# A Flower-like Cadmium Cobaltite Architecture for Efficient Degradation of Crystal Violet using a Photo-Induced Catalytic Method: Insight into the Degradation Pathway

**Samota Jayanti[1]*, Sharma Suraj[1], Prajapat Prakash[2] and Intodia Kumud[1]**
1. Department of Chemistry, Government Meera Girls College, Mohanlal Sukhadia University, Udaipur- 313001, Rajasthan, INDIA
2. Department of Chemistry, Ganpat University, Mehsana-384012, Gujarat, INDIA
*jayantisamota20@gmail.com

## Abstract

*The present study describes the potential use of cadmium cobaltite nano-flower (CCNF) as photocatalyst for the removal of organic dye. The CCNF was prepared through facile, one-pot and cost-effective hydrothermal approach. The designed CCNF was found to possess heterogeneous photocatalytic potential against the oxidative degradation of crystal violet dye taken as a model pollutant. The photocatalytic performance of CCNF was evaluated under visible light. The best photocatalytic performance was achieved under visible light with almost complete degradation (87.80%) exhibited within 2 hr of irradiation time.*

*Furthermore, the degradation efficiency of the prepared CCNF was determined in the presence and absence of quenchers and under different pH conditions. The intermediates and final products were investigated by FTIR analysis. The radical trapping studies show that holes ($h^+$), superoxide radicals ($\bullet O_2^-$) and hydroxyl radicals (•OH) were identified as the main active species in the reaction. The plausible catalytic mechanism and process were proposed. Finally, this technique can be effortlessly scaled-up for the removal of various polycyclic organic wastes that may be of potential industrial and environmental interests.*

**Keywords:** Active Species, Aromatic ring destruction, CCNF, Crystal Violet, Photocatalysis, Photo-induced Catalytic Degradation.

## Introduction

An enormous number of materials of various sources have been found in groundwater, surface, sewage and even drinking water as a significant class of organic pollutants over a couple of decades. The greatest concern is their harmful health impacts for the human and environment[3,18,27,29]. Dyes are one of the most essential classes of organic pollutants. The vast majority of organic pollutants includes dyes shown in water and are originating from a wide range of resources taking in consideration wastewater sources. All types of dyes show forthright direct influence on human health as well as show extremely high toxic activity[2,9].

Approximately 10,000 unique pigments and dyes are created per year all around the world. These dyes are enormously used in the tannery, textile and dyeing, cosmetic and paint ventures. They are chemically resistant, non-biocompatible and cancer-causing due to the presence of aromatic ring structures[1,5]. As indicated by Ecological and Toxicological Association of the Dyestuffs (ETAD) Manufacturing Industry overview, a progression of tests was led on almost 4000 dye sample and LD$_{50}$ values were found more prominent than $2 \times 10^3$ mg/kg for over 90% of dyes[4,24]. Because of toxicological, environmental and chemical perspectives, scientists are currently centering to find most suitable strategies for the treatment of textile industry effluents[21].

Crystal violet is an industrial synthetic cationic dye with applications in biological staining, dermatological specialist, veterinary medicine and dye processing. It is an individual from the tri-phenylmethane family[25]. The crystal violet effectively communicates with the negatively charged cell film surfaces in mammals and enters into cells. The excess inhalation of crystal violet dye causes numerous harmful impacts on humans such as irritation of the respiratory tracts, diarrhoea, headache, dizziness and long-term exposure that might damage the mucous membrane. Some conventional protocols adsorption, flocculation, coagulation and reverse osmosis are applied for the treatment of organic dyes[8,22,23]. In spite of the fact that this strategy was discovered successfully for the expulsion of contaminations, yet it is costly and frequently insufficient in evacuating recalcitrant compounds[10].

Recently, photocatalytic degradation has got world consideration as green innovation for the removal of contaminants from wastewater. The magnificent picture of this technique is its ability to transform the toxic dyes into harmless products[12]. Semiconductor photocatalysts have been found exceptionally relevant for compelling wastewater treatment such as photocatalytic degradation of organic dyes under UV light and visible light has been achieved through ZnO, $TiO_2$ and SnO[7]. Spinels are a significant class of material due to their catalytic and magnetic properties. Spinel cobaltites show significant catalytic activity[11].

Researchers have given considerable attention in synthesizing the cobaltite system by exploring different factors such as the precursors used, preparation methods, processing control and firing temperatures. Among the binary spinel oxides of transition metals with the general formula $MCo_2O_4$, $MFe_2O_4$ and $MCr_2O_4$ where M is a divalent cation of a d-block element, Ni, Cu and Zn cobaltites have attracted interest due to their diverse applications as oxide electrode materials, magnetic materials, thermistors and catalysts[16,17].

