Calcium substituted Nickel ferrite have been synthesised by co-precipitation method. The composition was characterized by XRD, SEM, FTIR and EDX. The application of synthesized ferrite was also studied in the photo degradation of methylene blue under visible light irradiation. In FTIR, highest and lowest absorption band were observed. XRD revealed the formation of cubic spinel structure with average size of 17nm. Surface morphology was studied by SEM and the particles are in cubic nature. The purity and stoichiometry of the composition were confirmed by Energy Dispersive X-ray (EDX) analysis. The photo catalytic property of \( \text{Ni}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles was calculated during the Methylene blue degradation with different time interval under solar light irradiation and found that \( \text{Ni}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{O}_4 \) having good Photocatalytic properties for Methylene blue degradation.

**KEY WORDS:** Photocatalytic, inverse, nanoparticles.

1. INTRODUCTION

Nickel ferrite (\( \text{NiFe}_2\text{O}_4 \)) with inverse spinel structure is an important soft magnetic material, prominently known for its high magnetic permeability, low coercive force, high saturation magnetisation, high Curie temperature and large magnetostriction constant. These outstanding properties make \( \text{NiFe}_2\text{O}_4 \) attractive for a wide variety of applications, such as ferro fluids, microwave absorbing materials, supercapacitor electrode materials and sensors. The properties of nickel ferrite can be varied by changing the identity of the trivalent Fe\(^{3+}\) and divalent Ni\(^{2+}\)cations. Even though, \( \text{NiFe}_2\text{O}_4 \) has a band gap of 2.19 eV, little research has been conducted on its photocatalytic activity. Although \( \text{NiFe}_2\text{O}_4 \) alone is photocatalytically inactive under visible light irradiation, it is possible to improve the efficiency of the photo induced charge separation in \( \text{NiFe}_2\text{O}_4 \) by substituting metals, resulting in enhanced photocatalytic performance.

To the best of our knowledge, as per the literature, no reports have been cited on the photocatalytic properties of Calcium substituted nickel ferrite nanoparticles under solarlight irradiation to date. Although, investigations on the structural, morphology and the identification of functional groups of Ni–Ca ferrite has been reported earlier, but the simultaneous detailed study of these properties of Ni–Ca ferritesynthesized using co-precipitation method, along with photo catalyticactivity has not been reported so far. Therefore, the present work reports a systematic investigation of structural, morphology, and composition of Ni–Ca ferrite prepared using co-precipitation method as well as its application as a photo catalyst.

2. EXPERIMENTAL METHOD

Nickel chloride, ferric chloride and calcium chloride were dissolved in deionized water with constant stirring and kept at 60°C for 30 minutes. NaOH (used as a precipitating agent) solution is mixed with the above solution, till the pH value becomes 12. The final solution was maintained at 85°C for 1 hour, this time is sufficient for the transformation of hydroxides into spinel ferrite. Brown color precipitate thus formed, filtered and washed several times using deionised water. Collected particle were then dried at 80°C. The product was then milled in an agate mortar and calcinated 800°C for 4 hrs, to form fine calcium substitute nickel ferrite nanoparticles.

3. RESULTS AND DISCUSSIONS

3.1. FTIR study: Figure.1 & 2 shows the FT-IR absorption spectra of nano crystalline \( \text{NiFe}_2\text{O}_4 \) and \( \text{Ni}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{O}_4 \) samples which were recorded in the range of 400-4000 cm\(^{-1}\). 700- 550 cm\(^{-1}\) the tetrahedral-metal stretching vibration frequency (Td) M tetra ↔O [A site] and 480-400 cm\(^{-1}\)corresponds to intrinsic stretching vibrations of the metal at the octahedral site (To) MOcta →O [B site]. The spectra shows prominent bands near 3394cm\(^{-1}\) and 1627cm\(^{-1}\) which are attributed to the stretching modes and H-O-H bending vibrations of the free or absorbed water. The band near 1481cm\(^{-1}\) is due to the anti symmetric NO stretching vibrations. The tetrahedral Stretching vibration frequency of \( \text{NiFe}_2\text{O}_4 \)is604cm\(^{-1}\) and for \( \text{Ca}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4 \)is594cm\(^{-1}\), show that as the Ca concentration increases the absorption bands value decreases.

3.2. Structural study: XRD of \( \text{NiFe}_2\text{O}_4 \) and \( \text{Ni}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles are given in Figure.3 & 4. \( \text{NiFe}_2\text{O}_4 \) and \( \text{Ni}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{O}_4 \) showed the main diffraction patterns characterized for cubic spinel. The spectra did not show any other peaks for impurities. The crystallite size was estimated using Debye–Scherrer formula:

\[
D = 0.9l/\beta\cos\theta
\]  

\[\text{(1)}\]
Where $D$ is the mean crystallite size, $\lambda$ is the x-ray wavelength, $\beta$ is the full width at half maximum (FWHM) of the diffraction peaks and $\theta$ is the Bragg’s angle. The average crystallite size of pure nickel ferrite and calcium substitute nickel ferrite is found to be about 22 and 17 nm. The lattice parameters of samples are calculated using the formula, $a = d \sqrt{h^2 + k^2 + l^2}$  

\[ \text{(2)} \]

Where $d$ is the inter planar distance and (hkl) is the plane of the concern 2θ value. The calculated lattice constant value of nickel ferrite and calcium substitute nickel ferrite is 8.23Å and 8.34Å.

