



Synthesis, Characterization and Photocatalytic Properties of $(\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3)$ Perovskite-Like Nanoparticles Synthesized by Co-Precipitation Method

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ABSTRACT

Potassium and barium doped perovskite nanoparticles ($\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$) have been synthesized using the co-precipitation process. The synthesized powders were calcined at 400°C and then different portions were separately tempered at annealing temperatures of 400, 600, 700 and 800°C for 4 hours each. The resultant nanopowders were then characterized using scanning electron microscopy (SEM) and were observed to be nanorods at high annealing temperature. Powder X-ray diffraction (XRD) showed that the powders crystallized in rhombohedral R3c lattice. Diffuse reflectance spectroscopy (DRS) showed that the materials are all visible light active with materials annealed at higher temperatures displaying higher absorption. Fourier transform infrared spectrometer (ATR-FTIR) was used to analyse the surface structure of the powder particles. The photodegradation efficiency of the dye was found to increase with an increase in irradiation time and annealing temperature having percentage removal of 29.9, 45.4, 59.1 and 65.7% for the powders annealed at 400, 600, 700 and 800°C respectively after 120 minutes of visible light irradiation, which makes them suitable for photodegradation applications. Addition of 1M peroxide (H_2O_2) was found to improve the performance of the powders very significantly with the powder annealed at 800°C having the best activity.

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INTRODUCTION

Perovskite-like materials, with the ABO_3 structure are widely investigated because of their fascinating properties which makes them useful for application in piezo and pyroelectric [1], photocatalytic [2], spintronic and memory devices [3]. They also display photocatalytic properties [4] which make them useful for applications in environmental remediation. The structure provides a robust basic skeleton with broad space for the mixture of elemental compositions and variation of electronic band structures in nanomaterials [5][6][7].

Due to the fact that the released dyestuff from industries used in textile materials has become one of the environmental problems. Several methods have been employed to lessen or eliminate these dyes from industrial coloured wastewater. Among them, photocatalysis is recognized as one of the viable alternatives that can be used to abate the increase in environmental danger caused by the release of dyes through industrial wastewater [4]. Studies on barium doped bismuth ferrite (BiBaFeO_3) nanoparticles have stimulated an extensive research on the modification, preparation and application of

perovskite-like semiconductors for photodegradation of organic waste products, due to its narrow bandgap energy of (1.79 eV) [8]. Studies have revealed that bismuth ferrite BiFeO_3 (BFO) and BFO related nanopowders are capable of exhibiting a good deal of photocatalytic activities [9] [10]. Orthoferrites as well, have shown promise in this area. The synthesis conditions (annealing temperature) have been shown to influence the magnetic, structural as well as photocatalytic properties of the materials [11]. The photocatalytic degradation of toluene and benzene using Ba doped BFO under visible light irradiation has been reported by Soltani *et al.* [12]. The material showed a photodegradation efficiency of 97% after 60 min of irradiation. The photoactivity of Ba and Na/K doped BFO have also been recently reported for methylene blue photodegradation. The materials have been synthesized via the sol gel method and was able to degrade most of the methylene blue present after 2 hours of irradiation [13].

The present work deals with the synthesis, characterization and photocatalytic properties of ($\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$) perovskite-like nanoparticles using co-precipitation method.

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MATERIALS AND METHOD

Materials

All the chemicals used for the preparation of $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ nanoparticles are analytical grade reagents and were used without any further treatment. Ferric nitrate nonahydrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ (98%), barium nitrate $[\text{Ba}(\text{NO}_3)_2]$ (99%), bismuth nitrate pentahydrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ (97%), potassium nitrate $[\text{KNO}_3]$ (99%), 30% H_2O_2 , 30% ammonia solution $[\text{NH}_3]$, sodium dodecyl sulfate (SDS) $[\text{NaC}_{12}\text{H}_{25}\text{SO}_4]$ as surfactant were used as received without further purification. Methylene blue dye $[\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}]$ was used for photocatalytic degradation study. Distilled water was used throughout the work.