Photocatalytic degradation of reactive brilliant red X-3B was studied with copper cobaltite nanocomposites. Results suggested that more than 85% of reactive brilliant red X-3B was mineralized by copper cobaltite nanocomposite. The chestnut husk-like nickel cobaltite hollow microspheres investigated the adsorption of Congo red[6]. The urchin-like copper cobaltite was investigated for the degradation of methyl orange and rhodamine B dye solutions[13]. The composite of copper cobaltite/graphitic carbon nitride also reported the photocatalytic degradation of methyl orange[14].

Herein we have investigated CCNF potential for photocatalytic degradation of organic dye. The impact of different parameters like pH, the addition of quenchers on the degradation of dye using the synthesized CCNF has also been investigated. This CCNF results in an efficient photocatalyst for visible-light-driven mineralization of aqueous solution of crystal violet dye with a degradation rate of 87.80% in 2 hrs. Moreover, these lab scale tests can effortlessly scaled-up to a business scale and can resolve enormous mechanical and ecological concerns.

## Material and Methods

**Materials:** The precursors used in our experiments were of analytical grade. $Cd(NO_3)_2$ (Merck 98%), $Co(NO_3)_2$ (Merck 98%) and crystal violet (Merck 97%) were purchased from Merck and used as received.

**Synthesis of CCNF:** The binary spinel CCNF has been synthesized from precursor $Cd(NO_3)_2$ and $Co(NO_3)_2$. For the synthesis of CCNF, stoichiometry amounts of cadmium nitrate and cobalt nitrate were dissolved in separate beakers in distilled water. Then these solutions were mixed and stirred further for half an hour to obtain a mixed metal nitrate solution. The cadmium nitrate was used as Cd source and cobalt nitrate was used as Co source. The molar ratio of nitrates was fixed to be a curtained ratio of 1:2.

The 2 M NaOH solution was added continuously drop-wise into the vigorously stirred solution mixture till the pH is 10. The brown precipitate was collected and washed with distilled water (twice) and ethanol (thrice) to make it free of nitrate ions. The dried brown precipitate was calcined in a ceramic crucible in the furnace at 500°C for 5 hr[26].

$$Co(NO_3)_3(aq) + NaOH\,(aq) \rightarrow Co(OH)_3\,(cp) + NaNO_3\,(l) + H_2O \qquad (1)$$

$$Cd(NO_3)_2\,(aq) + NaOH(aq) \rightarrow Cd(OH)_2\,(cp) + NaNO_3(l) + H_2O \qquad (2)$$

$$Co(OH)_3(cp) + Cd(OH)_2(cp) + NaOH\,(l) \rightarrow CdCo_2O_4(p) + Na^+ + OH^- + H_2O \qquad (3)$$

**Degradation experiments:** The degradation of aqueous crystal violet under visible light in the presence of CCNF (0.002 g/L) was carried out. The irradiation was carried out by the experimental reaction mixture deferment to a 200 W tungsten lamp, its light intensity is measured by solarimeter (60.0 mW $cm^{-2}$). A stock solution of crystal violet dye $1.0 \times 10^{-3}$ M standard concentration was prepared. This standard solution of crystal violet dye was diluted and achieved the different desirable concentration of the solution. The maximum absorbance of crystal violet dye solution was determined with the help of a UV–Visible spectrophotometer giving $\lambda_{max}$ at 576 nm.

The progression of the reaction was investigated by measuring the absorbance of crystal violet dye and CCNF containing reaction mixture at standard time intervals during exposure. A decrease in absorbance of the crystal violet experimental reaction solution was observed with increasing time of exposure. A plot between (1 + log A) and time was found linear for CCNF which indicates the pseudo-first-order kinetics followed by photodegradation of crystal violet dye. The rate constant for photocatalytic degradation of crystal violet using CCNF was measured with the help of the relation: $k = 2.303 \times Slope$.

**Active species:** The impact of active and inactive species was evaluated by trapping experiments on the photocatalytic activity of CCNF catalyst. To detect the active species during the whole process, hydroxyl radicals (•OH), superoxide radicals ($\bullet O_2^-$) and holes ($h^+$) were investigated by 6 mM isopropyl alcohol[28] (IPA, a quencher of •OH), 0.5 mM benzoquinone[15] (BQ, a quencher of $\bullet O_2^-$) and 6 mM disodium ethylenediaminetetraacetate[19] (EDTA- 2Na, a quencher of $h^+$) respectively. The method was similar to the former degradation test except the addition of scavengers before switching on the lamp.

