Synthesis, characterization and environmental remediation studies of Bi-substituted Li-Co spinel ferrites

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**ABSTRACT**

Photocatalytic ability of Lithium-Cobalt ferrites was improved by doping with Bi. For the synthesis of different compositions of Bi-doped Li-Co Ferrites, the Micro-Emulsion method was used. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) and Scanning Electron Microscopy (SEM) analyses confirmed its spinel structure and morphology. Bi-substituted Li-Co ferrites exhibit 93.8% and 83.9% degradation of methylene blue and crystal violet, respectively. While using scavenger this value of degradation of crystal violet exceeds up to 98.5%. The rate constants of LiCo\textsubscript{0.5}Bi\textsubscript{0.4}Fe\textsubscript{1.6}O\textsubscript{4} for methylene blue (MB) and crystal violet (CV) are 0.0203 and 0.01615 min\textsuperscript{-1}, respectively.

The band gap energy value calculated using tauc plot is 2.70 eV and 3.95 eV for Li-Co ferrites and Bi-doped Li-Co ferrites, respectively. Electrochemical impedance spectroscopy (EIS) studies confirmed that the doping of Bi in Li-Co spinel ferrites enhances its conductance. The use of these ferrites for photocatalytic degradation is more beneficial because they can be easily separable afterwards due to their magnetic nature which is confirmed by studying the re-usability of the as-synthesized samples.

**Highlights**

- Li-Co ferrites and Bi-substituted Li-Co ferrites were synthesized by the micro-emulsion method.
- XRD and FTIR confirmed their spinel structural features.
- The prepared catalyst successfully degraded the MB (> 90%) and CV (> 80%).
- Antibacterial studies of as-synthesized samples were also done for \textit{S. aureus} (Positive Strain) and \textit{P. aeruginosa} (Negative Strain) microorganisms.

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1. Introduction

Energy crisis and environmental pollution are the major consequences of the world with emerging industries. Organic dyes, such as methylene blue, rhodamine b and congo red, are the main components of industrial waste water\cite{1}. Scientists are striving to develop certain methods to overcome the increase in the release of organic dyes from different industries, including food...
and textile industry, directly into water bodies [2]. The best way for the degradation of these pollutants is photocatalysis, as it uses solar energy for the removal of these contaminants [3]. Photocatalysis plays a vital role in areas such as hydrogen production through water splitting, photoreduction and degradation of water contaminants. Besides, the energy crisis can be solved by an economic and environmentally safe photocatalysis technique [4]. Photocatalysis gained great attention for environmental remediation after 1972 when water splitting by UV light was done by using TiO2 photoanode [5], due to its high efficiency and abundance [6]. There are various factors such as higher value of band gap and lesser absorption energy, which limit the applications of TiO2. So, it is the main concern of scientists to explore cheap nanomaterials that will help them to meet their required needs. The assembly for various composites for the photocatalytic degradation of pollutants has also gained much attention during the last few years [7,8]. Different photocatalysts, such as pristine TiO2, WO3, CdS, Fe2O3, ZnS or TiO2 composites, N-Doped ZnO, Ag-based compounds and their composites, can be used for the removal of contaminants owing to their outstanding properties [9–11].

Owing to their chemical, electrical and physical properties, nanomaterials have attained great attention for the last few decades [12,13]. The properties of these nanomaterials are greatly dependent on their size and shape [14]. Among various ferromagnetic materials, ferrites are the most important due to the presence of double oxides between iron and other metals [15,16]. The key feature of ferrites includes the separation of sample from the solution due to their distinctive magnetic properties [17]. Additionally, these materials can be used as alternative catalyst supports due to their magnetic properties (high surface area, high dispersion and outstanding stability) [18]. Metal ferrites find their applications in water treatment, gas sensors, microwave and medical devices etc. because of their composition, high resistivity, grain size and magnetic nature etc. [19–21]. The electromagnetic properties of ferrites can be altered by changing the operating conditions such as frequency, temperature, pressure and time [22–24]. The spinal ferrites, such as MFe2O4 (M = Cu, Co, Mn and Ni), exhibit unique catalytic effectiveness [25]. These spinal ferrites were initially prepared by using the ceramic method with very low yield at micrometric scale. Currently, wet chemical methods, such as co-precipitation, sol–gel and micro-emulsion, are used for the synthesis of ferrites [26]. The spinal ferrites manufactured by the wet chemical method have more distinctive properties than those made by the ceramic method [27,28]. There are various methods, such as reverse micelle, sol–gel and citrate gel that can be used for the preparation of metal-substituted Li-Co ferrites [29–31]. The micro-emulsion route has more merits than other methods due to their low cost, simplicity and good control on particle size. At present, various shapes of ferrites have been produced (it may be thin films or in the form of powder). In a variety of electrical instruments, such as voltage-controlled rectifiers, low noise amplifiers and filters, ferrites find its applications as inductive components [32,33]. Typically, Fe-based spinal or Fe d-orbital materials show narrow band gap that causes extension of visible light absorption region [25]. The capability of ferrites can be increased by decreasing the eddy current and enhancing the electrical resistivity. Different types of bismuth and bismuth-substituted compounds are presently used in various fields including photocatalysis [34–36]. The semiconductors, based on Bi doping or BiO3 structure, exhibit better properties due to their suitable band potential and considerable chemical stability [37]. At present, several bismuth-substituted compounds with different band gap energy values are developed that could lessen the recombination rate of e/h and be used for the photocatalytic degradation of various dyes/contaminants [5].

Nanotechnology plays a vital role in controlling the microbial activities. On the basis of microbial growth or potential ability for the inhibition of biofilm formation, various NPs have been investigated. It is concluded that these NPs generate the reactive oxygen species (ROS) by reducing the adhesion of cells caused by electrostatic force neutralization rendered by nanostructured surfaces [38]. The antibacterial activity depends mainly on its properties such as high surface area, reactive sites and unique crystal morphology.

