Lanthanum-substituted Cobalt Ferrite Established by the Co-precipitation Process: Annealing Temperature Adjustment of Structural, Magnetic, and Dye Removal Characteristics

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Abstract

Co-precipitation process was used for the synthesis of lanthanum-substituted cobalt ferrite nanoparticles at several annealing temperatures (T\text{a}), i.e., 200 °C, 300 °C, and 400 °C, for 5 h. XRD spectral depicted that the produced nanoparticles sample indicates a single phase of fcc inverse spinel conforming to ICDD No 22-1086. The crystallite size (D) calculation at the strongest peaks shows the increase in enhancing the T\text{a} i.e., 18.99 nm, 19.90 nm, and 23.21 nm for 200 °C, 300 °C, and 400 °C, respectively. The FTIR results showed absorption band at the tetrahedral site, v₁ ~575 cm⁻¹ and the octahedral site, v₂ ~474 cm⁻¹. The absorption bands indicate that the lanthanum ions have successfully replaced the Fe³⁺ cations in the original cobalt ferrite structure. According to the hysteresis loop, the coercive field's (H\text{C}) magnitude falls from 700 Oe down to 550 Oe as T\text{a} increases. This result is consistent with the anisotropy constant which decreased from 0.77×10⁴ erg/cm³ to 0.56×10⁴ erg/cm³. The obtained nanoparticles also showed superior performance (much larger than 95%) for dye removal of Congo red.

Keywords: Cobalt Ferrite; Co-precipitation; Nanoparticles; Dye Removal


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1. Introduction

Magnetic ferrite are generally classified into four subgroups; spinel ferrite, hexagonal ferrite, garnet, and orthoferrite [1]. Individual material exhibits its own unique structural, magnetic, and electrical properties. Spinel ferrite is one material that is currently widely studied in research. The fundamental formula for spinel ferrite is MFe₂O₄; M is the divalent cation, which includes Co, Mg, Mn, Ni, and Zn [2]. Spinel ferrite is also a member of the Fd-3m space group face-centered cubic (fcc) crystal [3]. Two interstitial sites can be discovered in spinel ferrite: the tetrahedral site (A-site) and the octahedral site (B-site) [4]. The distribution of anions between

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sites A and B dependence on annealing temperature \((T_a)\), synthesis procedure as well as substitution other metal cation \([5,6]\). The number of available states at A-site \((\text{Fe}^{3+})\) in cobalt ferrite is 64, yet only 8 cations are occupied. While B-site \((\text{Fe}^{3+} + \text{Co}^{2+})\) has 32 states, it only has 16 cations \([7]\). So, either the cations redistribution due to physical treatment or the other metal cations substitution will modify their magnetic properties \([3]\).

Theoretically, the magnetic moment associated with saturation magnetization is 3 nB overall, with 5 nB and 8 nB at both of the A and B sites, respectively \([8]\). In the case of other metal cation substitutions, the suitability of the ionic radius and size of the interstices determines the mechanism of magnetic characteristics modification. Metal cations owing zero magnetic moments, such as Lanthanum, are an intriguing research material that can be substituted in cobalt ferrite \([9]\).

The \(\text{Co}^{2+}\) and \(\text{Fe}^{3+}\) ions occupy the octahedral site of cobalt ferrite. \(\text{La}^{3+}\) tends to replace ions at octahedral sites. When \(\text{La}^{3+}\) enters an octahedral site, it tends to displace the \(\text{Fe}^{3+}\) ion, because it has the same ion size. In the case of inverted spinel at the tetrahedral site, ion charging is more dominant over the \(3^+\) ion so that \(\text{Fe}^{3+}\) moves to the tetrahedral site after \(\text{La}^{3+}\) replaces the \(\text{Fe}^{3+}\) ion at the octahedral site \([10]\). Cobalt ferrite has interesting characteristics that open up application opportunities \([7]\), such as; permanent magnets \([11]\), magnetic sensors \([12]\), photocatalyst \([13]\), antibacterial \([14]\), drug delivery \([15]\), and MRI agent contrast \([16]\).

