostructured composites were highly efficient photocatalysts or not. Figure 4.5 reveals that absorption edge was red shifted for Nd substituted samples. As Nd content increases, the absorption edge shifted towards longer wavelength. The sample at x=1.5 showed the largest red-shift and revealed a higher intensity overall visible light absorbance spectrum in comparison with other samples (x=0.0, 1.0 and 2.0). This means that the Nd substituted NiFe$_2$O$_4$ were sensitive to visible light. Enhanced visible light absorption may result from the following: NiFe$_2$O$_4$ was characterized by a inverse spinel structure in which the tetrahedral and octahedral sites within the lattice of cubic close packing were occupied by Ni$^{2+}$ and Fe$^{3+}$ cations, [47] and the energy band structures of NiFe$_2$O$_4$ were generally defined by considering the O-2p orbital as the valence band and the Fe-3d orbital as the conduction band. Therefore, the absorption of NiFe$_2$O$_4$ in the visible region can be ascribed to the photoexcited electron transition from O-2p level into Fe-3d level [48]. In NiFe$_2$O$_4$, band gap between the O-2p level and the Fe-3d level was 2.29 eV, has large band gap compared to that of neodymium substituted samples. The band gap between O-2p and Fe-3d level decreases as 1.96, 1.76 eV with respect to x=1.0 and 1.5 as shown in Figure 4.6. Due to decrease in Eg, energy required to excite the electron from O-2p into the Fe-3d level goes on decreasing [36]. Along with the increasing Nd$^{3+}$ concentration, the absorbance increases. The absorbance gradually increases with the increase of neodymium content upto x=1.5. For the sample at x=2.0 the absorbance
decreases. The sample at $x=1.5$ shows a quite broad absorption due to the charge-transfer transition between the Nd $f$-electrons and the NiFe$_2$O$_4$ conduction or valence band [49]. It has been reported that Nd doping could form a dopant energy level within the band gap of NiFe$_2$O$_4$. The electronic transitions from the valence band to the dopant level or from the dopant level to the conduction band can effectively lower the electron-hole pair recombination rate, which shifts the broad absorption band toward the visible region. Meanwhile, sample at $x=0.2$ shows blue shift of absorption in comparison with other samples. Because octahedral Fe$^{3+}$ cations were completely replaced by the Nd$^{3+}$ ions, as a result dopant energy levels were not formed within the energy gap. This leads to the faster recombination of electron-hole pair, which was unfavorable for the photocatalytic reaction. Therefore, optimized Nd substituted nickel ferrite makes it possible to utilize more percent of solar energy. So, for NiFe$_{2-x}$Nd$_x$O$_4$ samples, a better photocatalytic capability under solar light was expected.

\[\text{Figure 4.5. Optical absorption spectra of NiFe}_{2-x}\text{Nd}_x\text{O}_4 \text{ samples}\]
4.3.5. **Energy band gap studies**

The optical energy band gap (Eg) of NiFe$_{2-x}$Nd$_x$O$_4$ catalysts were determined from the absorbance spectra, where a steep increase in the absorption was observed due to the band–band transition using the general relation. The absorption coefficient $\alpha$ of the NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticle catalysts have been determined from the absorption data by using the fundamental relationships [50,51].

\[
1 = I_0 e^{-\alpha t} \quad (1)
\]

\[
A = \log(I_0/I) \quad (2)
\]

and

\[
\alpha = 2.303(A/t) \quad (3)
\]