In the current research, Li-Co ferrites and different concentrations of Bi-substituted Li-Co spinal ferrites have been synthesized by the micro-emulsion method. All these spinal ferrites were tested for their ability to degrade various dyes under solar light and their results were also compared with Bi-substituted Li-Co spinal ferrites. We can assume that Bi-substituted Li-Co spinal ferrites will depict better antibacterial and photocatalytic activities.

2. Experimental details

2.1. Materials

Lithium chloride (LiCl) Sigma Aldrich (≥ 99.98%), Cobalt (II) acetate tetrahydrate (CH3COO)2Co.4H2O Sigma Aldrich (≥ 98.0%), Bismuth (III) nitrate pentahydrate (Bi(NO3)3.5H2O Sigma Aldrich (98%), Iron (III) nitrate nonahydrate Fe(NO3)3.9H2O Sigma Aldrich (≥ 99.95%). Cetyltrimethylammonium bromide (CTAB) Sigma Aldrich. All these chemicals of analytical grade were obtained from Sigma Aldrich (Germany) and no further purification was required prior to use.

2.2. Micro-emulsion technique

By utilizing the micro-emulsion methodology, Li-Co spinal ferrites were doped with different concentrations of
bismuth LiCo$_{0.5}$Bi$_{a}$Fe$_{2-a}$O$_4$ (0.0 ≤ a ≤ 0.4) were synthesized. The chemical compounds utilized in the synthesis of these ferrites are as follows: Bismuth (III) nitrate pentahydrate Bi(NO$_3$)$_3$·5H$_2$O, Lithium chloride (LiCl), Iron (III) nitrate nonahydrate Fe(NO$_3$)$_3$·9H$_2$O, Cetyltrimethylammonium bromide (CTAB), Cobalt (II) acetate tetrahydrate (CH$_3$COO)$_2$Co·4H$_2$O and deionized water. By utilizing the appropriate amount of different salts, 0.1M solution of Lithium chloride, 0.05M solution of Cobalt (II) acetate tetrahydrate, 0.2M solution of Bismuth (III) nitrate pentahydrate, 0.2M Iron (III) nitrate nonahydrate and 0.36M solution of Cetyltrimethylammonium bromide were prepared in beakers separately and stirred continuously. The temperature of all the solutions was then raised up to 60°C. Then the ammonia solution was added until the pH of the solutions became 10 and then all the solutions were mixed and stirred continuously for 6 h. The solutions were kept for 24 h to wait for the precipitates to settle at the bottom of the beakers. Then they were washed using distilled water until the pH became neutral. The precipitates were then dried in an oven at a temperature of 100°C. Afterwards, the dried precipitates were ground into fine powder by pestle and mortar. To avoid the addition of impurities, pestle and mortar was washed by using acetone prior to the grinding of precipitates of each sample. At the end, the calcination of these ferrites was done in a muffle furnace (Vulcan-a-550) at 800°C for 7 h (Figure 1).

2.3. Characterization techniques

To obtain the XRD patterns of the as-prepared sintered powdered samples, XRD Phillips X’Pert Pro MPD diffractometer was used with Cu Kα (λ = 0.15406 nm). The XRD patterns were studied at room temperature. To understand the nature and structure of the prepared ferrites, the FTIR analysis was done. FTIR spectrometer with built-in Zinc Selenide ATR and Zinc Selenide optics for high humidity was used to carry out the FTIR analysis. To confirm the morphology thermal emission a scanning electron microscope was used. Optical properties of as-synthesized samples were studied by Agilent Cary 60 spectrophotometer having spectral range between 200 and 800 nm. Electrochemical impedance spectroscopy was carried out using Gamry interface 5000 under the frequency 10$^2$–10$^6$ Hz in 50 ml of 0.1 M KCl solution, containing 50 ml of 1 mM ferrocyanide/ferricyanide (1:1) electrolyte.

2.4. Photocatalytic degradation

The removal efficiency of methylene blue (MB) and crystal violet (CV) was examined by using LiCo$_{0.5}$Fe$_2$O$_4$ and Bi-doped LiCo$_{0.5}$Fe$_2$O$_4$ as a photocatalysts under visible light irradiation for 110 min. 5 mg of photocatalyst was added into 100 ml of (5 ppm) MB and CV solution. The whole solution was placed in the dark with continuous stirring for 60 min. This was done to attain the adsorption–desorption equilibrium between dye solution and photocatalyst. Then the whole solution was placed under visible light irradiation with constant stirring. 10 ml of this solution was taken after regular time intervals and the removal efficiency of dye was measured by using UV–VIS spectrophotometer. The percentage degradation of both dyes was calculated by using the following equation:

\[
\text{Percentage Degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)
\]

where $C_t$ is the concentration at time $t$ and $C_0$ is the initial concentration of dye solution.

2.5. Antibacterial activity

Disc diffusion method was used to carry out the antibacterial activity of as-synthesized magnetic samples. This method was employed against two test microorganisms S. aureus (Positive Strain) and P. aeruginosa (Negative Strain). Different concentrations of as-synthesized magnetic samples were sonicated with distilled water and placed on the surface of the nutrient agar plate by using forcep. The standard antibiotic Ciprofloxacin was taken as a positive control. The inhibition zone was seen clearly on the corners of agar plate after incubation at 37°C for 24 h. This zone of inhibition was measured in mm units.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The study of phases of the as-synthesized bismuth-doped Li-Co spinel ferrites LiCo$_{0.5}$Bi$_a$Fe$_{2-a}$O$_4$ (0.0 ≤ a ≤ 0.4) was done by using Kα radiations of Cu (λ = 1.5406 Å), on an X-ray diffractometer. XRD spectrum of LiCo$_{0.5}$Fe$_2$O$_4$ in 2θ range from 20° to 70° [39] shows diffraction peaks at 30.2°, 35.5°, 38.3°, 42.9°, 53.8°, 56.9° and 62.5° in Figure 2. These diffraction peaks correspond with the Miller indices (220), (311), (222), (400), (422), (511) and (440), which confirms their spinel structure [40]. An additional secondary peak is obtained at 33.1° which is shown by (α) in the graph. The as-synthesized ferrites have cubic structure containing small concentration of α-Fe$_2$O$_3$. By increasing the bismuth content the secondary peak vanishes and the crystal has spinel structure with single phase only [41]. The XRD pattern (ICDD No. 88-0671) was used to confirm the structure of the synthesized ferrites. The crystalline size can be calculated by using Sherre’s formula