**Stability and reusability:** The stability of CCNF photocatalyst is a critical factor in large-scale technology applications. To evaluate the stability of the CCNF photocatalyst, recycling experiments were conducted on the CCNF for the degradation of crystal violet under visible light irradiation. The CCNF was collected by simple decantation and then washed using distilled water and ethanol. Thereafter, it was dried in an oven at 80 °C. The sample was reused for subsequent degradation. The CCNF photocatalyst maintained a very high photocatalytic activity and the removal rate of crystal violet on the CCNF photocatalyst was 79.02% after 5 cycles.

## Results and Discussion

The photocatalytic performance of CCNF was examined by monitoring the decomposition of crystal violet pollutant solution in an aqueous solution under visible illumination (Fig. 1). According to this obtained result, it was found that the contribution of self-degradation was negligible. The percentage of pollutant decomposition was calculated as follows:

$$D\% = \frac{A_0 - A_t}{A_t} \times 100 \qquad (4)$$

where $A_0$ and $A_t$ are the absorbance values of pollutant solution before and after decomposition by a UV–vis spectrometer, respectively. The pollutant decomposition was about 87.80% in 2 hrs illumination of visible light.

**Influence of pH:** The pH value of natural and polluted water varies in a broad range which might affect the generation of free radicals. The photocatalytic degradation of crystal violet dye solution may be affected by the pH of the medium. The pH was varied from 5.0 to 10.5. The pH was measured using a digital pH meter (Systronics). pH of the solution was varied by adding 1 N $HNO_3$ and 1 N NaOH solution. The effect of pH on the dye degradation with CCNF is summarized in figure 2.

**Influence of crystal violet concentration:** The crystal violet concentration was varied from 4.0 × $10^{-4}$ M to 5.6 × $10^{-4}$ M. A regular increase in the rate of dye degradation was observed till dye concentration reached $5.0\times10^{-4}$ M and thereafter, there was a gradual fall in rate (Figure 3). The photocatalytic activity increases with the increase in the concentration of the crystal violet as greater numbers of dye molecules are available for excitation and energy transmission and thus, an enhanced photoactivity is observed. But with further increase in the dye concentration above this limit, the dye starts behaving as a filter and will not allow incident light to reach the surface of the composite and a decrease in photoactivity was observed.

