Cu$^{2+}$ doped nickel spinel ferrites (Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$) nanoparticles loaded on CNTs for degradation of crystal violet dye and antibacterial activity studies

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ABSTRACT

In the current work, Cu-doped Nickel ferrites (Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$) integrated on carbon nanotubes (CNTs) were synthesized by wet-chemical method. The synthesized composite Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs along with pristine NiFe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ were characterized by X-rays diffraction (XRD), Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). XRD data confirmed the synthesis of NiFe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ with tetragonal lattice structure. The crystallite size varied from 26 to 35 nm with the substitution of Cu$^{2+}$ ions in NiFe$_2$O$_4$ while Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs showed moderate crystallite size of 32 nm. SEM analysis showed spherical nanoparticles of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ which transformed to aggregated blocks on combining with high surfaced CNTs. The conductivity of pure NiFe$_2$O$_4$ raised up to 0.028 and 0.22 S/m upon modification to Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs, respectively. Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs showed maximum degradation efficiency (92.9%) for CV, which was 1.4 and 1.8 folds higher than NiFe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$, respectively.

1. Introduction

The discovery of exciting photocatalytic properties of TiO$_2$ in 1972 by Fujishima [1] laid the foundation for new era of photocatalysis, where semiconductor photocatalyst can be used for environmental remediation. Since this discovery, many new semiconductor photocatalysts have been developed, and used to overcome environmental pollution and energy crisis [2–5]. Recently, photodegradation of organic pollutants by semiconductors, in the presence of earth-abundant solar radiations, has become much popular among material scientists [2,6,7]. The mechanism of photocatalysis involves the photogeneration of redox species, their transport, meanwhile avoiding the reunion, adsorption of pollutants and redox reactions [8–10]. Another important concern
during photocatalysis is to maximize the absorption window of semiconductor working under solar radiations. Henceforth, stable and solar light efficient photocatalysts are high in demand. Until now, many light active photocatalysts such as CuS [11], MnO2 [12], Ag@WO3 [13], V2O5 [14], NiO2−TiO2 [15], Gd2O3−CdO [16], etc. have been developed. Yet, low photocatalytic response limits the in-field applications of some photocatalysts [17–19]. Consequently, it is still required to develop more and more efficient photocatalysts for the future environmental applications.

In the recent years, spinel ferrites have been explored as excellent photocatalyst by the researches due to their outstanding ability to degrade organic pollutants [19–23]. Generally, spinel ferrites are represented by the formula i.e. MFe2O4, where M is a metal representing Cu, Ni, Mg or Mn. M and Fe being metal ions occupy the tetrahedral and octahedral positions of crystal lattice [24]. Depending on the kind of application, spinel ferrite fosters exceptional properties like good recyclability, monodispersity and high adsorption ability [25]. Doping of spinel ferrites by other metal ions as mixed ferrites is considered an effective engineering strategy to increase the photocatalytic activity of nanostructures and improve the interaction among pollutants and photocatalytic surface [25–28]. Sharma et al. [29] studied La/Cu/Zr TNPs (trimetallic nanoparticles) as highly active photocatalysts against the degradation of ampicillin. Phor et al. [30] synthesized Mg1−xZnxFe2O4 and explored its photocatalytic properties. Paramesh et al. [31] investigated Ni1xZnx−0.5FeO4 for photocatalytic applications. Yahya et al. [32] investigated cobalt ferrite-supported activated carbon for the removal of heavy metal ions from tannery waste water. In this report, we have doped NiFe2O4 with Cu2+ ions to synthesize Cu1−yNi1−yFe2O4 mixed ferrite because of its good ferromagnetic and photocatalytic properties and stability towards chemicals and heat. Nickel ferrites have been widely used in electronic gadgets.