where, $A$ is the absorption and $t$ is the thickness of the NiFe$_{2-x}$Nd$_x$O$_4$ ferrite samples. To estimate the optical absorption edge for these nanoparticles, $(\alpha h\nu)^{1/n}$ was plotted as a function of the photon energy ($h\nu$ for different $n$ values ($n=1/2$, $3/2$, $2$, $3$) (Tauc plots) [52]. The best linear fit was obtained in the case of $n = 1/2$, which indicates a direct allowed optical transition in NiFe$_{2-x}$Nd$_x$O$_4$ ferrite nanoparticles. The Tauc plot was presented in Figure 4.6. The straight line fit to the $(\alpha h\nu)^{1/n}$ vs. $h\nu$ plot was obtained by using linear regression software with only very small standard deviation. The intercept of the line at $\alpha = 0$ gives the value of the optical absorption edge. Figure 4.6 shows, redshift of absorption edge with Nd substitution into nickel ferrite. Moreover, the extent of redshift increases evidently with the increase in the amount of neodymium substitution like in our previous report [36]. The calculated energy band gap for nickel ferrite was found to be 2.28 eV. This band gap value was nearly equal to experimental values.
reported in the literature [29]. The sample x=1.5 shows large redshift of 1.76 eV compared to other samples (for other samples x=1.0, 2.0 energy band gap were found to be 1.97 and 3.3 eV, respectively). The redshift in energy band gap was considered to be due to two factors in the study. One of these comes from the substitution of neodymium into NiFe$_2$O$_4$. A partial replacement of Fe$^{3+}$ ions by Nd$^{3+}$ ions causes some electronic states were introduced into the band gap of NiFe$_2$O$_4$ by Nd 4f electrons, which were located close to the lower edge of the conduction band to form the new lowest unoccupied molecular orbital. As a result a series of metastable energy levels were formed within the energy gap, resulting in the red shift of the apparent optical band gap [53,54]. Whereas, in the sample x=2.0, octahedral Fe$^{3+}$ cations were completely replaced by the Nd$^{3+}$ ions. As a result, the absorption edge transition can be from O-2p to Nd-4f instead of Fe-3d, as in pure NiFe$_2$O$_4$. The Nd–O bond length becomes smaller than that in the normal spinel structure using atomic pair distribution functions [55]. Therefore, sample x=2.0, the distance between O-2p and Nd-4f was large, corresponding to a wide energy band gap.

The other factors were considered to be high doping densities which cause the band gap to shrink. This effect was explained by the fact that the wave functions of the electrons bound to the impurity atoms start to overlap as the density of the impurities increase. This overlap forces the energies to form an energy band rather than a discreet level. If the impurity level is shallow, this impurity band reduces the energy band of the host material [56]. The band gap energies of NiFe$_{2-x}$Nd$_x$O$_4$ were greater than the theoretical energy required for water splitting ($\lambda > 1.23$ eV) [24] and the absorption covers the whole visible region due to the introduction of neodymium, indicating the
NiFe$_{2-x}$Nd$_x$O$_4$ materials can be used as efficient photocatalysts in practical environmental remediation under natural solar light irradiation.

**Figure 4.6.** Plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for NiFe$_{2-x}$Nd$_x$O$_4$ compositions

### 4.3.6. Photocatalytic activity

The photocatalytic activities of Nd substituted NiFe$_2$O$_4$ and pure NiFe$_2$O$_4$ photocatalysts were evaluated by the degradation of model organic pollutant rose bengal (RB) under natural solar light irradiation. In order to obtain the real photodegradation yield due to the photocatalysis in the presence of photocatalysts, the decreases in the dye concentration because of the adsorption and direct photolysis should be deducted. The
decrease due to adsorption can be deducted after the adsorption equilibrium was achieved. Therefore, photodegradation yield was defined as [57].

\[
\text{photodegradation yield} = \left( \frac{C_o - C_a - C_b}{C_o} \right) \times 100
\]

where, \(C_o\) is the initial concentration of dye, \(C_a\) is the concentration after photodegradation of dye, and \(C_b\) is the decrease concentration because of the direct photolysis. Figure 4.7 illustrates, the photodegradation rates of rose bengal (RB) on the as-obtained NiFe\(_{2-x}\)Nd\(_x\)O\(_4\) nanocomposite photocatalysts with differing neodymium content under natural solar light irradiation at different time intervals. Blank experiments indicate that the direct photolysis of RB was negligible when illuminated with solar light in the absence of catalysts. The adsorption–desorption equilibrium solution of RB and NiFe\(_{2-x}\)Nd\(_x\)O\(_4\) were used as starting solution (\(t = 0\) min). It was observed that, when compared to other samples, pure NiFe\(_2\)O\(_4\) and NiNd\(_2\)O\(_4\) nanoparticles were photocatalytically inert compounds (Figure 4.7 [A] and [D]). Interestingly the neodymium substituted nickel ferrite hybrid leads to dramatically enhancement of photocatalytic activity (Figure 4.7 [B] and [C]). With increasing neodymium content in NiFe\(_{2-x}\)Nd\(_x\)O\(_4\) photocatalyst, faster RB degradation were observed and neodymium concentration at \(x=1.5\) gave the best performance in photocatalytic activity (Figure 4.7 [C]). It can be clearly seen that almost all the RB molecules in the solution were decomposed near 180 min for the sample \(x=1.5\) under natural solar light irradiation.