The X-ray density are also calculated using the relation, 

\[ d_x = \frac{8MN}{V} \]

\[ \text{(3)} \]

Where $M$ is the molecular weight, $N$ is the Avogadro’s number and $V$ is the volume of unit cell. The estimated X-ray density value of two ferrites is 5.364 gm/cm$^3$ and 5.161gm/cm$^3$.

3.3. Elemental study: Figure 5 shows the EDX pattern obtained for calcium substitute nickel ferrite, which gives the elemental and atomic composition in the samples. No trace of impurity was found. The compounds show the presence of Ni, Fe, Ca,O and listed in Table 1. This table shows that the experimental values are related to theoretical values.

3.4. Morphological study: The SEM micrographs of the assynthesized samples $x= 0.0$ and $0.5$, are shown in Figure 6 and 7. It is evident from the SEM micrographs that the samples have uniform and cubic structural morphology with a narrow size distribution of the particles.

3.5. Photo catalytic study: Photocatalytic activity means the ability of some nano materials to speed up a certain reaction ("photoreaction") as a catalyst in combination with light (sunlight, ultraviolet light). To examine the photocatalytic degradation properties of the $\text{Ni}_{0.5}\text{Ca}_{0.5}\text{Fe}_2\text{O}_4$, we have selected the Methylene Blue which is one of the great Organic pollutants of dyes industries and not easily degraded, therefore we added 0.05 g of each nano ferrite samples in 50 ml of 10ppm of MB solution and stayed the each sample in dark for 30 minutes for equilibrium adsorption/desorption then sonicate for 10 minutes at ambient temperature and placed in sunlight at room temperature with continuous stirring then after different intervals of time the samples is centrifuged and determine the concentration of MB of each added sample against the calibration curve of 10 ppm of MB. The data is tabulated in the Table 2 and as a graphically shown in Figures 8&9.

In this figure gives, the neat spectrum of MB four characteristic peaks were observed at 246, 292, 617 and 663 nm. Then change the time interval, there was decrease in absorption intensity of the peak at 662nm and 665 nm, indicating degradation of MB at the end of 210 min and 180 min of irradiation. The photocatalytic degradation was calculated by applying following equation,

\[ \text{Degradation (%) = } \frac{c_0-c_t}{c_0} \times 100 \]

\[ \text{(5)} \]

Where $C_0$ is the initial MB concentration and $C_t$ is the concentration of MB at time t. It is clear that with increasing Ca content the degradation of MB occurs in lesser time. The dye degradation was accelerated due to larger band gap of $\text{NiFe}_2\text{O}_4$ (2.19ev) compared with $\text{CaFe}_2\text{O}_4$ (1.9 ev). From the literature, it was observed that the lower band gap higher the photocatalytic activity. Doping of Ca$^{2+}$ in NiFe$_2$O$_4$ reduces recombination of photo generated electrons and holes hence increasing the degradation of MB.

![Figure 1: FTIR Spectra of NiFe$_2$O$_4$](image1)

![Figure 2: FTIR Spectra of Ni$_{0.5}$Ca$_{0.5}$Fe$_2$O$_4$](image2)

### Table 1. EDX for Ni$_{0.5}$Ca$_{0.5}$Fe$_2$O$_4$

<table>
<thead>
<tr>
<th>Elements</th>
<th>Expected (wt %)</th>
<th>EDX (wt %)</th>
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<tbody>
<tr>
<td>Ni</td>
<td>7.15</td>
<td>11.81</td>
</tr>
<tr>
<td>Fe</td>
<td>28.57</td>
<td>24.39</td>
</tr>
<tr>
<td>O</td>
<td>57.13</td>
<td>50.00</td>
</tr>
<tr>
<td>Ca</td>
<td>7.15</td>
<td>13.80</td>
</tr>
</tbody>
</table>
Fig. 3. XRD Spectra of NiFe$_2$O$_4$

Fig. 4. XRD Spectra and Fig. 5. EDX Spectrum of Ni$_{0.5}$Ca$_{0.5}$Fe$_2$O$_4$

Fig. 6. Morphological image of NiFe$_2$O$_4$

Fig. 7. Morphological image of Ni$_{0.5}$Ca$_{0.5}$Fe$_2$O$_4$

Fig. 8. Photocatalytic activity of NiFe$_2$O$_4$

Fig. 9. Photocatalytic activity of Ni$_{0.5}$Ca$_{0.5}$Fe$_2$O$_4$

Table 2. Estimation of degradation & band gap

<table>
<thead>
<tr>
<th>Composition</th>
<th>Degradation (%)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>97.31</td>
<td>210</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Ca$</em>{0.5}$Fe$_2$O$_4$</td>
<td>99.22</td>
<td>180</td>
</tr>
</tbody>
</table>

4. CONCLUSION

Ni$_{0.5}$Ca$_{0.5}$Fe$_2$O$_4$ nanoparticles are successfully synthesized by co-precipitation technique. The particles were found to exhibit a spinel structure. The decrease in particle size and the lattice contraction with increasing zinc concentration in the nanoparticles were due to the occurrence of a metastable cation distribution different from their bulk counterpart. The compositional analysis confirmed the stoichiometry of the samples. FT-IR spectrum gives the octahedral and tetrahedral sites in the wave number range of 594 cm$^{-1}$ and 401 cm$^{-1}$. In SEM image shows that the particles are in cubic nature. With increasing Ca content photo degradation of dye occurs in lesser time due to wider band gap of nickel ferrite as compared to calcium substitute nickel ferrite.

REFERENCES