Carbon materials as supporting surface can improve the dispersion of nanoparticles, increase loading rate and surface area for the heterogeneous redox reactions [2,33,34]. Carbon nanotubes (CNTs) as a graphitic analogue of carbon family consists of benzene rings that provide an aromatic surface (rich in π electrons) for proper interaction towards metals and organic pollutants [33]. Electrical and mechanical properties of CNTs have made them a suitable candidate to be used in semiconductor photocatalysis [35]. For example, TiO2/CNTs [36], ZnO/CNTs [37], In2S3/CNTs [38], CuFe12O19/CNTs [39], TiO2@CNTs/Fe2O4 [40], etc. The heterojunction among nanoparticles and CNTs provides faster transport to photogenerated electrons from the conduction band (CB). In a similar way, the high surface area of CNTs provides stabilization to charge and prolong their recombination [41]. Furthermore, the impregnation of ferrites over CNTs prevents the aggregation of these magnetic nanoparticles in an aqueous solution [42].

Keeping in view the benefits of CNTs, we have synthesized Cu1−xNi1−xFe2O4/CNTs through a combined approach of co-precipitation and ultrasonication. The purpose of this research is to evaluate and compare the efficiency of NiFe2O4, Cu1−xNi1−xFe2O4 and Cu1−xNi1−xFe2O4/CNTs for photodegradation of an organic dye, crystal violet (CV). CV dye possesses poisonous nature and is mainly used in the textile industries. It causes very critical eye damages and is dangerous for the aquatic life. So, its removal from wastewater is very important by photodegradation.

The characterization of synthesized materials was done with XRD, FE-SEM, FT-IR and I–V.

2. Experimental work

2.1. Chemicals

Nickel Chloride (NiCl2.6H2O), Copper Acetate (Cu(COOCH3)2), Iron Nitrate (Fe(NO3)2), Aqueous Ammonia (NH4OH) and Carbon nanotubes (CNTs). All chemicals were of analytical grade and procured from Sigma Aldrich; Germany. Chemicals were used as received without any further processing.

2.2. Synthesis of NiFe2O4 and Cu1−xNi1−xFe2O4

Synthesis of un-doped and Cu doped NiFe2O4 was carried through co-precipitation procedure reported elsewhere [24]. Briefly, 200 mL of NiCl2.6H2O; 0.1, 20 mL of (Cu(COOCH3)2); 0.1 and 200 mL Fe(NO3)2; 0.2 M were mixed in 500 mL beaker and stirred on a hot plate at 50°C. pH of solution was increased upto 10 with aqueous ammonia. Solution was allowed to stir for 4 h and then left under static condition for overnight. Next, precipitates were collected and washed to the neutral pH. Obtained precipitates were dried at 60°C and grinded to smooth powder. At the end, powder was annealed at 900°C to obtain NiFe2O4 and Cu1−xNi1−xFe2O4 (x = 0.1).

2.3. Synthesis of Cu1−xNi1−xFe2O4/CNTs

To synthesize nickel doped spinel ferrite nanocomposite with CNTs, ultrasonication means was used as cost-effective approach. 90 mg of Cu1−xNi1−xFe2O4 was added into 20 mL distilled water and ultrasonicated for 2 h. Diluted solution of CNTs (1 mg/mL) was then mixed with Cu1−xNi1−xFe2O4 dispersion and mixture was ultrasonicated for 3 h at 50°C. Obtained composite was dried at 60°C and stored for photocatalytic applications. The whole procedure of synthesis of Cu1−xNi1−xFe2O4 and Cu1−xNi1−xFe2O4/CNTs is schematically illustrated in Figure 1.
2.4. Characterization

The physiochemical characterizations of NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs were carried out under various techniques. Crystal phase of synthesized materials was studied by Bruker D8 X-rays diffractometer. Morphological analysis was carried under JEOL-JSM-7401F FE-SEM. Functional groups were checked by PerkinElmer FT-IR spectrometer. Current–Voltage characteristic was determined by KEITHLEY voltage-source meter. The photocatalytic study was done on Carry 60 UV–Visible spectrophotometer in the range of 200–800 nm.

2.5. Photocatalytic measurements

Photocatalytic potential of each synthesized material was measured by the degradation of CV dye under the natural sunlight. The photocatalytic experiment was performed in April 2021 at 33°C temperature. For a typical experiment, 10 mg of photocatalyst was taken in 50 mL aqueous solution of CV having 5 ppm concentration. Before irradiation, the catalyst-dye suspension was stirred under dark for half an hour in order to establish the adsorption–desorption equilibrium. Next, the suspension was placed in sunlight for 90 min. The temperature of the photocatalytic medium was maintained by the cold-water supply. After each 15 min, 4 mL of dye suspension was removed from the photocatalytic medium and photocatalyst was extracted with the help of magnet and filtration. The absorption of CV was measured by UV–Visible spectrophotometer at a wavelength of 586 nm.