The photocatalytic activity increases with increase in neodymium concentration because of two reasons discussed in the following sections. First reason was the higher efficiency of the sample \(x=1.5\) in comparison with other samples (\(x = 0.0, 1.0, 2.0\)) can be correlated to its ability to absorb a larger fraction of visible light, [36] as demonstrated in Figure 4.5. Whereas, in comparison with other samples, \(x=1.0\) (NiFe\(_2\)O\(_4\)) and \(x=2.0\)
(NiNd$_2$O$_4$) shows little absorption in the visible light region due to large energy band gap (2.29 and 3.3 eV respectively). Considering the other ferrite samples, the sample at $x=1.5$ has narrow band gap energy (1.76 eV) due to new energy level appear at just below the conduction band, which were mainly derived from the electronic states of the introduced neodymium ion (i.e., energy level of introduced neodymium). The significant enhancement in photoactivity with neodymium can be attributed to the remarkable substitution effect of the combination of NiFe$_2$O$_4$ and the neodymium content, leading to the efficient separation of photogenerated carriers in the NiFe$_{2-x}$Nd$_x$O$_4$ coupling system. Once it reaches a limit value (such as $x=1.5$), the activity decreases (as shown in Figure 4.7), possibly because the surface species may also act as recombination centers for charge carriers and also due to wide band gap.

![Graph](image)

**Figure 4.7.** Degradation of rose bengal (10.0 mg L$^{-1}$) with different NiFe$_{2-x}$Nd$_x$O$_4$ photocatalysts under solar light irradiation: [A] $x=0.0$; [B] $x = 1.0$; [C] $x = 1.5$; [D] $x = 2.0$;
Second reason was the substitution of Fe$^{3+}$ by Nd$^{3+}$ in the lattice of NiFe$_2$O$_4$ was very interesting. The highest photocatalytic activity was showed by the Nd substituted nickel ferrites (NiFe$_{2-x}$Nd$_x$O$_4$). It seems that the octahedrally coordinated Nd$^{3+}$ ions have an important contribution to the formation of new types of defects which were beneficial for photodegradation process. The substitution of Fe$^{3+}$ with the isoelectric Nd$^{3+}$ does not create electrically charged lattice defects. But on the other hand, the replacement of small Fe$^{3+}$ ions (0.78 Å) with the significantly larger Nd$^{3+}$ ions (1.16Å) were likely to induce significant lattice strains. This affects the catalytic activity due to the stabilization of unusual oxidation states and to the simultaneous formation of structural defects [58]. Moreover, narrowed energy band gap can effectively reduce the recombination of photogenerated charge carriers and enhance the photocatalytic activity [59]. The photogenerated electrons from new conduction band due to Nd substitution get transferred to trapping sites of NiFe$_2$O$_4$ in presence of sunlight irradiation. Such subsequent transfer of electrons to lattice trapping sites of NiFe$_2$O$_4$ helps in separating the charge carriers effectively. These trapping sites also benefits by preventing the recombination to a large extent and facilitating the charge separation thereby activating the catalyst [60]. These factors contribute to the improved photocatalytic activity.

The success in synthesis of solar light active NiFe$_{2-x}$Nd$_x$O$_4$ by co-precipitation method and its unusual photocatalytic behavior encouraged us to extend this photocatalytic activity under natural solar light irradiation to another few organic pollutants. Figure 4.8 shows the photodegradation rates of Methylene blue (MB), Rhodamine B (RhB), Methyl orange (MO) and methyl red (MR) under the same conditions as for RB. The comparison of their photodegradation yields for the
degradation of the sample $x=1.5$ was summarized in Table 4.2. It was observed that photodegradation yield of these dyes exhibited similar results with small percent of variation, indicates the effectiveness of the Nd substituted nickel ferrite ($x=1.5$). The small percent of variation in the photodegradation yield may depend on the structure and complexity of the dyes, particularly on the nature and position of substituents in the aromatic rings [61]. These results suggest that NiFe$_{2-x}$Nd$_x$O$_4$ catalyst can be used to decompose different types of organic pollutants which were present in water.