Preparation of Photocatalysts

Powders of $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ were synthesized using the co-precipitation route as reported by Ghasdi and Alamdari [14]. In this method, stoichiometric proportions of $\text{Ba}(\text{NO}_3)_2$ (1.0454 g) (0.0063 mol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (5.82 g) (0.0119 mol), KNO_3 (0.40 g) (0.0039 mol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8.08 g) (0.020 mol) were dissolved in 100 ml of distilled water in a beaker until a homogeneous solution was formed. This was followed by addition of 5 g of SDS then few drops of freshly prepared 30 % ammonium hydroxide (NH_3) solution in order to adjust the pH at 7. Stirring and heating process continued at 90°C until white precipitates are form. The residue was filtered and washed, dried at 120°C for 6 hours in an oven. The powder obtained was then pre-calcined at 400°C and annealed at different temperatures of 600, 700 and 800°C for 4 hours in a Muffle furnace.

Evaluation of Photocatalytic Activity

The photocatalytic activity of $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ nanopowders were determined in a fabricated "continuous stir tank photoreactor" (CSTP) on a magnetic stirrer plate for the degradation of methylene blue dye solution. A 10 mg/L of the dye was prepared and the maximum wavelength absorbance was measured ($\lambda_{\text{max}} = 664 \text{ nm}$). After 20 min of exposure in the dark, the suspension (using 20 mg of the catalyst) was irradiated for 120 min and samples were taken for analysis at a time interval of 20 min using a 60W IP65 visible light lamp which was placed at a distance of 20 cm from the top of the beaker. The absorbance's of all the samples was measured using the UV-vis spectrophotometer (Agilent Technology, CARY series 300). The following equation was used for the calculation of the

photodegradation efficiency of the methylene blue dye:

$$\% \text{ efficiency} = \frac{C_0 - C}{C_0} \times 100 \dots\dots\dots (1)$$

where C_0 = the initial dye concentration, and C = the concentration of the dye.

The effect of peroxide (30 %) (three drops) addition on photodegradation efficiency of the dye was also monitored at intervals of 20 min for 120 min. using 20 mg each of the powders.

Characterization of the Nanomaterials

The powders were characterized using powder x-ray diffraction (PXRD) to determine the lattice structure as well as the crystallite sizes of the particles by using the Scherer equation. Scanning electron microscopy (SEM) was used to study the morphology of the crystallites. Fourier-transform infrared spectroscopy (FTIR) was used to analyse the surface structure of the crystallites and diffuse reflectance spectroscopy (DRS) was used to determine the visible light activities of the powders. Photocatalytic degradation of MB dye was evaluated using UV-VIS spectrophotometer (Agilent Technology, CARY series 300).

RESULTS AND DISCUSSION

The samples were labelled as BK2BFO followed by the temperature at which the powder was annealed.

X-ray Diffraction Analysis (XRD)

The structural properties of $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ nanomaterials were analyzed by powder X-ray diffraction (PXRD) machine using the $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) on Rigaku ultima IV X- ray diffractometer at 2θ angles from 10° to 80° . From the PXRD patterns (Figure 1), nucleation clearly had already begun at 400°C with peaks belonging to mixed oxides of the perovskite precursors, but as the annealing temperature increased, at 600°C , the peaks for the mixed oxides disappears and fully formed perovskite peaks are observed. At 700°C the peaks become narrower with increased intensity, indicating an increased in crystallite sizes and crystallinity. The appearance of tiny impurity peaks (indicated by *) at 13° and 17° for samples annealed at 800°C might be an indication of a phase separation phenomenon. The peak patterns show that the powders have crystallized in a rhombohedral perovskite structure.