\[
D = \frac{K\lambda}{\beta\cos\theta} \quad (2)
\]

where λ is the wavelength of X-rays (0.15406 nm), K is a crystallinity constant (0.9), β is the FWHM and θ is the angle of diffraction. The values of average crystalline size for LiCo$_{0.5}$Fe$_2$O$_4$ and LiCo$_{0.5}$Bi$_{0.4}$Fe$_{1.6}$O$_4$ are 14.063 and 7.786 nm, respectively.
Figure 1. Synthetic scheme of Li-Co ferrites and Bi-doped Li-Co ferrites.

Figure 2. XRD analysis of Li-Co ferrites and different concentrations of Bi-doped Li-Co ferrites.

Figure 3 shows the XRD spectra of the recovered photocatalyst. The characteristic peaks remain unchanged, but there is a slight variation in the intensity of the peaks.

3.2. SEM
The SEM analysis was performed for the study of structural and surface morphology of as-prepared nanoparticles. In Figure 4(a), aggregation is due to the
magnetic nature of spinal ferrites. While in Figure 4(b), the porosity of Li-Co ferrite has been increased; this indicates the formation of Bi-doped Li-Co ferrites. The average grain size calculated from the SEM analysis is 196.9 and 158.86 nm for LiCo0.5Fe2O4 and LiCo0.5Bi0.4Fe1.6O4, respectively.

3.3. FTIR

FTIR spectra of Bi-doped Li-Co spinel ferrites are shown in the figure. FTIR (Fourier transform infrared) spectroscopy has gained more attention than other methods of infrared spectroscopy. FTIR spectra give spectral analysis of the sample and clearly indicate about the position of bonds and ions in the crystal [42]. FTIR spectra also estimate the cationic distribution and chemical changes on both A and B sites. The absorption bands present at around 508 and 410 cm⁻¹, as shown in Figure 5, are the main characteristic bands which confirm the formation of spinel ferrites [43]. The absorption bands in given spectra show the stretching vibration of metal and oxygen atom present in the crystal lattice. The spinel structure of synthesized ferrites is also confirmed by the fact that all absorption bands of Bi-doped Li-Co ferrites are present between 400 and 600 cm⁻¹ [39].

3.4. Optical properties

UV–VIS spectroscopy is used to measure the optical properties of Bi-doped Li-Co ferrites. Figure 6 shows that Li-Co ferrites have absorption bands both in UV and in visible regions. Its absorption peaks were observed between 350 and 500 nm. The presence of absorption bands in the visible light area is the reason behind the photocatalytic activity of Li-Co ferrites. Absorption capacity in the visible region is enhanced in the case of Bi-doped Li-Co ferrites. It is the main reason behind the exceptional photocatalytic activity of Bi-doped Li-Co ferrites than pure Li-Co ferrites. Tauc plot is used to measure the direct band gap of as-synthesized samples by using the following equation:

\[(a\nu)^n = k(\nu - E_g)\]  

where \(\nu\) is the photon energy, \(a\) is the absorption coefficient, \(k\) is a constant value and \(n\) represents the transition type (For direct transition, \(n = 2\)) [44]. Extrapolation of the linear curve was done to find out the value of \(E_g\). The band gap value calculated for Li-Co ferrites and Bi-doped Li-Co ferrites is 2.70, 3.01, 3.03, 3.72 and 3.95 (Figure 7).

3.5. Photocatalysis

LiCo0.5Fe2O4 and different concentrations of Bi-doped LiCo0.5Fe2O4 were used as photocatalysts to measure the percentage degradation of MB and CV under visible
Figure 6. UV–VIS spectra of (a) Li-Co ferrites and different concentrations of Bi-doped Li-Co ferrites and (b) Tauc plot of as-synthesized samples.

Figure 7. General schematic diagram showing the process of photocatalysis.

Table 1. Comparison of % degradation of CV and MB with the prepared nanoparticles.

| Photocatalyst                  | % degradation of CV | % degradation of MB |
|--------------------------------|---------------------|---------------------|
| LiCo0.5Fe2O4                  | 47.9%               | 53.5%               |
| LiCo0.5Bi0.1Fe1.9O4           | 54.6%               | 78.8%               |
| LiCo0.5Bi0.2Fe1.8O4           | 63.8%               | 90.1%               |
| LiCo0.5Bi0.3Fe1.7O4           | 79.7%               | 90.5%               |
| LiCo0.5Bi0.4Fe1.6O4           | 83.9%               | 93.8%               |
| LiCo0.5Bi0.4Fe1.6O4 + scavenger | 98.5%               | –                   |

Percentage Degradation = \( \frac{C_0 - C_t}{C_0} \times 100 \)

where \( C_t \) is the concentration at time \( t \) and \( C_0 \) is the initial concentration of dye solution [45,46].