Cobalt ferrite nanoparticles can be synthesized using a variety of techniques. Most popular methods are co-precipitation \([17–19]\), sol-gel \([20–22]\), and hydrothermal \([23–25]\). As part of this study, the synthesis of cobalt ferrite material with lanthanum substitution carried out using the co-precipitation method due to well-controlled distribution of dopants and crystal size \([26]\). Additionally, the coprecipitation method was chosen because it can produce large \(H_c\) and smaller \(M_s\) as the particle size increases depending on the NaOH concentration \([27]\).

In this study, the synthesis of lanthanum substituted cobalt ferrite nanoparticles using variations in the \(T_a\) will be reported. The concentration taken is the most optimal which can maximally modify the structure and magnetic properties. Increasing the concentration above 10% will give rise to a secondary phase on sample \([28]\).

2. Materials and Methods

2.1 Experimental

Lanthanum substituted cobalt ferrite \((\text{CoLa}_{0.1}\text{Fe}_{1.9}\text{O}_4)\) nanoparticles were produced utilizing the co-precipitation method. \(\text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}\) (Merck), \(\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) (Merck), and \(\text{La(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}\) (Merck) were the components utilized in the synthesis; they were dissolved in double-distilled water and stirred for 10 min. In order to generate a precipitate, the NaOH solution \((4.8 \text{ M})\) was added dropwise while being continuously after being heated to 95 °C and stirred \((250 \text{ rpm})\) \([27]\). This precipitate was collected, cleaned with ethanol to get rid of the salts that had been dissolved, and then overnight dried at 100°C. The sample was then annealed for 5 h at temperatures of 200 °C, 300 °C, and 400 °C at a heating rate of 10 °C/s. The powder was then hand-milled in a marble mortar for 2 h to obtain the final product before being physically characterized.

2.2 Material Characterizations

The crystalline structure of the \(\text{CoLa}_{0.1}\text{Fe}_{1.9}\text{O}_4\) nanoparticles is evaluated using an X'Pert PRO PANalytical X-ray diffractometer (using Cu-Kα radiation with a wavelength of \(\lambda = 1.54\)). The XRD patterns were acquired in the 2θ = 20–70° range, with a step size of 0.02° and a duration of 0.7 s per step. A Shimadzu IR Prestige 21 FTIR spectroscope in the 350–4,000 cm\(^{-1}\) range was used to characterize the oxide bonds in the sample. The hysteresis loop of the M-H curve measurements was taken at room temperature using an Oxford VSM1.2 H vibrating-sample magnetometer.

2.3 Dye Removal Study

The Congo red dye removal properties were evaluated by using Ultraviolet Visible Spectroscopy (UV Vis). The dye removal performance was evaluated using a 20 ppm Congo red solution as a test dye model by considering both absorption and irradiated-ultraviolet-light-photocatalyst processes.

2.4 Equations for Calculations

The crystallite size can be calculated by Scherrer’s formula:

\[
D = \frac{0.9\lambda}{\beta\cos\theta}
\]

where, \(D\) is the crystallite size, the magnitude of wavelength \((\lambda, \text{Cu-K}\alpha) = 0.154060\ \text{nm}\), \(\beta\) is the full width at half maximum (FWHM), and...
θ is the Bragg angle of diffraction. Furthermore, the lattice parameters are obtained from the following equation.

\[ a = d_{\text{hkl}} \sqrt{h^2 + k^2 + l^2} \]  \hspace{1cm} (2)

where, \(a\) is the lattice parameters, \(d\) is the interplanar distance, and \((h, k, l)\) is the Miller indices of the nanoparticles. Other parameters that can be obtained from XRD analysis are density \((\rho_x)\) and lattice strain \((\varepsilon)\) which calculate the following equation [29].