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ATR - FTIR Spectra

The ATR-FTIR spectra of the powders were collected using a PerkinElmer Spectrum 100 Fourier spectrometer. From the results obtained (Figure 2), the appearance of absorption peaks between 850 and 1350 cm^{-1} is attributed to the powdered crystals due to adsorbed water molecules on the surface of the crystallites. The peaks located around 600 cm^{-1} could be attributed to the Fe-O or Bi-O and other M-O stretching bands as reported by Hu *et al.* [15]. The decrease in absorption peaks at this region is as a result of the incorporation of more of the metal oxides as annealing temperature increased until they are fully incorporated into the perovskite structures at 700 °C in agreement with the results of the XRD.

Morphology

The SEM images of the crystallites were recorded using the JEOL/EO Version 1.0 (JSM-6610) microscopy. The results are shown in figure 3 - 6. The SEM micrographs clearly showed the influence of annealing temperature on the morphology of the powders. As can be seen the crystallite sizes increase with increase in annealing temperature from 400 to 800 °C. This observation agrees with the increase in peaks intensity of the PXRD patterns with increase in temperature. The particles were heavily aggregated and polycrystalline at the temperatures 400 and 600 °C. When the annealing temperature was increased to 700 °C however, the particles grew into a tube-like shape with few nanorods. When the annealed temperature was further increased to 800 °C, only tube-like particles were observed with varying size.

UV-Vis DRS Spectrum

Figure 7 shows the diffuse reflectance spectra of the powdered samples. The absorption edges and band gaps were determined from the diffuse reflectance spectra of the powders measured using UV-Vis spectrophotometer (Shimadzu UV-2450). The absorption spectrum shows that the powders can absorb considerable amounts of visible light, indicating that the powders could be a kind of visible-light-driven photocatalytic materials. The

steep shape of the spectra for all the samples indicates that the visible light absorption was due to the electronic transition from the valence band (VB) to conduction band (CB) ($\text{O}^{2-} 2p \rightarrow \text{Fe}^{3+} 3d$) in crystallite lattice as reported by Wang *et al.* [16]. The band gap of the powders was determined by the equation $E_g = 1239.8/\lambda$ [17], where E_g the band gap energy (eV) is and λ (nm) is the wavelength of the absorption edges in the spectra. The calculated band gaps of the powders are 2.09, 2.04, 2.03 and 2.01 eV for 400, 600, 700 and 800 °C respectively. The powder annealed at 800 °C was found to display the smallest band gap energy of 2.01 eV, which was confirmed to be the most active one with the highest percentage (65.7 %) of methylene blue dye removal after 120 minutes.

Photocatalytic Activities

The photocatalytic activity of the powders was analyzed and evaluated as shown in Figure 8. From these results, it can be seen that all the powders were able to adsorb water molecules thereby lowering the concentration of the dye. The photodegradation efficiency of the dye increased significantly with an increase in irradiation time and annealing temperature. Powders annealed at higher temperatures (700 °C and 800 °C) showed higher photocatalytic activity. The percentage removal of the dye was found to be 29.9, 45.4, 59.1 and 65.7 % for the powders annealed at 400, 600, 700 and 800 °C respectively after 120 minutes of irradiation, which makes them suitable for photodegradation application.

Effect of hydrogen peroxide (H_2O_2) addition

Figure 9 shows the effect of hydrogen peroxide (H_2O_2) addition to the reaction mixture. Careful observation of the effect of hydrogen peroxide addition (H_2O_2) shows that addition of H_2O_2 increases the number of radical species which are believed to be responsible for the degradation of the dye; and subsequently increases the photocatalytic performance of the powders. The powders annealed at 700 °C and 800 °C were found to be more active.