Table 1 shows the comparison between % degradation of MB and CV by using as-synthesized products as photocatalysts. Figures 8(g,h) and 9(g,h) show the plots between \( \ln(C_0/C_t) \) and irradiation time (\( t \)). According to the first-order kinetic law: \( \ln(C_0/C_t) = kt \), from the slope of the straight line drawn using linear regression, the value of degradation rate constant \( k \) can be determined [47]. All these values show that Bi-doped LiCo0.5(Fe2O4) exhibit phenomenal photocatalytic performance. The reason behind this increased photocatalytic activity is the increased number of reacting species, greater surface area and large number of active sites (Figures 10 and 11).

Table 2 shows the comparison of photocatalytic degradation of the already reported literature and the current work, which confirms the novelty of the current work.

3.5.1. Mechanism of photocatalysis

The very first step involved in the mechanism of photocatalytic degradation of dyes is the adsorption of dye molecules on the surface of NPs of catalyst. When samples are irradiated with solar radiations, the electrons (e\(^-\)) in the valence band (VB) of LiCo0.5(Fe2O4)
and Bi-doped LiCO$_{0.5}$(Fe$_2$O$_4$) are excited to the conduction band (CB) [52]. This will ultimately create a gap with positive charge in the VB [53]. The charge separation occurs due to the difference in energy bands between LiCO$_{0.5}$(Fe$_2$O$_4$) and Bi-doped LiCO$_{0.5}$(Fe$_2$O$_4$). It will also hinder the recombination process. The photogenerated electron will react with O$_2$ present in the solution to give O$_2^-$ ions which will form OH hydroxyl radical on reaction with H$_2$O [54,55]. In photocatalytic reaction, these photocatalytic reactive species are able to attack and degrade the organic pollutants and convert it into simple compounds such as CO$_2$, H$_2$O and other by-products. In LiCO$_{0.5}$(Fe$_2$O$_4$), the low degradation efficiency is due to the immediate recombination of photogenerated electron and hole pairs which will not allow the electron and hole pairs to move and interact with dye solutions. It is clear from the literature that when solar radiation irradiates the photocatalyst, the photons directly cause the breakdown of bonds of dyes and cause an enormous enhancement in the kinetic energy of free radicals formed [56,57] (Table 3).

The whole mechanism behind this photocatalytic activity can easily be understood by Figure 12 and equations.

\[
\text{Bi - doped LiCO}_{0.5} (\text{Fe}_2\text{O}_4) + h\nu \rightarrow \text{Bi - doped LiCO}_{0.5} (\text{Fe}_2\text{O}_4) (e^-_{(\text{CB})} + h^+_{(\text{VB})}) \quad (1)
\]

\[
O_2 + e^- \rightarrow O_2^- \quad (2)
\]

\[
H_2O + h^+ \rightarrow H^+ + \cdot OH \quad (3)
\]

\[
\text{MB - Bi doped LiCO}_{0.5} (\text{Fe}_2\text{O}_4) + O_2^- + h^+ + \cdot OH \rightarrow \text{Bi - doped LiCO}_{0.5} (\text{Fe}_2\text{O}_4) + H_2O + CO_2 + \text{other by - products} \quad (4)
\]

**3.5.2. EIS**

Electrochemical impedance spectroscopy was performed using the frequency range of $10^2$–$10^6$ Hz and 50 mL of 0.1M KCl solution containing 50 mL of 1 mM ferrocynide/ferricyanide (1:1) electrolyte. Platinum wire and silver/silver chloride Ag(s)/AgCl(s) were utilized as counter and reference electrodes, respectively. For the preparation of working electrode, slurry was made by mixing 5 mg of as-synthesized samples with nafion and it was coated on Indium-Tin oxide (ITO)-coated glass substrates. The prepared working electrode was then dried for 1 h at room temperature. The main purpose
behind this EIS analysis is to analyse the charge transfer properties of as-prepared photocatalysts. It can be seen in Figure 13 that the diameter of Nyquist semicircle of Bi-doped Li-Co ferrites is much smaller than that of undoped Li-Co ferrites. The main reason behind this smaller diameter is the lower charge transfer resistance that causes the effective separation of photogenerated $e^- - h^+$ pair, transport charges between interfaces and lessens the chances of recombination of electron/hole. On the other hand, greater impedance of undoped Li-Co ferrites causes less conductive transfer of photogenerated $e^-$ which plays an important role in photocatalytic reaction.

Table 2. Comparison of photocatalytic degradation of the already reported literature and current work.

| Sr.no | Photocatalyst       | Light | Time     | Rate constant | % degradation | Dye         | Reference |
|-------|---------------------|-------|----------|---------------|---------------|-------------|------------|
| 1.    | LiFe$_2$O$_4$ (rod like) | visible | 180 min. | 0.00497       | 62.4%         | MB          | [48]       |
| 2.    | Li$_2$Fe$_5$O$_8$   | UV-VIS | 30 min.  | —             | 95%           | MO          | [49]       |
| 3.    | CoFe$_2$O$_4$       | visible | 100 min. | 0.022         | 90%           | Remazol deep red | [50] |
| 4.    | CuFe$_2$O$_4$       | visible | 35 min.  | 0.010         | 43%           | MB          | [51]       |
| 5.    | Bi$_2$O$_3$/CuFe$_2$O$_3$ | visible | 35 min.  | 0.053         | 91%           | MB          | [51]       |
| 6.    | LiCo$_{0.5}$Bi$_{0.4}$Fe$_{1.6}$O$_4$ | visible | 120 min. | 0.0203        | 93.8%         | MB          | Current work |
| 7.    | LiCo$_{0.5}$Bi$_{0.4}$Fe$_{1.6}$O$_4$ + Scavenger | visible | 90 min.  | 0.0203        | 83.9%         | CV          | Current work |
|       |                     |       |          |               | 98.5%         | CV          | Current work |
3.5.3. Role of scavenger