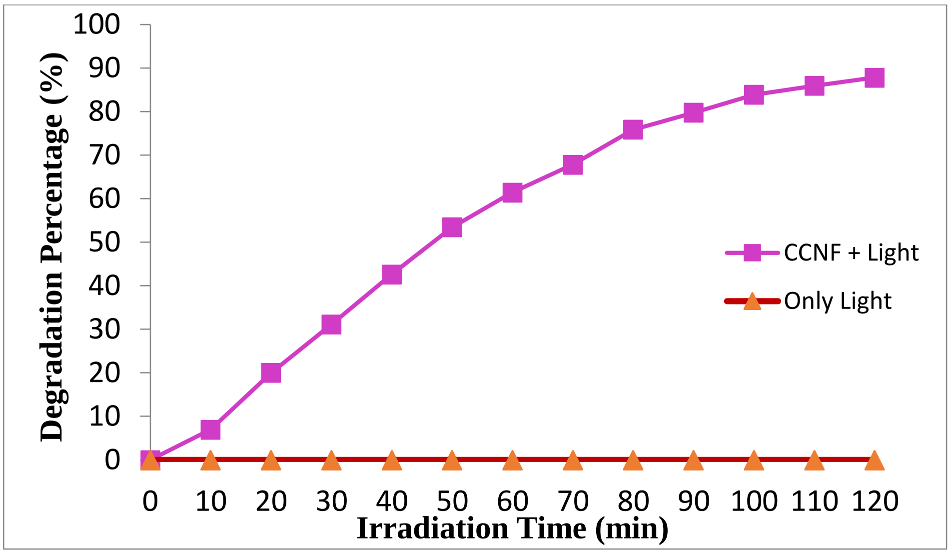

**Figure 1: Photocatalytic Degradation of Crystal Violet Pollutant by CCNF.**

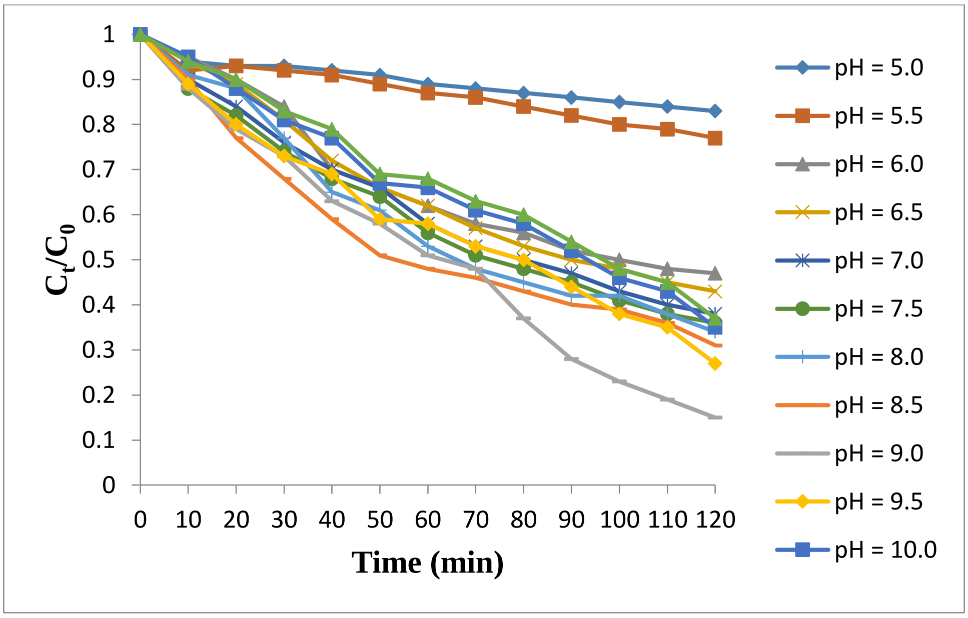

**Figure 2: Influence of pH on photocatalytic degradation of crystal violet pollutant.**

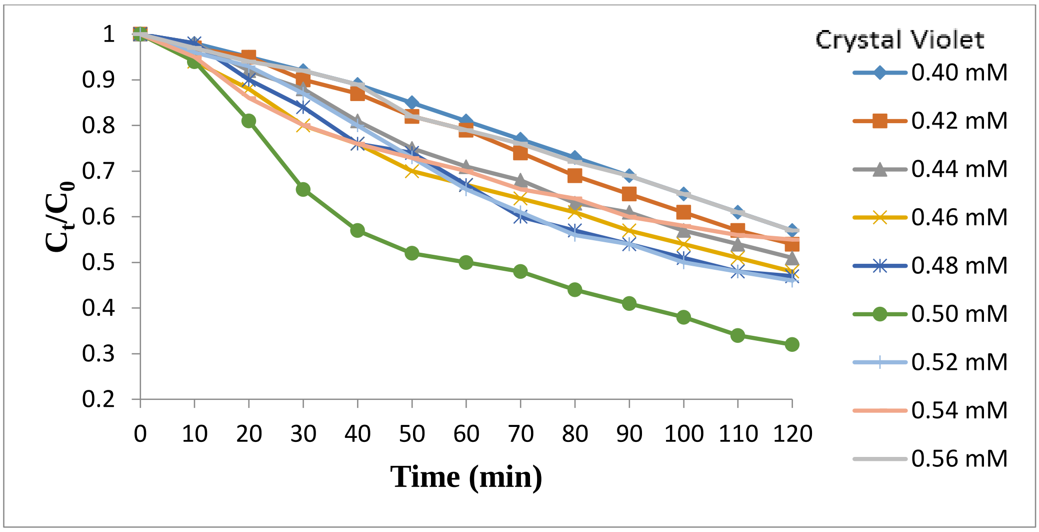

**Figure 3: Influence of Crystal Violet Concentration on Photocatalytic Degradation**

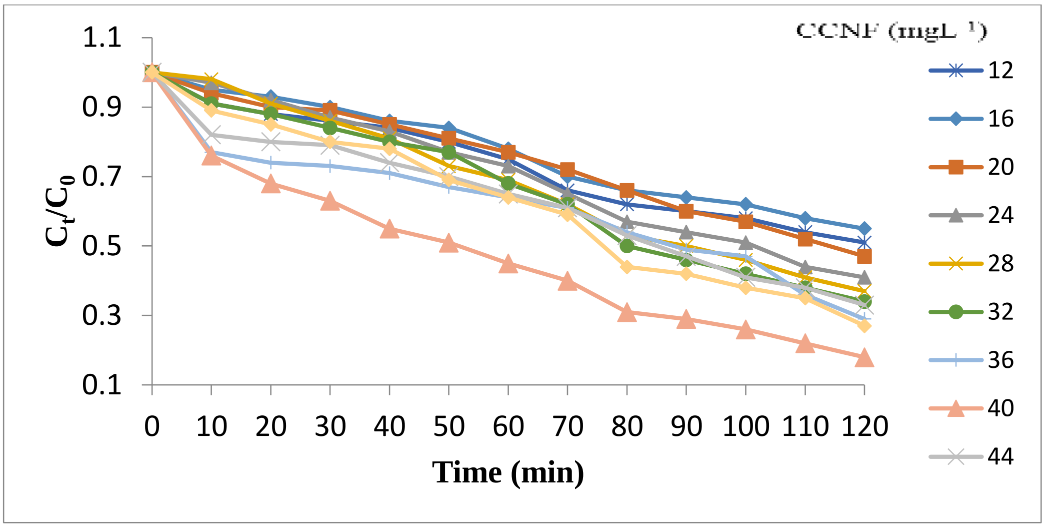

**Figure 4: Influence of CCNF Amount on Photocatalytic Degradation.**

**Influence of the amount of CCNF:** The amount of CCNF photocatalyst may also affect the photocatalytic degradation of crystal violet. The amount of the catalyst was varied from 12 mg to 48 mg. It was observed that the rate of photodegradation of crystal violet increases with an increase in the amount of catalyst to a certain extent reaching a maximum value. Any further increase in the amount of CCNF results in a decrease in the rate of degradation. The results are represented in figure 4.

**Influence of light intensity:** The intensity of the light also influences the rate of photodegradation. The light intensity was measured by solarimeter (Suryamapi CEL 201). The light intensity was varied from 20.0 to 70.0 mW/cm$^2$ and the results are tabulated in figure 5.