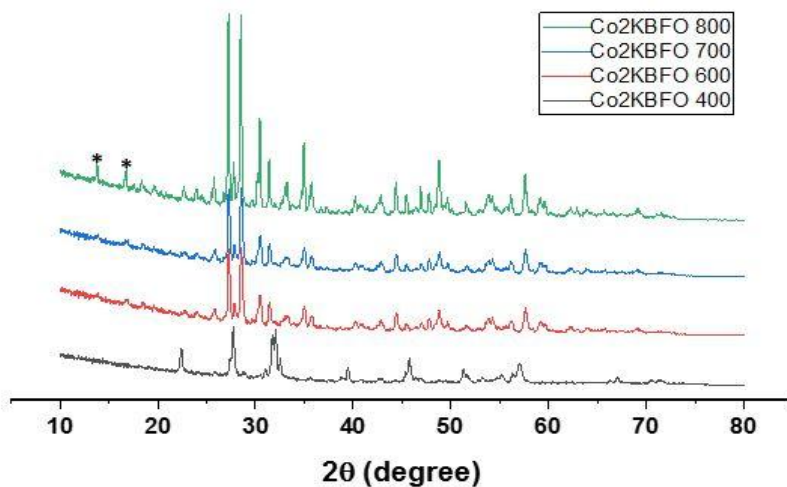


Figure 1: PXRD diffractogram of Bi_{0.6}K_{0.2}Ba_{0.2}FeO₃ nanoparticles

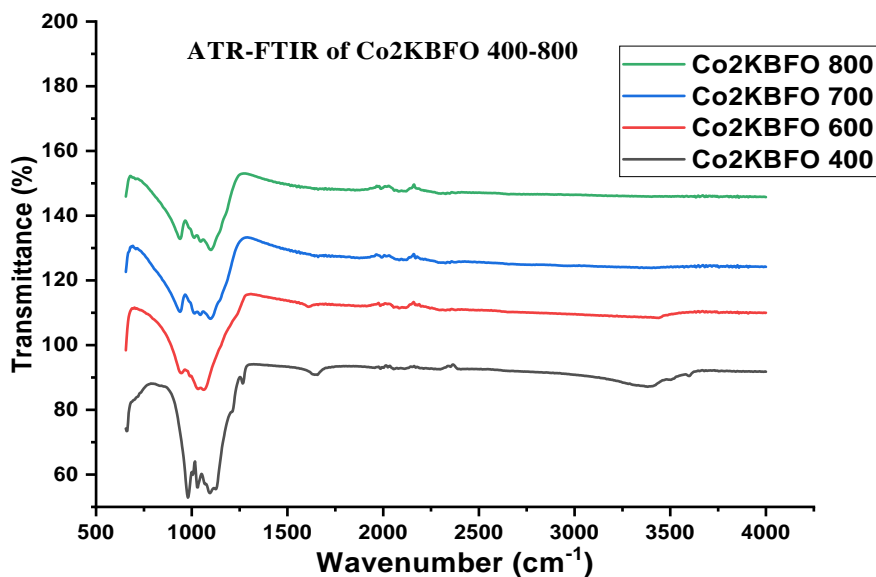


Figure 2: ATR - FTIR spectrum of Bi_{0.6}K_{0.2}Ba_{0.2}FeO₃ nanoparticles

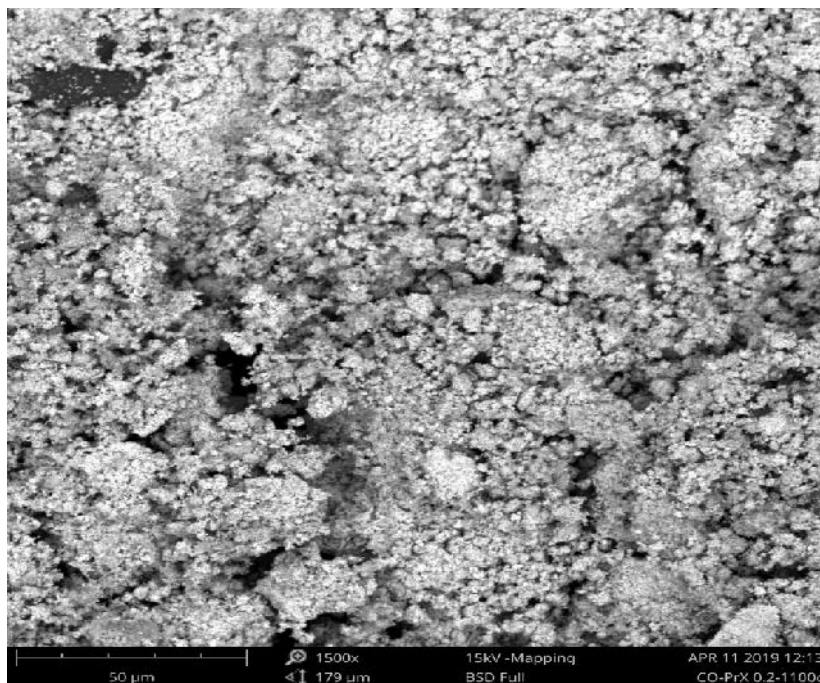