\[ \rho_x = \frac{8M}{2a^3} \]  \hspace{1cm} (3)

\[ \varepsilon = \frac{\beta}{4\tan\theta} \]  \hspace{1cm} (4)

where, \(M\) is the molecular weight of the nanoparticles and \(a^3\) is the cell volume of the \(\text{CoLa}_{0.1}\text{Fe}_{1.9}\text{O}_4\) nanoparticles using various the \(T_a\) treatments. Meanwhile, the specific surface area \((S)\) can be obtained from the relationship between \(D\) and \(\rho_x\), i.e., \(S = 6/(\rho_x XD)\) [30]. The results of the calculation are summarized in Table 2.

Using the approach described by Waldron, the force constants for the tetrahedral site \((k_t)\) and octahedral site \((k_o)\) were calculated [31]:

\[ k_t = 7.62 \times M_1 \times v_1^2 \times 10^{-7} \text{ N/m} \]  \hspace{1cm} (5)

\[ k_o = 10.62 \times \left( \frac{M_2}{2} \right) \times v_2^2 \times 10^{-7} \text{ N/m} \]  \hspace{1cm} (6)

where, \(M_1\) and \(M_2\) are the molecular weights of the cations on the tetrahedral and octahedral sites, respectively. Additionally, the FTIR data can be applied to determine the average force constants magnitude \((F)\) using the following equation [32]:

\[ F = \frac{2k_x + h_i}{3} \]  \hspace{1cm} (7)

The netto moment magnetic, \(n_B\) and magnetic anisotropy, \(K\) calculate following the equation [33].

\[ n_B = \frac{M \times Ms}{5585} \]  \hspace{1cm} (8)

\[ K = \frac{Hc \times Ms}{0.98} \]  \hspace{1cm} (9)

In multidomain, the relationship between the coercivity field and the anisotropy constant is expressed in the following equation:

\[ H_c = e + \frac{f}{D} \]  \hspace{1cm} (10)

where, \(e\) and \(f\) are constants, and \(D\) is the size of the crystallite. Therefore, the coercivity decreases as the crystallite size increases, causing the anisotropy constant to also decrease [34].

Furthermore, the results of the percentage reduction \((\eta)\) in the photocatalyst test are calculated using the following equation [30]:

\[ \eta = \left( \frac{A_o - A_s}{A_o} \right) \times 100\% \]  \hspace{1cm} (11)

where, \(A_o\) is the initial absorbance and \(A_s\) is the final absorbance. The percentage reduction re-

Figure 1. (a) XRD patterns of the \(\text{CoLa}_{0.1}\text{Fe}_{1.9}\text{O}_4\) nanoparticles at 200 °C, 300 °C, and 400 °C; (b) The strongest peak shift of the \(\text{CoLa}_{0.1}\text{Fe}_{1.9}\text{O}_4\) nanoparticles at 200 °C, 300 °C, and 400 °C.
3. Results and Discussion

3.1 XRD Analysis of CoLa$_{0.1}$Fe$_{1.9}$O$_4$ Nanoparticles

Figure 1(a) presents XRD patterns of the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles using various the Ta treatments (200 °C, 300 °C, and 400 °C). All patterns conform to ICDD 22-1086 which indicates that all samples belong to the face-centered cubic (fcc) crystal structure with the space group Fd-3m [35]. Rietveld refined results using Fullprof™ software have also confirmed that CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles have a fcc crystal structure with a space group Fd-3m (Figure 2), refinement parameters are provided in Table 1. The results show the magnitude of $\chi^2$ (goodness of fit) CoLa$_{0.1}$Fe$_{1.9}$O$_4$ at 200 °C, 300 °C, and 400 °C were 1.67, 1.65, and 1.63, respectively; this result is close to a magnitude of 1 which means it supports the goodness of refinement [6]. The results of the analysis using ICDD and Fullprof™ software justify that La$^{3+}$ ions can successfully replace Fe$^{3+}$ ions in cobalt ferrite nanoparticles.