**Infrared spectra of crystal violet and irradiated crystal violet**: Spectral analysis of organic compounds was studied in prime important range (400 cm$^{-1}$- 4000 cm$^{-1}$). FTIR spectra of original crystal violet dye and visible light irradiated CCNF containing crystal violet dye solution are depicted in figure 6 and figure 7 respectively. The detailed FTIR spectra show changes in the crystal violet dye original solution and irradiated solution. The N-R stretching modes were observed in the frequency region 3100-3500 cm$^{-1}$ of the spectrum.

The absorption peak at 2983 cm$^{-1}$ could be assigned as C-H stretching vibration. The absorption band at 1586 cm$^{-1}$ in FTIR spectra is assigned as C−C=C symmetric stretching vibration which forms a conjugated bond with the benzene ring. Two sharp bands at 2390 cm$^{-1}$ and 2310 cm$^{-1}$ are due to C=C stretching vibration. The absorption peaks in the frequency region 622 cm$^{-1}$ to 820 cm$^{-1}$ indicate the aromatic ring bending mode. A strong peak around 1366 cm$^{-1}$ indicates the presence of the methyl group (-CH$_3$).

The O-H absorption band peak (3273 cm$^{-1}$) in the IR spectrum indicates that irradiated Crystal violet contains hydroxyl group in degraded by-products. A medium broad peak at 2128 cm$^{-1}$ could be assigned as C=C stretching vibration. A strong peak around 1637 cm$^{-1}$ firmly indicates an N-H bending vibration or C−C=C symmetric stretching vibration.