Different types of scavenger have been used during the photocatalysis process such as 2-butanol, H₂O₂, Ascorbic acid (Vit.C) etc [44]. And their effect on the photocatalytic activity of the synthesized particles is studied. In the present study, Ascorbic acid or Vit.C is used as a scavenger with CV dye and its effect is studied. Ascorbic acid enhances the photocatalytic activity of Bi-doped LiCo₀.₅(Fe₂O₄) photocatalyst. Table 1 shows that the photocatalytic degradation of CV is less than that of MB which is 83.9% and 93.8%, respectively, with Bi-doped LiCo₀.₅(Fe₂O₄) but with the addition of Vit.C as a scavenger the degradation of CV is enhanced up to 98.5%. Figure 10 shows the comparison of %degradation of LiCo₀.₅Fe₂O₄ and Bi-doped LiCo₀.₅(Fe₂O₄). The increased photocatalytic degradation can be explained by the effective charge separation by the addition of scavenger. Due to the addition of Vit.C, the electrons present at the surface of Bi-doped LiCo₀.₅(Fe₂O₄) react efficiently with the oxygen molecules; as a result, superoxide radicals are formed, which then undergo reaction with the water molecules and form hydrogen peroxide. The electrons and hole on the surface of the photocatalyst then undergo redox reaction with hydrogen peroxide and form hydroxyl radicals which then degrade the organic dyes to the degradation products like CO₂ and H₂O. The photocatalytic degradation of methylene blue in the presence of Ascorbic acid is highly reversible. As the light source is removed, the oxidized product changes rapidly to its coloured reduced form at such velocity to make the study of photocatalytic degradation by using spectrophotometer difficult [58] (Figures 14 and 15).

Table 3. Values of conduction band valance band of LiCo₀.₅Fe₂O₄ and LiCo₀.₅Bi₀.₄Fe₁.₆O₄.

| Photocatalyst     | χ (eV) | E₃ (eV) | E⁰ (eV) | E₈ (eV) | E₉ (eV) |
|-------------------|--------|---------|---------|---------|---------|
| LiCo₀.₅Fe₂O₄      | 5.42   | 2.70    | 4.5     | −0.43   | 2.27    |
| LiCo₀.₅Bi₀.₄Fe₁.₆O₄ | 5.421  | 3.95    | 4.5     | −0.196  | 2.896   |

Figure 11. Comparison of photocatalytic degradation of methylene blue (MB) and crystal violet (CV).

Figure 12. Mechanism for photocatalytic degradation of the dyes by using LiCo₀.₅Bi₀.₄Fe₁.₆O₄ as a photocatalyst.

Figure 13. EIS of the LiCo₀.₅Fe₂O₄ and LiCo₀.₅Bi₀.₄Fe₁.₆O₄.
Figure 14. Suspension of crystal violet and LiCo$_{0.5}$Bi$_{0.4}$Fe$_{1.6}$O$_4$ by using scavenger (a) before degradation (b) after degradation.

Table 4. Antibacterial activity of Li-Co ferrites and different concentrations of Bi-doped Li-Co ferrites.

| Sr. No. | Sample | Concentrations | $S. aureus$ (Pos-Strain) | $P. aeruginosa$ (Neg-Strain) |
|---------|--------|----------------|--------------------------|-----------------------------|
| 1       | AZ-1   | 10 mg/ml       | 06 mm                    | 06 mm                       |
|         |        | 20 mg/ml       | 06 mm                    | 08 mm                       |
|         |        | 40 mg/ml       | 06 mm                    | 07 mm                       |
|         | Ciprofloxacin (control) | 4 $\mu$g/ml | 12 mm                    | 11 mm                       |
| 2       | AZ-2   | 10 mg/ml       | 06 mm                    | 06 mm                       |
|         |        | 20 mg/ml       | 06 mm                    | 06 mm                       |
|         |        | 40 mg/ml       | 06 mm                    | 06 mm                       |
|         | Ciprofloxacin (control) | 4 $\mu$g/ml | 11 mm                    | 12 mm                       |
| 3       | AZ-3   | 10 mg/ml       | 06 mm                    | 06 mm                       |
|         |        | 20 mg/ml       | 06 mm                    | 06 mm                       |
|         |        | 40 mg/ml       | 06 mm                    | 08 mm                       |
|         | Ciprofloxacin (control) | 4 $\mu$g/ml | 12 mm                    | 12 mm                       |
| 4       | AZ-4   | 10 mg/ml       | 06 mm                    | 07 mm                       |
|         |        | 20 mg/ml       | 06 mm                    | 07 mm                       |
|         |        | 40 mg/ml       | 06 mm                    | 07 mm                       |
|         | Ciprofloxacin (control) | 4 $\mu$g/ml | 15 mm                    | 15 mm                       |
| 5       | AZ-5   | 10 mg/ml       | 07 mm                    | 07 mm                       |
|         |        | 20 mg/ml       | 07 mm                    | 07 mm                       |
|         |        | 40 mg/ml       | 09 mm                    | 08 mm                       |
|         | Ciprofloxacin (control) | 4 $\mu$g/ml | 14 mm                    | 12 mm                       |

3.5.4. Reusability

The structure stability and reusability are the important requirements for the development of a photocatalyst. The recycling experiments of repetitive cycles were performed for the photodegradation of methylene blue to evaluate the durability and stability of as-prepared material [59,60]. The Bi-doped Li-Co ferrites showed similar photocatalytic efficiency after three successive cycles (Figures 16 and 17). It is also noticed that the XRD patterns did not show certain variations after three cycles. It suggests that Bi-doped Li-Co ferrites can be widely utilized for the treatment of industrial waste water.