The strongest peak (311) was used to calculate the crystallite size (Equation (1)) and lattice parameters (Equation (2)) shown in Table 2. Other parameters that can be obtained from XRD analysis are density (Equation (3)) and lattice strain (Equation (4)). The molar mass of the material created in all materials is the same according to stoichiometry. However, in Table 2, when the annealing temperature treatment causes changes in structural parameters such as crystallite size and lattice parameters, the impact on other parameters also changes.

### Table 1. The Rietveld analysis by Fullprof of the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles.

<table>
<thead>
<tr>
<th>Ta(°C)</th>
<th>$a=b=c$ (Å)</th>
<th>$R_{wp}$</th>
<th>$R_{exp}$</th>
<th>$R_B$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>8.359</td>
<td>40.1</td>
<td>28.7</td>
<td>15.8</td>
<td>1.67</td>
</tr>
<tr>
<td>300</td>
<td>8.373</td>
<td>36.9</td>
<td>26.5</td>
<td>14.9</td>
<td>1.65</td>
</tr>
<tr>
<td>400</td>
<td>8.370</td>
<td>33.0</td>
<td>23.7</td>
<td>12.3</td>
<td>1.63</td>
</tr>
</tbody>
</table>

### Table 2. The crystallite size ($D$), lattice parameters ($a$), density ($\rho$), lattice strain ($\varepsilon$), and specific surface area ($S$) of the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles.

<table>
<thead>
<tr>
<th>Ta(°C)</th>
<th>$D$ (nm)</th>
<th>$a$ (Å)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$\varepsilon$ $10^{-3}$</th>
<th>$S$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>18.99</td>
<td>8.338</td>
<td>5.568</td>
<td>5.96</td>
<td>56.74</td>
</tr>
<tr>
<td>300</td>
<td>19.90</td>
<td>8.316</td>
<td>5.613</td>
<td>5.67</td>
<td>53.71</td>
</tr>
<tr>
<td>400</td>
<td>23.21</td>
<td>8.343</td>
<td>5.559</td>
<td>4.88</td>
<td>46.50</td>
</tr>
</tbody>
</table>
The crystallite sizes of the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles using various $T_a$ treatments at 200 °C, 300 °C, and 400 °C was 18.99 nm, 19.90 nm, and 23.21 nm, respectively. With an increase in a certain $T_a$, the crystallite sizes may increase $([(19.90−18.99)/18.99]×100\% = 4.79\%$ and $[(23.21−19.90)/19.90]×100\% = 15.53\%$), which may be related to an increase in the internal energy of the crystal structure that can lead to atomic diffusion. Atomic diffusion particles may aggregate into larger particles [36]. Other, increasing the $T_a$ speeds up the crystallization process resulting in a larger crystallite size [37,38]. Furthermore, the lattice parameters acquire random magnitudes with an increase in the $T_a$ around ~8.3 Å which is confirmed by the random shift of the strongest peak in Figure 1(b). Similar results were obtained when calculating the density magnitudes. This randomness is allegedly due to the formation of random oxygen vacancies so that the compaction of the material becomes less regular [35]. Meanwhile, the lattice strain decreased with increasing the $T_a$ at 200 °C, 300 °C, and 400 °C were $5.96×10^{-3}$, $5.67×10^{-3}$, and $4.48×10^{-3}$, respectively. The decrease that occurred was 5.11% $([(5.96×10^{-3}−5.67×10^{-3})/5.67×10^{-3}]×100\%$ and 26.56% $([(5.67×10^{-3}−4.48×10^{-3})/4.48×10^{-3}]×100\%$. This difference is attributed to the change in crystallite size, which cause lattice strain. A decrease in lattice strain and an increase in crystallite size are caused by the material’s improved crystallization [39].