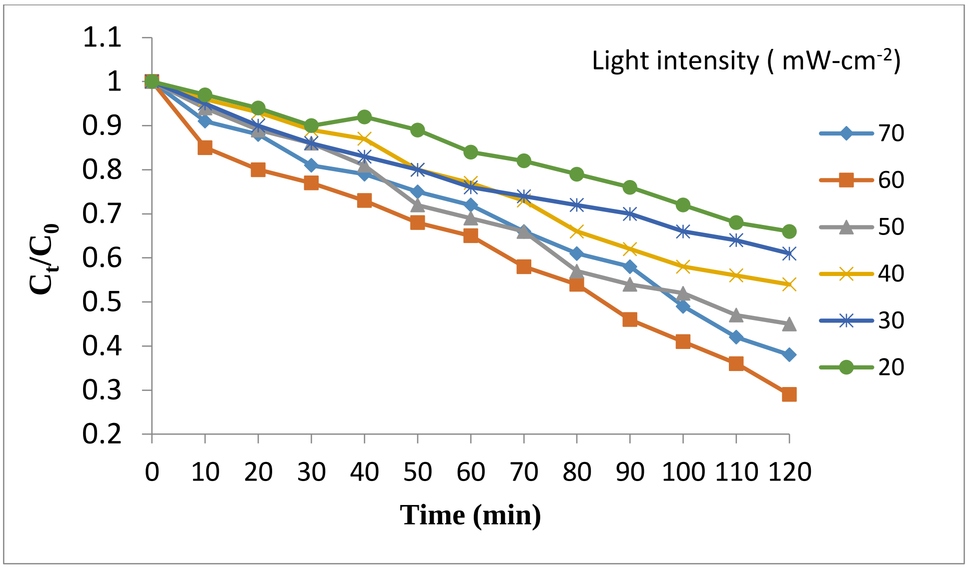

**Figure 5: Influence of Light Intensity on Photocatalytic Degradation**

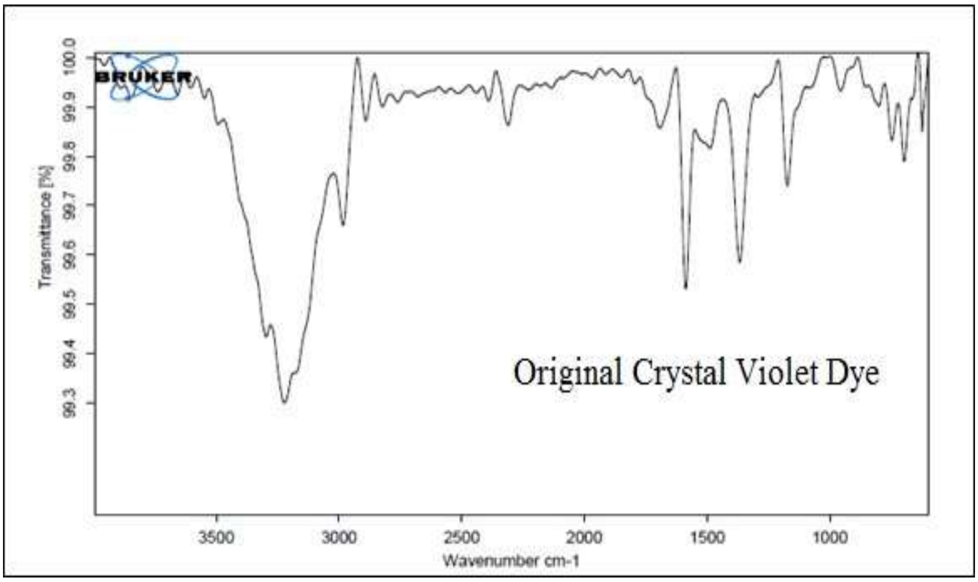

**Figure 6: FTIR spectra of original crystal violet dye.**

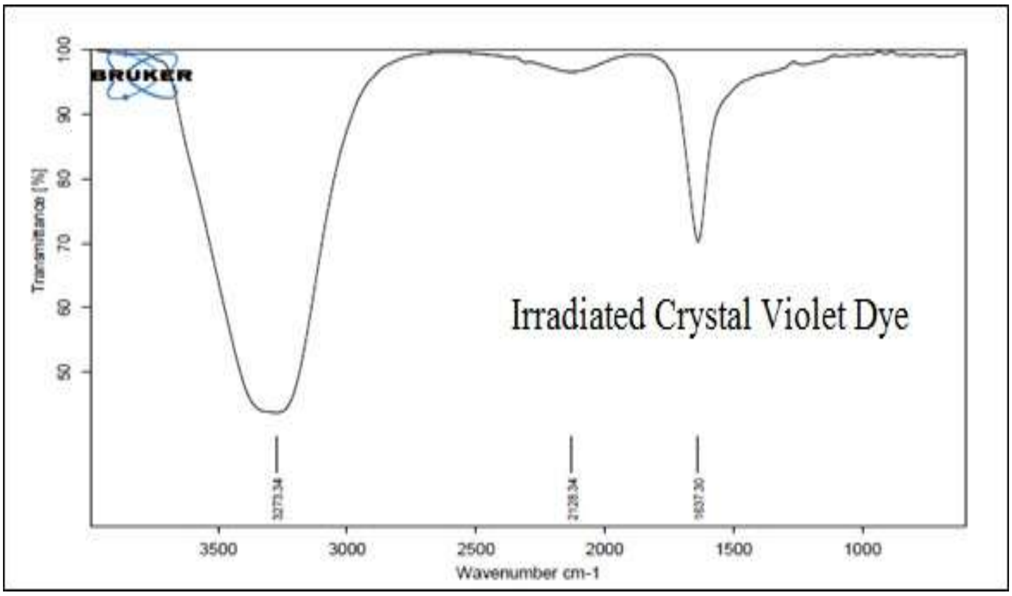

**Figure 7: FTIR spectra of irradiated crystal violet dye.**

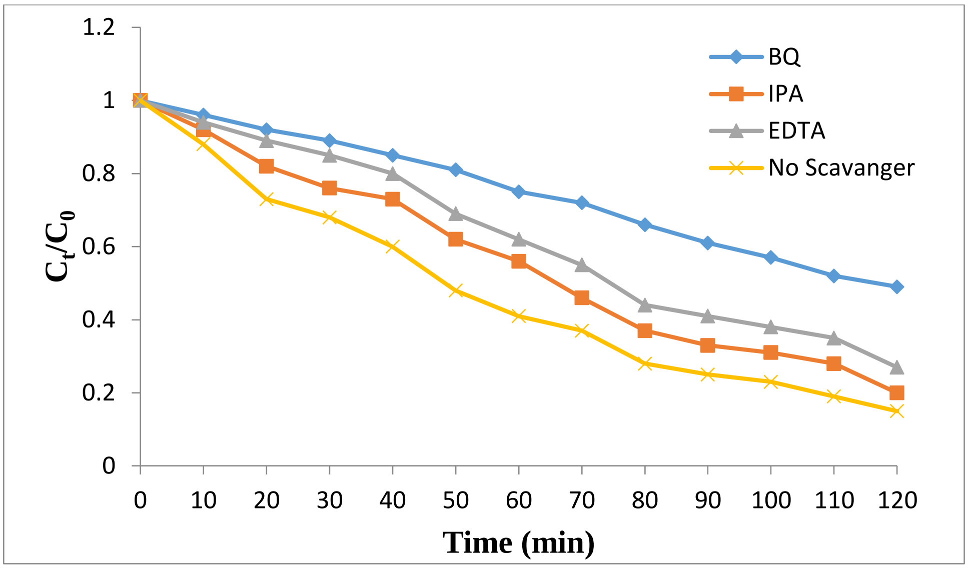

**Figure 8: Influence of various scavengers on crystal violet degradation.**

**Scavenger test:** To further investigate the responsible radical for crystal violet dye degradation radical trapping experiments were performed. In this study, different scavengers i.e. ethylenediaminetetraacetate (EDTA- 2Na) for $h^+$, isopropyl alcohol (IPA) for •OH and p-benzoquinone (BQ) for $•O_2^-$ were used.

It is evident from figure 8 that all scavengers were capable of decreasing the degradation of crystal violet to some extent. The degradation of crystal violet reduced from 58.78%, 14.97% and 12.48% in the presence of BQ, EDTA and IPA respectively.

**Plausible mechanism:** The manner of photocatalytic degradation of crystal violet using CCNF was proposed based on the above observations. An experimental mechanism is proposed for the crystal violet molecule. A light of suitable wavelength was absorbed by the crystal violet dye and it gets excited to its first