3. Results and discussions

3.1. X-rays diffraction analysis

XRD spectra of undoped and Cu-doped NiFe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs nanocomposite are represented in Figure 2. Pure NiFe$_2$O$_4$ showed prominent peaks at 18.79°, 30.73°, 35.90°, 37.65°, 43.64°, 54.09°, 57.83°, 63.32°, 71.87°, 75.01° and 75.81°. The characteristic peaks correspond to reflections from (111), (220), (311), (222), (400), (422), (511), (440), (620), (533) and (622) plans respectively (Reference card# 00-003-0875). Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ showed almost similar reflections and no extra peaks other than aforementioned were detected which ensured the purity of samples. Peak intensity of (222) plane of Cu doped sample was increased while intensity of peaks due to (220), (400), (440) planes were decreased in comparison to that of the undoped sample. This decrease in peak intensity might be due to the variation in electron density and point defects. The findings confirmed tetragonal crystal structure of spinel ferrites (space group; I41/amd). Similar diffraction pattern for Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ was observed by Rao et al. [43] and Khalifeh et al. [44]. The sharpness of peaks indicates good crystallinity of synthesized nanostructures. When Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ was combined with carbonaceous material (CNTs) a broad bump near 25.70° was observed corresponding to CNTs. Addition of CNTs has no effect on the crystal lattice of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$. The lattice parameters $a$, $b$, $c$ and cell volume for NiFe$_2$O$_4$ were 5.84, 5.84, 8.63 and 294.79 Å, respectively. While Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ showed slightly higher lattice parameters with shifting of peaks toward lower 2θ values. The results indicate Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ has crystal defects. The average crystallite size ($D$) for all samples was calculated by Debye–Scherrer equation as given below [10]:

$$D = \frac{n\lambda}{\beta \cos \theta}$$

where $\lambda$, $\beta$ and $\theta$ represent wavelength of X-rays used (1.54 Å), full width at half maximum and diffraction angle. Crystallite size of pure NiFe$_2$O$_4$ was 26.97 nm that was increased to 35.46 nm in Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$. This is likely due to the fact that the substitution of Cu$^{+2}$ in NiFe$_2$O$_4$ caused lattice expansion. However, the addition of CNTs to Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ caused a decrease in crystallite size to 32.01 nm.

3.2. FE-scanning electron microscopy analysis

To determine the shape and surface morphology of NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs, low and high magnification FE-SEM micrographs are shown in Figure 3(a–f). SEM image of NiFe$_2$O$_4$ at 1000× and 2000× magnification clearly showed spherical nanoparticles (Figure 3(a,b)). Slight aggregation can be seen in micrographs due to high surface energy of individual particles. Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ showed same morphology as that of NiFe$_2$O$_4$, indicating Cu$^{+2}$ substitution in NiFe$_2$O$_4$ has no effect on its morphology (Figure 3(c,d)). Figure 3(e,f) demonstrates the presence of thread-like CNTs in a fabricated sample. Unlike to other samples, Cu$_x$Ni$_{1-x}$Fe$_2$...
Figure 2. XRD spectrum of NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs.

Figure 3. SEM micrographs of NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs taken at high and low magnifications.
Figure 4. FTIR spectra of NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs.

O$_4$/CNTs showed most merged particles giving up the appearance of block-like structure that may be caused by the larger surface area of CNTs. This large surface area of CNTs will provide more active sites to pollutants to get adsorbed for degradation, with concomitant faster transport to photogenerated charged species. Hence, higher photocatalytic activity can be expected from Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs.