3.6. Antibacterial activity

Antibacterial activity of as-synthesized magnetic samples was carried out by using the disc diffusion method. The results of this method are reported in Table 4. On the basis of zone of inhibition, Bi-doped LiCo (Fe2O4) showed maximum antibacterial activity against both microorganisms $S. aureus$ (Positive Strain) and $P. aeruginosa$ (Negative Strain) among all the synthesized nanoparticles [61]. This happened due to the doping of Bismuth with LiCo(Fe2O4). The enhanced antibacterial activity of Bismuth nanoparticles and Bismuth-doped compounds is already reported in the literature [62,63]. The whole scenario behind this increase in antibacterial activity is the presence of attraction between positively charged heavy metal ions and negatively charged cell membrane. These ions penetrate in the cell membrane and inactivate the proteins present on the surface of the bacterial cell. This results in reduction in membrane permeability and ultimately causes the demise of microbes (Figures 18 and 19).
Figure 16. (a,b,c) Photocatalytic degradation of methylene blue by recovered LiCo_{0.5}Fe_{2}O_{4} after the first, second and third cycles, respectively (d) shows the recyclability of the LiCo_{0.5}Fe_{2}O_{4} photocatalyst.

Figure 17. (a,b,c) Photocatalytic degradation of methylene blue by recovered LiCo_{0.5}Bi_{0.4}Fe_{1.6}O_{4} after the first, second and third cycles, respectively (d) shows the recyclability of the LiCo_{0.5}Bi_{0.4}Fe_{1.6}O_{4} photocatalyst.
Figure 18. Antibacterial activity of as-synthesized materials *Pseudomonas aeruginosa* (Negative Strain).

Figure 19. Antibacterial activity of as-synthesized materials *Staphylococcus aureus* (Positive Strain).
4. Conclusion

Micro-emulsion method was used to synthesize magnetically recyclable Bi-doped Li-Co ferrites. Characterization of these spinel ferrites was done by using XRD, SEM and FTIR for structure morphology and spectral analysis, respectively. The antibacterial activity of these ferrites was studied by using S. aureus (Positive Strain) and P. aeruginosa (Negative Strain) and it can be clearly seen that Bi-doped Li-Co ferrites exhibit more antibacterial activity than pure Li-Co ferrites. The photocatalytic degradation of methylene blue and crystal violet was studied by using as-synthesized samples as photocatalysts. The results show that Bi-doped Li-Co ferrites exhibit exceptional photocatalytic activity than bare Li-Co ferrites which is confirmed by the EIS analysis. These Bi-doped Li-Co ferrites find their potential applications in both environmental and biological fields due to their sustainability, recyclability and cost effectiveness.

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References

[1] Ebrahimzadeh MA, Mortazavi-Derazkola S, Zazouli MA. Eco-friendly green synthesis of novel magnetic Fe3O4/SiO2/ZnO-PryO11 nanocomposites for photocatalytic degradation of organic pollutant. J Rare Earths. 2020; 38(1):13–20.

[2] Elgorban AM, Bahkali AH, Syed A. Construction of Ag2WO4 decorated CoWO4 nano-heterojunction with recombination delay for enhanced visible light photocatalytic performance and its antibacterial applications. Colloids Surf A. 2021;629:127416.

[3] Feizipoor S, Habibi-Yangjeh A. Ternary TiO2/Fe3O4/CoWO4 nanocomposites: novel magnetic visible-light-driven photocatalysts with substantially enhanced activity through pn heterojunction. J Colloid Interface Sci. 2018;524:325–336.

[4] Janani B, Al-Kheraif AA, Thomas AM, et al. Construction of nano-heterojunction AgFeO2–ZnO for boosted photocatalytic performance and its antibacterial applications. Mater Sci Semicond Process. 2021;133:105924.

[5] Janani B, Syed A, AL-Shwaiman HA, et al. Performance analysis of novel Bi6Cr2O15 coupled Co3O4 nano-heterostructure constructed by ultrasonic assisted method: visible-light driven photocatalyst and antibacterial agent. Colloids Surf A. 2021;622:126671.

[6] Fujishima A, Honda K. Electrochemical photocatalysis of water at a semiconductor electrode. Nature. 1972; 238(5358):37–38.

[7] Asadzadeh-Khaneghah S, Habibi-Yangjeh A, Nakata K. Decoration of carbon dots over hydrogen peroxide-treated graphite carbon nitride: exceptional photocatalytic performance in removal of different contaminants under visible light. J Photochem Photobiol A. 2019;374:161–172.

[8] Rauf A, Ma M, Kim S, et al. Mediator- and co-catalyst-free direct Z-scheme composites of Bi3WO6–Cu2S for solar-water splitting. Nanoscale. 2018;10(6):3026–3036.

[9] Lakshmi S, Renganathan R, Fujita S. Study on TiO2-mediated photocatalytic degradation of methylene blue. J Photochem Photobiol A. 1995;88(2–3):163–167.

[10] Kokilavani S, Al-Kheraif AA, Thomas AM, et al. Novel NiS/Ag2MoO4 heterostructure nanocomposite: synthesis, characterization and superior antibacterial and enhanced photocatalytic activity. Physica E. 2021;133:114767.

[11] Kokilavani S, Syed A, AL-Shwaiman HA, et al. Preparation of plasmonic CoS/Ag2WO4 nanocomposites: efficient visible light driven photocatalysts and enhanced anti-microbial activity. Colloid Interface Sci Commun. 2021;42:100415.

[12] Shirzadi-Ahodashti M, Mortazavi-Derazkola S, Ebrahimzadeh MA. Biosynthesis of noble metal nanoparticles using crateagus monogyna leaf extract (CML@X-NPS, X = Ag, Au): antibacterial and cytotoxic activities against breast and gastric cancer cell lines. Surf Interfaces. 2020;21:100697.

[13] Mortazavi-Derazkola S, Yousefina A, Naghizadeh A, et al. Green synthesis and characterization of silver nanoparticles using E. angustifolia bark extract and study of its antibacterial effect. J Polym Environ. 2021;1–9.