La$^{3+}$ and Fe$^{3+}$ have differences in ionic radius. The rare earth metal La$^{3+}$ is a nonmagnetic cation because it does have 3d electrons, but the ion size is larger than Fe$^{3+}$ and Co$^{2+}$. So, a small amount of the element La$^{3+}$ in cobalt ferrite can cause lattice strains in the material and cause structural changes that impact its magnetic properties. Substituting larger ions limits the very high nucleation rate of cobalt ferrite due to lattice [40]. Thus, the size of the crystallites is one of the factors that causes changes in the lattice strain. Furthermore, the specific surface area magnitude of the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ decreased with increasing the $T_a$ at 200 °C, 300 °C, and 400 °C were 56.74 m$^2$/g.

![Figure 3. FTIR Spectrum of the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles at 200 °C, 300 °C, and 400 °C.](image)

Table 3. Absorption bands of FTIR the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles.

<table>
<thead>
<tr>
<th>$T_a$ (°C)</th>
<th>Absorption (cm$^{-1}$)</th>
<th>Mode of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>3393.9</td>
<td>O–H stretching</td>
</tr>
<tr>
<td></td>
<td>1631.85</td>
<td>C=O stretching</td>
</tr>
<tr>
<td></td>
<td>1505.51</td>
<td>C=C stretching</td>
</tr>
<tr>
<td></td>
<td>1379.16</td>
<td>O–H bending</td>
</tr>
<tr>
<td></td>
<td>589.28</td>
<td>Me–O tetrahedral site</td>
</tr>
<tr>
<td></td>
<td>471.62</td>
<td>Me–O octahedral site</td>
</tr>
<tr>
<td>300</td>
<td>3417.04</td>
<td>O–H stretching</td>
</tr>
<tr>
<td></td>
<td>1633.78</td>
<td>C=O stretching</td>
</tr>
<tr>
<td></td>
<td>1506.47</td>
<td>C=C stretching</td>
</tr>
<tr>
<td></td>
<td>1380.13</td>
<td>O–H bending</td>
</tr>
<tr>
<td></td>
<td>575.78</td>
<td>Me–O tetrahedral site</td>
</tr>
<tr>
<td></td>
<td>474.51</td>
<td>Me–O octahedral site</td>
</tr>
<tr>
<td>400</td>
<td>3417.04</td>
<td>O–H stretching</td>
</tr>
<tr>
<td></td>
<td>1631.85</td>
<td>C=O stretching</td>
</tr>
<tr>
<td></td>
<td>1515.15</td>
<td>C=C stretching</td>
</tr>
<tr>
<td></td>
<td>1382.06</td>
<td>O–H bending</td>
</tr>
<tr>
<td></td>
<td>571.92</td>
<td>Me–O tetrahedral site</td>
</tr>
<tr>
<td></td>
<td>493.8</td>
<td>Me–O octahedral site</td>
</tr>
</tbody>
</table>

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53.71 m²/g, and 46.50 m²/g, respectively. This decrease is due to the expansion of the crystals and the sample’s high surface-to-volume ratio [41,42].

3.2 FTIR Analysis of CoLa₀.₁Fe₁.₉O₄ Nanoparticles

Figure 3 shows the FTIR spectrum of the CoLa₀.₁Fe₁.₉O₄ nanoparticles with the Ta at 200 °C, 300 °C, and 400 °C. The FTIR analysis obtained absorption band results as shown in Table 3. The absorption bands appeared at the tetrahedral site, ν₁ of 471.62 cm⁻¹, 474.51 cm⁻¹, and 493.80 cm⁻¹; the octahedral site, ν₂ of 589.28 cm⁻¹, 575.78 cm⁻¹, and 571.92 cm⁻¹ at the Ta of 200 °C, 300 °C, and 400 °C, respectively. The primary absorption band range supports the cobalt ferrite-based structure [19,43]. It is also claimed that the La⁺⁺ cation has been successful in switching the Fe³⁺ cations from the cobalt ferrite’s initial structure [2].