3.3. Fourier transform infrared spectroscopy studies

FT-IR spectra for pure and mixed spinel ferrites along with CNTs nanocomposite were recorded in the range of 400–4000 cm$^{-1}$. Spinel ferrites usually show their characteristic bands for ionic vibrations in the range of 400–1000 cm$^{-1}$ [45] as shown in Figure 4. Typically, two kinds of Metal–Oxygen (M$\leftrightarrow$O) vibrational bands are present in FT-IR spectra of spinel ferrites [46]. The bands near $\sim$ 400 cm$^{-1}$ are aroused by $M_{\text{octahedral}}$$\leftrightarrow$O stretching, while bands around $\sim$ 500 cm$^{-1}$ represent $M_{\text{tetrahedral}}$$\leftrightarrow$O stretching [45,47]. In Figure 4, NiFe$_2$O$_4$ showed two lower bands at 449 and 489.7 cm$^{-1}$, and one highest band at 540.8 cm$^{-1}$ that can be assigned to $M_{\text{octahedral}}$$\leftrightarrow$O and $M_{\text{tetrahedral}}$$\leftrightarrow$O vibrations, respectively. In Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$, a new band appeared at 460.7 cm$^{-1}$ and remaining bands shifted towards lower wavenumber at 438.8, 459 and 523 cm$^{-1}$, respectively [48]. These results suggest the successful inclusion of Cu$^{2+}$ in the crystal lattice of NiFe$_2$O$_4$. The FT-IR spectra of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs represented similar four bands as present in unsupported Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$. However, change in peak intensities and peak shifting are ascribed to crystalline field effect and change in lattice strain due to the introduction of graphitic components (CNTs) [49].

Figure 5. Current–Voltage plots for NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs taken at ambient temperature.
3.4. Current–voltage measurements

The current–voltage behaviour of synthesized samples is shown in Figure 5. Clearly, all samples showed ohmic response during I–V measurements. The slope obtained by graphs of "I vs. V" gave out the value of resistance for each sample that was used to calculate the resistivity of corresponding undoped NiFe2O4, Cu-doped NiFe2O4 and CuNi1−xFe2O4/CNTs by the following equation [24]:

$$\rho = \frac{RA}{l}$$  \hspace{1cm} (2)

where "\(\rho\)" denote resistivity of the material, "\(R\)" is the resistance obtained from slope, and "\(A\)" and "\(l\)" are the area and thickness of the pellet used for IV measurements. The resistivity values for NiFe2O4, CuNi1−xFe2O4 and CuNi1−xFe2O4/CNTs were 35.68, 32.70 and 4.42 Ω m, respectively. The reciprocal of resistivity gave conductivity values. DC-conductivity for NiFe2O4 was 0.028 S/m that was increased to 0.0305 S/m in CuNi1−xFe2O4. While CuNi1−xFe2O4/CNTs showed highest value of conductivity i.e. 0.22 S/m (Figure 6). This exceptional increase in conductivity is due to the generation of new energy excitations due to the presence of Cu2+ ions in the peak position which signifies the degradation of aromatic chromophores is mainly due to photocatalysts [50]. The increase in photocatalytic efficiency from 48.9% to 63.4% is likely due to the presence of Cu2+ contents in CuNi1−xFe2O4 that facilitates the electronic excitations due to the generation of new energy levels in the band gap structure host [51,52]. Also, Cu2+ acts as a trapping centre for photoinduced electrons and therefore prolongs the recombination of electron–hole pair [53,54]. Lengthening of electron–hole life span increased the number of charged species per unit time at the surface of photocatalyst, which in turn speed up the photodegradation process. In addition, the marked increase in photocatalytic activity (92.9%) of CuNi1−xFe2O4/CNTs was observed due to the synergy effect by the existence of the Cu2+ and CNTs in CuFe2O4. Besides the factors contributed by substitution of Cu2+, addition of CNTs creates the heterojunctions among CuNi1−xFe2O4 and CNTs that give rise to electronic interphase among the two [55]. Visible in Figure 7(c), another influence on CuNi1−xFe2O4/CNTs photocatalytic activity is the higher adsorption capability contributed by attraction among the aromatic parts of dye and CNTs [56]. DRS UV visible spectroscopy analysis was performed for the synthesized photocatalysts.

The band gap energy of prepared photocatalysts is exhibited in Figure 8.