[14] Ebrahimzadeh MA, Naghizadeh A, Mohammad-Aghdam S, et al. Enhanced catalytic and antibacterial efficiency of biosynthesized Convolvulus fruticosus extract capped gold nanoparticles (CFE@AuNPs). J Photochem Photobiol B. 2020;209:111949.

[15] Khan MA, Zaman MQ, Majeed A, et al. Structural, spectral, dielectric and magnetic properties of Sr2CuxNi2-xFe28-xCrO46 (0 ≤ x ≥ 0.5) ferrites synthesized via micro-emulsion route. Vol. Vol. 259Mater. Chem. Phys.; 2021. p. 124066.

[16] Wang LG, Wang XX, Zhu CM, et al. Influences of annealing temperature on dielectric, magnetic and magnetoelectric properties of 0.7 BiO.5Na0.5TiO3-0.3 NiFe2O4 ceramics. J Magn Magn Mater. 2020;494:165773.

[17] Smart JS. The Néel theory of ferrimagnetism. Am J Phys. 1955;23(6):356–370.

[18] Ebrahimzadeh MA, Mortazavi-Derazkola S, Zazouli MA. Eco-friendly green synthesis and characterization of novel Fe 3 O 4/SiO2/Co3O4 nanocomposites: novel magnetic visible-light-driven photocatalysts and characterization of organic contaminants. J Mater Sci Mater Electron. 2019;30(12):10994–11004.

[19] Meyers MA, Mishra A, Benson DJ. Mechanical properties of nanocrystalline materials. Prog Mater Sci. 2006;51(4):427–556.

[20] Singh A, Pathak S, Kumar P, et al. Tuning the magnetic and electric properties of nanocrystalline materials. Prog Mater Sci. 2006;51(4):427–556.

[21] Singh A, Pathak S, Kumar P, et al. Tuning the magnetic and electric properties of nanocrystalline materials. Prog Mater Sci. 2006;51(4):427–556.
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[22] Naito Y, Suetake K. Application of ferrite to electromagnetic wave absorber and its characteristics. IEEE Trans Microw Theory Tech. 1971;19(1):65–72.

[23] Sugimoto M. The past, present, and future of ferrites. J Am Ceram Soc. 1999;82(2):269–280.

[24] Arteaga-Cardona F, Pal U, Maria Alonso J, et al. Tuning magnetic and structural properties of MnFe2O4 nanostructures by systematic introduction of transition metal ions M2+ (M = Zn, Fe, Ni, Co). J Magn Magn Mater. 2019;490:165496.

[25] Janabi B, Syed A, Thomas AM, et al. A simple approach for the synthesis of bi-functional pn type ZnO@CuFe2O4 heterojunction nanocomposite for photocatalytic and antimicrobial application. Physica E. 2021;130:114664.

[26] Phansamdaeng P, Kheparmit J. Structural, magnetic and dielectric properties of chromium substituted copper ferrite ceramics. Mater Today Proc. 2019;17:1644–1651.

[27] Chaudhuri A, Mitra S, Mandal M, et al. Nanostructured bismuth ferrites synthesized by solvothermal process. J Alloys Compd. 2010;491(1–2):703–706.

[28] Anjum S, Rashid A, Bashir F, et al. Effect of Cu doped nickel ferrites on structural, magnetic and dielectric properties. Mater Today Proc. 2015;2(10):5559–5567.

[29] Sivakumar N, Narayanasamy A, Greneche J-M, et al. Electrical and magnetic behaviour of nanostructured MgFe2O4 spinel ferrite. J Alloys Compd. 2010;504(2):395–402.

[30] Mansour S, Elkestawy M. A comparative study of electric properties of nano-structured and bulk Mn–Mg spinel ferrite. Ceram Int. 2011;37(4):1175–1180.

[31] Mosivand S, Kazeminezhad I. A novel synthesis method for manganese ferrite nanopowders: The effect of manganese salt as inorganic additive in electrosynthesiscell. Ceram Int. 2021;47(9):13517–13526.

[32] Liu F, Yang C, Ren TL, et al. Fully integrated ferrite-based inductors for RF ICs. The 13th International Conference on Solid-State Sensors, Actuators and Microsystems, 2005. Digest of Technical Papers. TRANSUDERS’05. Seoul: IEEE; 2005.

[33] Pardavi-Horvath M. Microwave applications of soft ferrites. J Magn Magn Mater. 2000;215–216:171–183.

[34] Verma A, Alam MI, Chatterjee R, et al. Development of a new ferrite core for power applications. J Magn Magn Mater. 2006;300(2):500–505.

[35] Zhou X, Jiang J, Li L, et al. Preparation and magnetic properties of La-substituted Zn–Cu–Cr ferrites via a rheological phase reaction method. J Magn Magn Mater. 2007;314(1):7–10.

[36] Rosnan RM, Othaman Z, Hussin R, et al. Effect of Mg substitution on the structural and magnetic properties of Co0.5Ni0.5Mg0.5Fe2O4 nanoparticles. Chin Phys B. 2016;25(4):047501.

[37] Balasurya S, Das A, Alyousef AA, et al. Facile synthesis of Bi2O2Mo6O19 and Ag2MoO4 nanocomposite for the enhanced visible light photocatalytic removal of methylene blue and its antimicrobial application. J Mol Liq. 2021;374(1):116390.

[38] Chinnathambi A, Nasif O, Alharbi SA, et al. Enhanced optoelectronic properties of multifunctional MnFe2O4 nanorods decorated Co3O4 nanoheterostructure: photocatalytic activity and antibacterial behavior. Mater Sci Semicond Process. 2021;134:105992.

[39] Junaid M, Khan MA, Hashmi ZM, et al. Structural, spectral, magnetic and dielectric properties of Bi substituted Li-Co spinel ferrites. J Mol Struct. 2020;1221:128859.