Table 4 shows that the tetrahedral force constant decreased with an increase in the Ta, i.e., 148.58 N/m, 141.85 N/m, and 139.95 N/m; whereas the octahedral force constant increased, i.e. 151.57 N/m, 153.43 N/m, and 166.16 N/m, at the Ta of 200 °C, 300 °C, and 400 °C, respectively. The decrease in the tetrahedral force constant is caused by a decrease in the interatomic distance (Me–O) at the tetrahedral sites, while the increase in the octahedral force constant is affected by an increase in the bond length (Me–O) [44]. The movement of ions to these two sites causes the absorption to change.

3.3 VSM Analysis of CoLa₀.₁Fe₁.₉O₄ Nanoparticles

Figure 4 presents the hysteresis loop of the CoLa₀.₁Fe₁.₉O₄ nanoparticles with the Ta at 200 °C, 300 °C, and 400 °C. Table 5 displays the findings from the evaluation of the hysteresis loop, including the coercive field (Hc), saturation magnetization (Ms), remanent magnetization (M₀), magnetic moment (n₀), and magnetic anisotropy constant (K).

The Hc of the CoLa₀.₁Fe₁.₉O₄ nanoparticles obtains a decrease with increasing the Ta, i.e., 700 Oe, 560 Oe, and 550 Oe at the Ta of 200 °C, 300 °C, and 400 °C, respectively. The calculations of the magnetic anisotropy constant, which decreases with increasing the Ta, provide support for the Hc results. The squareness ratio magnitudes for the CoLa₀.₁Fe₁.₉O₄ at the Ta were 200 °C, 300 °C, and 400 °C were 0.43, 0.44, and 0.49, respectively; the results obtained have a magnitude smaller than 0.5 implies that all nanoparticles are multi-domain [6,45]. The reduction of the Hc can occur due to changes in particle size and domain-wall pinning might cause crystalline imperfections in the multi-domain state [34]. The magnetic properties resulting from La⁺⁺ substitution which carries 4f electron spins on cobalt ferrite are caused by the dominant super exchange in-

Table 4. FTIR parameters of the CoLa₀.₁Fe₁.₉O₄ nanoparticles.

<table>
<thead>
<tr>
<th>Ta (°C)</th>
<th>ν₁ (cm⁻¹)</th>
<th>ν₂ (cm⁻¹)</th>
<th>k₁ (N/m)</th>
<th>k₀ (N/m)</th>
<th>F (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>589.28</td>
<td>471.62</td>
<td>148.58</td>
<td>151.57</td>
<td>150.57</td>
</tr>
<tr>
<td>300</td>
<td>575.78</td>
<td>474.51</td>
<td>141.85</td>
<td>153.43</td>
<td>149.57</td>
</tr>
<tr>
<td>400</td>
<td>571.92</td>
<td>493.80</td>
<td>139.95</td>
<td>166.16</td>
<td>157.42</td>
</tr>
</tbody>
</table>

Table 5. Magnetic parameters of the CoLa₀.₁Fe₁.₉O₄ nanoparticles samples.

<table>
<thead>
<tr>
<th>Ta (°C)</th>
<th>Hc (Oe)</th>
<th>Mₛ (emu/g)</th>
<th>Mᵣ (emu/g)</th>
<th>M₀/Mₛ</th>
<th>n₀ (µB)</th>
<th>K(×10⁴) (erg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>700</td>
<td>19.05</td>
<td>8.37</td>
<td>0.43</td>
<td>0.83</td>
<td>0.77</td>
</tr>
<tr>
<td>300</td>
<td>560</td>
<td>20.30</td>
<td>8.99</td>
<td>0.44</td>
<td>0.88</td>
<td>0.67</td>
</tr>
<tr>
<td>400</td>
<td>550</td>
<td>17.45</td>
<td>8.70</td>
<td>0.49</td>
<td>0.76</td>
<td>0.56</td>
</tr>
</tbody>
</table>
teration via oxygen ions between cations in A-site and B-site. This magnetic behavior is largely regulated by 3d electron spin coupling. The emergence of 3d-4f electron spin coupling can be expected through the substitution of small amounts of rare earth cations [40].