3.5. Photocatalytic study

The photocatalytic efficiency of NiFe2O4, CuNi1−xFe2O4 and CuNi1−xFe2O4/CNTs was measured and compared for degradation of an aqueous solution of CV under the direct sunlight at the catalytic amount of 10 mg/50 mL. After predetermined intervals, a fraction of dye volume was removed from mixture and its concentration was determined under the UV–Visible spectrophotometer. The UV–Visible time-dependent profiles for degradation of CV in the presence of NiFe2O4, CuNi1−xFe2O4, CuNi1−xFe2O4/CNTs are shown in Figure 7(a–c).

Referring to Figure 7, it is clear that CuNi1−xFe2O4/CNTs showed the maximum decline in the peak intensity at 586 nm under 90 min of solar light irradiation. CuNi1−xFe2O4/CNTs exhibited highest photodegradation efficiency compared to NiFe2O4 and CuNi1−xFe2O4 (Figure 7(d)). More accurately, 48.9%, 63.4% and 92.9% degradation were achieved in the presence of NiFe2O4, CuNi1−xFe2O4 and CuNi1−xFe2O4/CNTs. Furthermore, there was no hypsochromic shift in the peak position which signifies the degradation of aromatic chromophores is mainly due to photocatalysts [50]. The increase in photocatalytic efficiency from 48.9% to 63.4% is likely due to the presence of Cu2+ contents in CuNi1−xFe2O4 that facilitates the electronic excitations due to the generation of new energy levels in the band gap structure host [51,52]. Also, Cu2+ acts as a trapping centre for photoinduced electrons and therefore prolongs the recombination of electron–hole pair [53,54]. Lengthening of electron–hole life span increased the number of charged species per unit time at the surface of photocatalyst, which in turn speed up the photodegradation process. In addition, the marked increase in photocatalytic activity (92.9%) of CuNi1−xFe2O4/CNTs was observed due to the synergy effect by the existence of the Cu2+ and CNTs in CuFe2O4. Besides the factors contributed by substitution of Cu2+, addition of CNTs creates the heterojunctions among CuNi1−xFe2O4 and CNTs that give rise to electronic interphase among the two [55]. Visible in Figure 7(c), another influence on CuNi1−xFe2O4/CNTs photocatalytic activity is the higher adsorption capability contributed by attraction among the aromatic parts of dye and CNTs [56]. DRS UV visible spectroscopy analysis was performed for the synthesized photocatalysts.

The band gap energy of prepared photocatalysts is exhibited in Figure 8.

3.6. Kinetic study

The photo-efficiency of prepared photocatalysts was also evaluated in terms of first-order apparent rate constant (kapp) by the following equation:

$$\ln C_t/C_0 = -k_{app}t$$  \hspace{1cm} (3)

where "\(C_t/C_0\)" denotes the ratio of dye concentration and "\(t\)" is the corresponding time. As expected, the decay of \(C_t/C_0\) vs. "\(t\)" was increased in order of NiFe2O4 > CuNi1−xFe2O4 > CuNi1−xFe2O4/CNTs (Figure 9(a)). Figure 9(b) shows graph of \(-\ln C_t/C_0\) vs. "\(t\)". The curve among \(-\ln C_t/C_0\) and "\(t\)" was subjected to linear fitting using Origin software to determine the value of kapp equal to the slope of straight line. The value of kapp was maximum for CuNi1−xFe2O4/CNTs (0.0261 min⁻¹), moderate for CuNi1−xFe2O4 (0.0087 min⁻¹) and minimum for NiFe2O4.
In addition, the recycling performance of Cu$_{x}$Ni$_{1-x}$Fe$_2$O$_4$/CNTs was analysed to predict its feasibility for practical applications. For this purpose, Cu$_{x}$Ni$_{1-x}$Fe$_2$O$_4$/CNTs was recovered after each photocatalytic test by centrifugation, washed with distil water and dried at 60°C. The recovered photocatalyst was reapplied for degradation of CV under the same conditions as mentioned beforehand. Figure 10 shows the recycling
Figure 9. Kinetic study of photocatalytic degradation of MB under NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs; (a) Plot of $C_t/C_0$ vs. time, (b) linear fitting plot of $-\ln (C_t/C_0)$ vs. time and (c) bar graph of comparative $k_{app}$ values.