excited singlet state. This first excited singlet state of the crystal violet dye undergoes intersystem crossing (ISC) and gets converted to its triplet state. CCNF also absorbs the incident light energy and excites its electron from the valence band to the conduction band leaving a hole in the valence band.

$$^1CV_0 \xrightarrow{hv} {}^1CV_1 \quad (5)$$

$$^1CV_1 \xrightarrow{ISC} {}^3CV_1 \quad (6)$$

$$CdCo_2O_4 \xrightarrow{hv} CdCo_2O_4\,[h^+\,(VB) + e^-(CB)] \quad (7)$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad (8)$$

$$e^- + O_2 \rightarrow \bullet O_2^- \quad (9)$$

$$^3CV_1 + \bullet O_2^- \rightarrow \text{Leuco CV} \quad (10)$$

$$\text{Leuco CV} \rightarrow \text{Mineralization Products} \quad (11)$$

On the other hand, the CCNF photocatalyst also utilizes the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. The hole (CCNF) reacts with hydroxyl ion (aqueous solution) which generates hydroxyl radicals. The electron (CCNF) reacts with oxygen (aqueous solution) which generates electrophilic oxygen radical anions. The oxygen radical anions will oxidize the crystal violet dye to its leuco form which may ultimately degrade to products. The possible degradation products of crystal violet dye by LC-MS were also investigated[20]. Identified intermediate products are shown in figure 9.