Redistribution of cations is related to changes in magnetization. Meanwhile, changes in physical properties can be associated with He due to changes in the magneto crystalline anisotropy constant. The anisotropy constant depends on the size of the crystallites. Heat treatment increases the annealing temperature, and it can reduce the anisotropy constant because the crystallite size decreases. This is possible because of the existence of multi magnetic domains in the material.

3.4 Dye Removal Analysis of CoLa$_{0.1}$Fe$_{1.9}$O$_4$ Nanoparticles

Figure 5 shows the dye removal characteristic of the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles. Figure 5(a) can be seen that there was a decrease in the degradation results of the Congo red pollutant for overnight time. Furthermore, the photocatalyst test was performed by irradiating UV light for 10 min and the results were obtained in the form of a decrease in the degradation magnitude of all the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles (Figure 5(b)).

Table 6 shows that the total reduction of Congo red dye using the CoLa$_{0.1}$Fe$_{1.9}$O$_4$, i.e., 95.98% (54.61% with photocatalysis), 97.32% (60.00% with photocatalysis), and 97.90% (40.35% with photocatalysis) at the $T_a$ of 200 °C, 300 °C, and 400 °C, respectively. Physical changes that occur in the absorption and photocatalyst process are the color change of the congo red test material from red to clear (Figure 5(c)). Furthermore, the mechanism that occurs in the dye removal process is the absorption of the material caused by the surface properties of the material. The surface properties of the material are related to the crystallite size, the smaller the crystallite size causes a large surface area, this is one of the indicators supporting the absorption process [46]. The results obtained are different due to other factors, i.e., magnetic properties such as $H_C$. $H_C$ supports the absorption mechanism, the smaller the $H_C$, the smaller the induced magnetism that occurs in the absorption pro-

<table>
<thead>
<tr>
<th>$T_a$ (°C)</th>
<th>Dye Removal Properties (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>95.98</td>
</tr>
<tr>
<td>300</td>
<td>97.32</td>
</tr>
<tr>
<td>400</td>
<td>97.90</td>
</tr>
</tbody>
</table>

Figure 5. Dye removal characteristic of the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles, (a) adsorption properties for different the $T_a$ at 200 °C, 300 °C, and 400°C; (b) typical photocatalytic properties for the $T_a$ of 200 °C; (c) Visual photograph of the best Congo red dye removal for the $T_a$ of 300 °C.
cess, and the greater the absorption speed. Meanwhile, in the photocatalyst process, the mechanism that occurs follows the S-scheme, in which La$^{3+}$ ions help in slowing down the recombination of electrons (e$^{-}$) from the conduction band (CB) to the valence band (VB) in cobalt ferrite material. Thus, the formation of reactive oxygen species (•OH, O$_2^-$, and H$_2$O$_2$) becomes more, especially the formation of hydroxyl ions (•OH). This formation is used to degrade pollutants in this case, namely Congo red pollutant [47], the more •OH radicals formed, the better the degradation results obtained [48].

4. Conclusions

Lanthanum-substituted cobalt ferrite (CoLa$_{0.1}$Fe$_{1.9}$O$_4$) nanoparticles with the annealing temperature ($T_a$) treatment have been successfully synthesized using the co-precipitation method. XRD analysis shows that all the samples crystallized indicate a cubic spinel-type structure with an Fd-3m space group. FTIR analysis shows that the main absorption band range corresponds to the cobalt ferrite-based structure. VSM results show that the CoLa$_{0.1}$Fe$_{1.9}$O$_4$ nanoparticles decrease the magnitude of the $H_c$ with increasing the $T_a$. This is directly correlated with the change in the anisotropy magnetic constant ($K$). The obtained nanoparticles also performed well for Congo red dye removal. The effect of temperature will change the physical properties which affect its application. So, as the annealing temperature increases, the crystal growth gets better.

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References