Figure 3: SEM image of $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ nanoparticles annealed at 400 °C

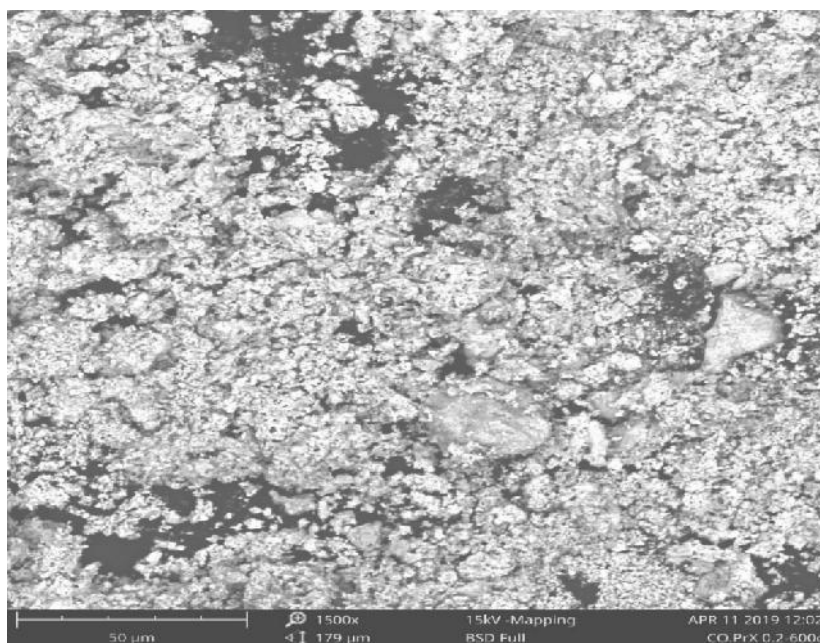


Figure 4: SEM image of the of $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ nanoparticles annealed at 600 °C