Table 1. Comparison of photocatalytic performance of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs photocatalyst with other ferrite materials under solar light irradiation for the photodegradation of CV dye.

| Photocatalyst                  | Dye | Percentage degradation (%) | Reference |
|-------------------------------|-----|---------------------------|-----------|
| Gd doped BiFeO$_3$            | CV  | 84.5                      | [57]      |
| CaFe$_2$O$_4$                 | CV  | 90                        | [58]      |
| CuFe$_2$O$_4$                 | CV  | 90                        | [59]      |
| MgFe$_2$O$_4$/ZnS             | CV  | 91                        | [60]      |
| Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs | CV  | 92.9                      | Present work |

Table 1. Comparison of photocatalytic performance of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs photocatalyst with other ferrite materials under solar light irradiation for the photodegradation of CV dye.

results of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs for four consecutive cycles. No considerable decline in photocatalytic activity was observed after each experimental run. Results confirmed that Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs is regeneratable and quite stable to be applied again for photocatalytic degradation.

3.7. Plausible mechanism

The superior photocatalytic activity of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs is determined with the help of a plausible mechanism. Represented in Figure 11, under the solar light, electrons from CB of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ get excited to higher energy levels, leaving the positive holes behind. Cu$^{+2}$ contents in Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ trap the electrons that are then captured by highly conductive surface of CNTs. These electrons react with the oxygen molecules (O$_2$) molecules on the surface of photocatalyst and produce...
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Figure 11. Plausible mechanism for photocatalytic degradation of MB in presence of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ /CNTs.

superoxide radical (•O$_2^-$). Holes (h$^+$) from the CB react with H$_2$O molecules and generate hydroxide radicals •OH$^-$. Primary reactive species (electrons/holes) are converted to secondary reactive species (•O$_2^-$/•OH$^-$) by the redox process. These secondary species attack the dye molecules (CV) to give CO$_2$ and H$_2$O. This whole process can be summarized in the following reactions:

$$hv + Cu_xNi_{1-x}Fe_2O_4/CNTs \rightarrow e^- + h^+$$

$$e^- \rightarrow CNTs(e^-)$$

$$e^- + O_2 \rightarrow •O_2^-$$

$$H_2O + h^+ \rightarrow •OH^-$$

$$•O_2^- + CV \rightarrow CO_2 + H_2O$$

$$•OH^- + CV \rightarrow CO_2 + H_2O$$

3.8. Bacterial activity

The bacterial activity of NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs was verified for S. aureus and P. vulgaris by varying the concentrations of synthesized nanoparticles (Figure 12). Bacteria were cultivated and transferred to 9 g/300 mL agar gel nutrient medium in a petri dish. Whatmann filter paper were cut down into small disks and dipped into the aqueous solution of nanoparticles. Later on, dipped disks were submerged into a nutrient medium. Petri dishes were incubated at 37°C for 24 h. The inhibition of bacterial growth was observed which clarifies that NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs were active nanomaterials for killing S. aureus and P. vulgaris. However, antibacterial activity of Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs was superior than NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$. Measurements of the inhibition zones and their comparative results are exhibited in Table 2. Another observation was S.
The antibacterial activity of NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs was studied by XRD, FT-IR and SEM. The effect of Cu$_x$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs was mainly contributed to the generation of reactive oxygen species (ROS) and damage to the bacterial cell membrane. Damaged membraned failed to carry the cellular contents which eventually killed the bacterial strains.

### 4. Conclusion

In summary, pure and mixed copper spinel ferrites as NiFe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ were prepared by co-precipitation route. Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs nanocomposite was prepared by ultrasonication means. The physiochemical properties of pristine NiFe$_2$O$_4$, Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs were studied by XRD, FT-IR and SEM. The effect of Cu$_{1-2}$ substitution and CNTs on photocatalytic properties of NiFe$_2$O$_4$ was studied by the photocatalytic degradation of CV under direct sunlight. The photodegradation percentage of CV for the three photocatalysts was increased in order NiFe$_2$O$_4$ < Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ < Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs which showed the sequential upgradation of photocatalytic activity upon addition of Cu$_{1-2}$ and CNTs contents, respectively. Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$/CNTs gave 92.9% degradation of CV while Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ and NiFe$_2$O$_4$ showed 63.4% and 48.9% dye removal within 90 min.

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### Disclosure statement

No potential conflict of interest was reported by the author(s).

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