Figure 4.8. Comparison of percent degradation of different dyes (10.0 mg L$^{-1}$) over the sample at $x=1.5$
Table 4.2. Summary of photodegradation yields for degradation of different dyes over the sample at $x=1.5$ under natural solar light irradiation

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular structure</th>
<th>Irradiation light</th>
<th>Photodegradation yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rose Bengal (RB)</td>
<td><img src="image" alt="Structure" /></td>
<td>Solar</td>
<td>98.1</td>
</tr>
<tr>
<td>Methylene Blue (MB)</td>
<td><img src="image" alt="Structure" /></td>
<td>Solar</td>
<td>93.4</td>
</tr>
<tr>
<td>Rhodamine B (RhB)</td>
<td><img src="image" alt="Structure" /></td>
<td>Solar</td>
<td>91.9</td>
</tr>
<tr>
<td>Methyl Red (MR)</td>
<td><img src="image" alt="Structure" /></td>
<td>Solar</td>
<td>96.7</td>
</tr>
<tr>
<td>Methyl Orange (MO)</td>
<td><img src="image" alt="Structure" /></td>
<td>Solar</td>
<td>94.5</td>
</tr>
</tbody>
</table>

4.3.7. Effect of catalyst concentration

The effect of photocatalyst concentration on the photodegradation of rose bengal (RB) were investigated by employing different concentrations of the sample $x=1.5$, varying from 0.025 to 0.15g L$^{-1}$ as shown in Figure 4.9. This revels that the photodegradation percent of the model compound under investigation were found to increase with the increase in catalyst concentration. As the catalyst amount continues to
be increased upto 0.1 g, the degradation increases to 95%. This indicates a higher catalyst dosage cause to an elevated reaction rate, because the increase of catalyst amount provides more active sites for RB, leading to a increase of OH\(^-\) radical responsible for the degradation of RB. At lower catalyst loading much of light may be transmitted through the solution, which restricts the catalytic activity. However, when the catalyst amount exceeds 0.1 g, the degradation rate decreases due to the scattering of light and reduction in light penetration through the solution [62,63]. Based on this for instance, we found that the optimum catalyst loading for the best photodegradation was 0.1 g L\(^{-1}\).

![Figure 4.9. Influence of catalyst concentration on the degradation of Rose Bengal](image)

**Figure 4.9.** Influence of catalyst concentration on the degradation of Rose Bengal
4.3.8. Hydroxyl radical analysis

To understand the active species involved in the photocatalytic process, hydroxyl radicals (OH') were detected on the surface of photoilluminated NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticles by the photoluminescence (PL) technique [62,64]. Figure 4.10 shows the comparison of PL intensity for NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticles. Usually, PL intensity was proportional to the amount of OH' radicals produced. It could be easily seen that at a fixed time, the concentration of OH' radicals formed in the order is as follows: $x=1.75 > x=1.0 > x=0.0 > x=2.0$. This is consistent with the order of photocatalytic activities of these samples, indicating that the greater the formation rate of OH' radicals, the higher the photocatalytic activity achieved. Moreover, the above results also showed that the OH' radicals were the main active species in the photochemical process of the organic dyes/ NiFe$_{2-x}$Nd$_x$O$_4$ system.

![Figure 4.10. Photoluminescence emission spectra of NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticles](image)
4.3.9. Photocatalytic mechanism

On the basis of the above discussions and the literature reports, [64-66] a possible mechanism of photodegradation over NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticles can be proposed. As shown in Scheme 4.1, comparison with other samples, pure NiFe$_2$O$_4$ can hardly be excited by visible light due to its large band gap (2.28eV), which leads to a low visible-light activity for the photodegradation of organic pollutants. The modification of nickel ferrite by neodymium substitution results in high visible light activity due to reduction in band gap. The band gap reduction might be due to the formation of metastable energy levels within the band gap of NiFe$_2$O$_4$ by Nd 4f electrons, which were located close to the lower edge of the conduction band. Under visible-light irradiation electrons can be excited from the valence band to the energy levels of NiFe$_{2-x}$Nd$_x$O$_4$ system (conduction band) as shown in Scheme 4.1 and simultaneously the same amount of holes were generated in the VB. Meanwhile, it is highly possible for the photogenerated electrons in the conduction band of nickel ferrite to fall into the energy levels of NiFe$_{2-x}$Nd$_x$O$_4$ system. As a result, the photogenerated electrons and holes can be separated efficiently [67].