[40] Abu El-Fadl A, Hassan AM, Mahmoud MH, et al. Synthesis and magnetic properties of spinel Zn1−xNixFe2O4 (0.0 ≤ x ≤ 1.0) nanoparticles synthesized by microwave combustion method. J Magn Magn Mater. 2019;471:192–199.

[41] Satakkar M, Ghodke N, Kane S. Influence of high temperature sintering on the structural and magnetic properties of Mn1−xZnxFe2O4. J Phys Conf Ser. 2014;534:012016.

[42] Khan MA, Sabir M, Mahmood A, et al. High frequency dielectric response and magnetic studies of Zn1−xTbFe2O4 nanocrystalline ferrites synthesized via micro-emulsion technique. J Magn Magn Mater. 2014;360:188–192.

[43] Slimani Y, Güngüneş H, Nawaz M, et al. Magneto- optical and microstructural properties of spinel cubic copper ferrites with Li-AI co-substitution. Ceram Int. 2018;44(12):14242–14250.

[44] Abdur R, Muhammad A, Mehwish A, et al. Magnetically recyclable Ni1−xCdxFe2O4-yO4–xNGO nanocomposite photocatalyst for visible light driven photocatalysis. Ceram Int. 2020;46(9):13517–13526.

[45] Adeleke JT, Theivisanthi T, Thiruppathi M, et al. Photocatalytic degradation of methylene blue by ZnO/NiFe2O4 nanoparticles. Appl Surf Sci. 2018;455:195–200.

[46] Tao J, Yang T, Liu Q, et al. Designing 0d/2D CdS nanoparticles/g-C3N4 nanosheets heterojunction as efficient photocatalyst for improved H2-evolution. Surf Interfaces. 2021;26:101312.

[47] Kokilavani S, Al-Farraj SA, Thomas AM, et al. Enhanced visible light driven photocatalytic and antibacterial activities of Ag2WO4 decorated Zn5Sn3 nanoparticle. Ceram Int. 2021;47(9):12997–13006.

[48] Zhang D, Zhang L. Construction of a three-dimensional nest-like lithium ferrite/reduced graphene oxide composite with enhanced visible-light photocatalytic activity. New J Chem. 2016;40(8):7171–7180.

[49] Gandomi F, Peymani-Motlagh SM, Rostami M, et al. Simple synthesis and characterization of Li 0.5 Fe 2.5 O 4, LiMg 0.5 Fe 2 O 4 and LiNi 0.5 Fe 2 O 4, and investigation of their photocatalytic and anticancer properties on hela cells line. J Mater Sci: Mater Electron. 2019;30(22):19691–19702.

[50] Singh S, Singhal S. Transition metal doped cobalt ferrite nanoparticles: efficient photocatalyst for photodegradation of textile dye. Materials Today: Proceedings. 2019;14:453–460.

[51] Munir S, Rasheed A, Zulfiquar S, et al. Synthesis, characterization and photocatalytic parameters investigation of a new CuFe2O4/Bi2O3 nanocomposite. Ceram Int. 2020;46(18):29182–29190.

[52] Balasurya S, Syed A, Raju LL, et al. Elucidation of photocatalysis, photoluminescence and antibacterial studies of Ag2MoO4 decorated NiM0.5O4 nano-heterostructure. Opt Mater. 2021;113:110856.

[53] Lassoued A, Li J. Magnetic and photocatalytic properties of Ni–Co ferrites. Solid State Sci. 2020;104:106199.

[54] Janabi B. The effect of various capping agents on surface modifications of CdO NPs and the investigation of photocatalytic performance, antibacterial and anti-biofilm activities. J Nanorg Organomet Polyrm Mater. 2020;30:1865.  

[55] Akhil K, Jayakumar J, Gayathri G, et al. Effect of various capping agents on photocatalytic, antibacterial and antibiofilm activities of ZnO nanoparticles. J Photochem Photobiol B. 2016;160:32–42.

[56] Hezam F, Nur O, Mustafa M. Synthesis, structural, optical and magnetic properties of NiFe2O4/MWCNTs/ZnO hybrid nanocomposite for solar radiation driven photocatalytic degradation and magnetic separation. Colloids Surf A. 2020;592:124586.
[57] Janani B, Syed A, Raju LL, et al. Synthesis of carbon stabilized zinc oxide nanoparticles and evaluation of its photocatalytic, antibacterial and anti-biofilm activities. J Inorg Organomet Polym Mater. 2020;30(6):2279–2288.

[58] Butler AM, Cushman M, MacLachlan E. The determination of ascorbic acid in whole blood and its constituents by means of methylene blue; macro-and micromethods. J Biol Chem. 1943;150(2):453–461.

[59] Janani B, Syed A, Thomas AM, et al. Designing spinel NiCr2O4 loaded Bi2O3 semiconductor hybrid for mitigating the charge recombination and tuned band gap for enhanced white light photocatalysis and antibacterial applications. J Alloys Compd. 2021;865:158735.

[60] Kokilavani S, Syed A, Thomas AM, et al. Integrating Ag2WO4 on VS4 nanoplates with synergy of plasmonic photocatalysis and boosted visible-light harvesting and its antibacterial applications. J Alloys Compd. 2021;865:158810.

[61] Kirankumar VS, Sumathi S. Photocatalytic and antibacterial activity of bismuth and copper co-doped cobalt ferrite nanoparticles. J Mater Sci Mater Electron. 2018;29(10):8738–8746.

[62] Mao Z, Xie R, Fu D, et al. PAN supported Ag-AgBr@Bi20TiO32 electrospun fiber mats with efficient visible light photocatalytic activity and antibacterial capability. Sep Purif Technol. 2017;176:277–286.

[63] Aggrawal S, Chauhan I, Mohanty P. Immobilization of Bi2O3 nanoparticles on the cellulose fibers of paper matrices and investigation of its antibacterial activity against E. coli in visible light. Mater Express. 2015;5(5):429–436.