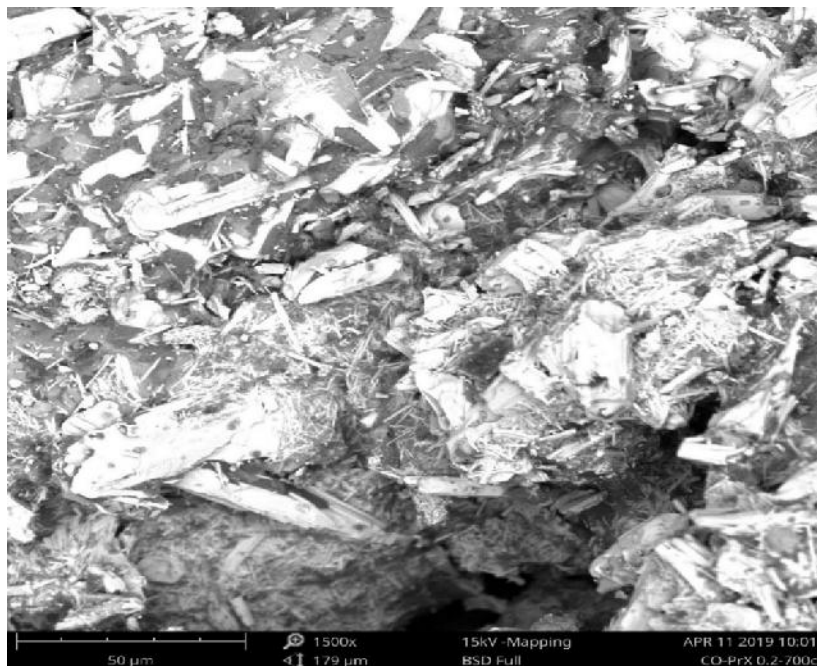


Figure 5: SEM image of $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ nanoparticles annealed at 700 °C



Figure 6: SEM image of $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ nanoparticles annealed at 800 °C

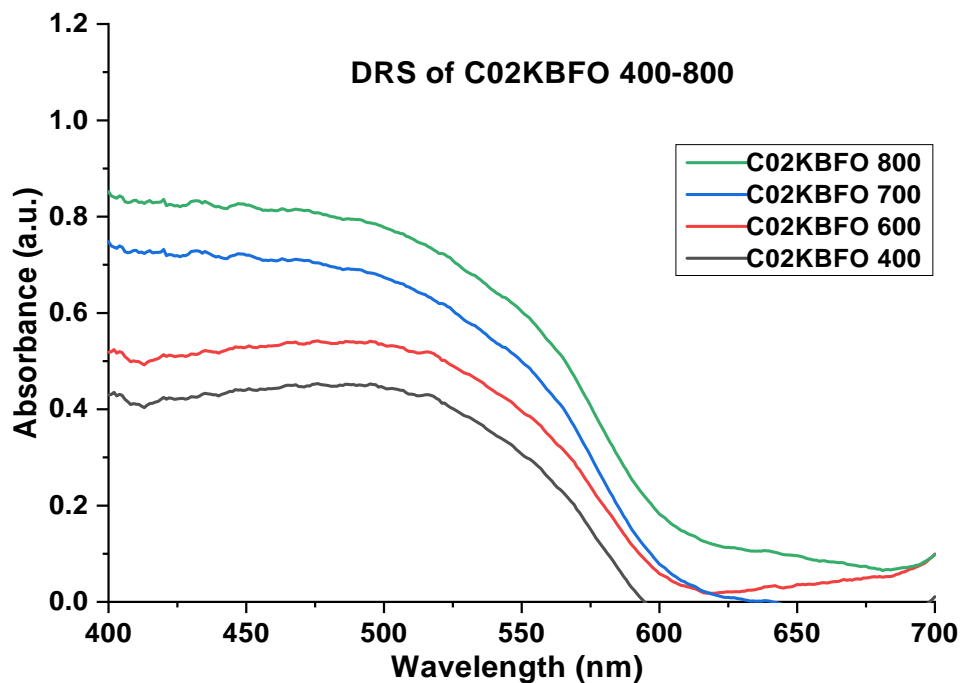


Figure 7: UV-Vis DRS spectrum of $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ nanoparticles annealed at 400, 600, 700 and 800°C