The photo-induced holes directly react with organic dyes or interact with surface-bound H$_2$O or OH$^-$ to produce the OH$^-$ radical species which were extremely strong oxidant for the mineralization of organic dyes. Meanwhile, the electrons which were formed can react with the adsorbed molecular oxygen to yield O$_2^-$.$^*$ The generated O$_2^-$ then further combine with H$^+$ to produce HO$_2^*$, [68] which can react with the trapped electrons to generate OH$^-$ radicals [69]. All the reactive species, such as OH$^-$, HO$_2^*$,
and holes, could oxidize organic pollutants to some degree. Based on the above analysis, the photocatalytic reaction can be expressed as follows:

\[
\text{NiFe}_{2-x}\text{Nd}_x\text{O}_4 + \text{hv} \rightarrow \text{NiFe}_{2-x}\text{Nd}_x\text{O}_4 (e_-^\text{cb} + h_+^\text{vb}) \rightarrow \text{NiFe}_{2-x}\text{Nd}_x\text{O}_4 + \text{energy} \tag{4}
\]

\[
\text{NiFe}_{2-x}\text{Nd}_x\text{O}_4 (h_+^\text{vb}) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \tag{5}
\]

\[
\text{NiFe}_{2-x}\text{Nd}_x\text{O}_4 (h_+^\text{vb}) + \text{OH}^- \rightarrow \text{OH}^- \tag{6}
\]

\[
\text{NiFe}_{2-x}\text{Nd}_x\text{O}_4 (e_-^\text{cb}) + \text{O}_2 \rightarrow \text{O}_2^- \tag{7}
\]

\[
\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^- \tag{8}
\]

\[
2 e_-^\text{cb} + \text{HO}_2^- + \text{H}^+ \rightarrow \text{OH}^- + \text{OH}^- \tag{9}
\]

\[
\text{OH}^-, \text{HO}_2^-, \text{O}_2^-, h_+^\text{vb} + \text{organic pollutants} \rightarrow \text{degradation product} \tag{10}
\]

**Scheme 4.1.** Possible mechanism of the photocatalytic degradation of organic pollutants over NiFe$_{2-x}$Nd$_x$O$_4$ photocatalysts under natural solar light irradiation
4.3.10. Recycle ability

The regeneration of the photocatalyst was one of the key steps in the photocatalysis technology for practical applications. NiFe$_2$O$_4$ is a soft magnetic material that possesses good magnetic properties, which gives it good performance in magnetic separation for the NiFe$_{2-x}$Nd$_x$O$_4$ photocatalysts using an external magnet (see the inset of Figure 4.11). Herein, the stability of the sample $x=1.5$ was investigated and this catalyst can be reused without considerable amount of mass loss. As shown in Figure 4.11 during the usage of five cycles the photocatalytic activity was almost as high as the first cycle. These results illustrated that NiFe$_{2-x}$Nd$_x$O$_4$ as a novel magnetically separable, highly solar light response photocatalyst can be reused for several times efficiently. It exhibits potential application in continual and long-term processes.

![Figure 4.11. The photodegradation rate of RB in solution for five cycles using NiFe$_{2-x}$Nd$_x$O$_4$ (sample at $x=1.5$) photocatalyst under solar light irradiation. Inset reveals the magnetic separation property of NiFe$_{2-x}$Nd$_x$O$_4$ nanoparticle catalysts](image-url)
4.4. Conclusion

In summary, for the first time, we have reported that the neodymium substituted nickel ferrite system could be a promising material for photocatalysis under natural solar light irradiation. The neodymium substitution into nickel ferrite results in a dramatic conversion of the inert NiFe$_2$O$_4$ into a highly solar light active photocatalyst. This may be due to the reduction of the nickel ferrite band gap by Nd$^{3+}$ substitution. It should be pointed out that, the NiFe$_{2-x}$Nd$_x$O$_4$ photocatalysts were cost saving, magnetically recoverable, recyclable photocatalysts that exhibit high photocatalytic efficiency (upto 98%) to decompose different types of organic pollutants. In an attempt to design the efficient solar light active photocatalyst, we were successful in optimizing the concentration of Nd$^{3+}$ substitution, large visible light absorption and energy band gap of the materials. On the basis of experimental results, the strategy for future improvement in the photocatalytic properties of ferrites under solar light irradiation should take into consideration the finding of suitable substitutional elements for Fe$^{3+}$. This could open new uses for substituted ferrites in application such as larger scale waste water treatment plants.
References


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