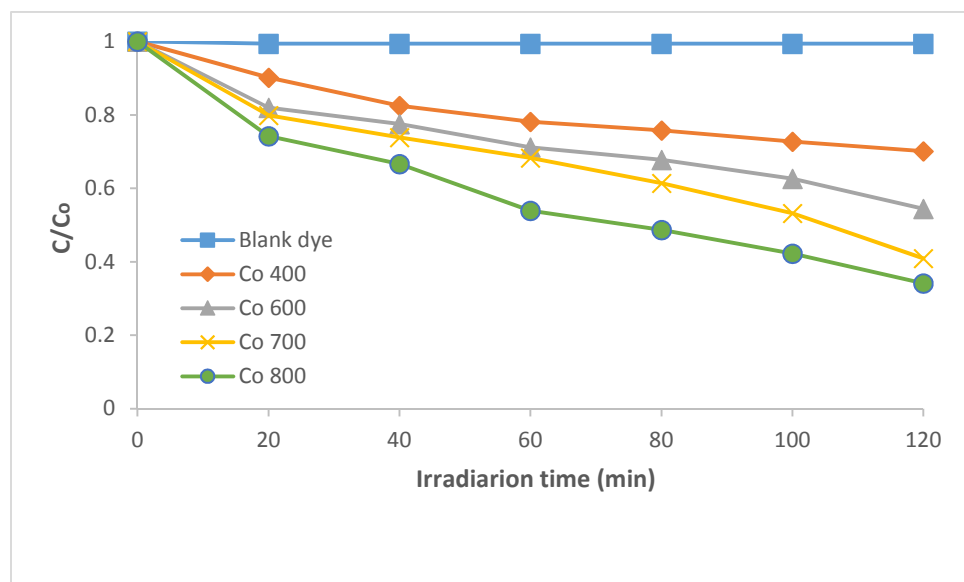


Figure 8: Photodegradation rate of methylene blue dye with $\text{Bi}_{0.6}\text{K}_{0.2}\text{Ba}_{0.2}\text{FeO}_3$ nanoparticles

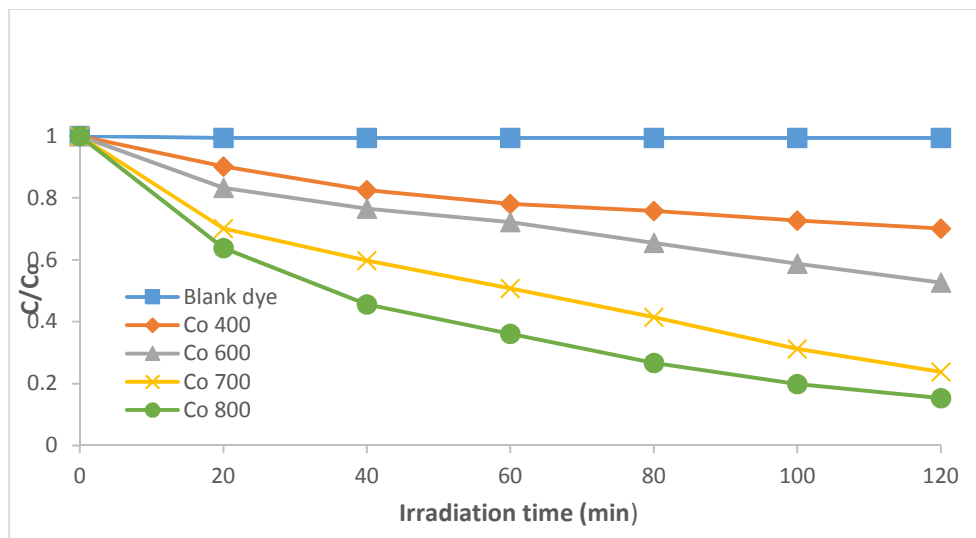


Figure 9: Effect of peroxide (H_2O_2) addition on the photodegradation efficiency of methylene blue with $Bi_{0.6}K_{0.2}Ba_{0.2}FeO_3$ nanoparticles

CONCLUSION

In conclusion, perovskite-like material ($Bi_{0.6}K_{0.2}Ba_{0.2}FeO_3$) annealed at 400, 600, 700 and 800 °C were successfully synthesized via co-precipitation method and characterizes by XRD, SEM, DRS and FTIR. From the XRD data, all powders were found to have rhombohedral perovskite structures. The morphology, size and annealing temperature had remarkably affected the photocatalytic activities of nanopowders. The photodegradation efficiency of the methylene blue dye was calculated to be 29.9, 45.4, 59.1 and 65.7 % for the powders annealed at 400, 600, 700 and 800 °C respectively after 120 minutes of irradiation, which makes them suitable for photodegradation applications.

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