**Stability and reusability:** For practical applications of a photocatalyst, the reusability is as important as its efficiency. To evaluate the reusability of CCNF, five consecutive photocatalytic experimental runs were performed, adding recycled CCNF photocatalyst to fresh crystal violet solutions. The activity of CCNF particles for the degradation of crystal violet was observed for up to five cycles. The stability and reusability of CCNF evaluate by the successive tests of crystal violet degradation using the same batch CCNF catalyst.

As represented in figure 10, the degradation efficiency for crystal violet photodegradation was 98.20% on the first run and 89.42% on the fifth run. The slight decrease in efficiency suggested that the CCNF synthesized would be a promising catalyst in the practical application.

## Conclusion

CCNF was prepared and investigated for the application of photocatalytic degradation of crystal violet dye. The contemplation showed that crystal violet dye could be degraded successfully by using CCNF photocatalyst under visible light. The optimum reaction conditions were obtained as: pH = 9.0, [Crystal Violet] = $5.0 \times 10^{-4}$ M, [CCNF] = 40 mg and light intensity = 60 mW $cm^{-2}$. This CCNF could be reused 5 times without any significant loss in its photoactivity which is essential in practical environment protection.

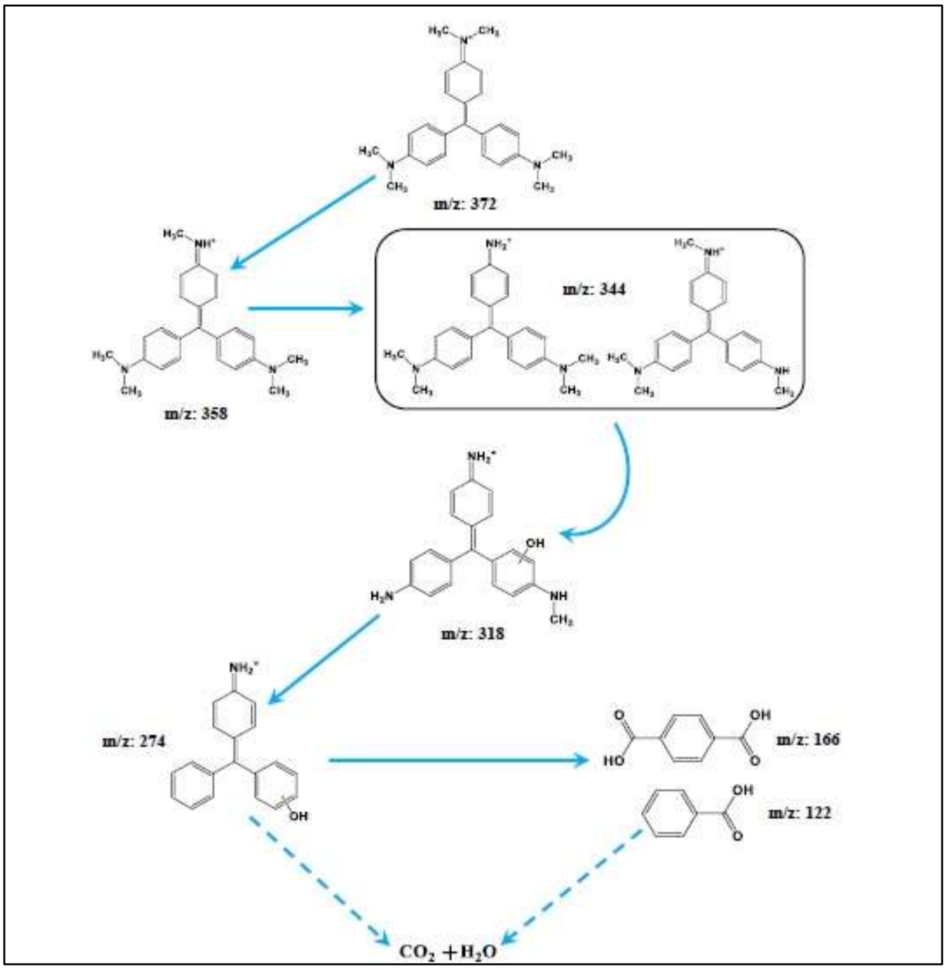

**Figure 9: Degradation pathway of crystal violet pollutant.**

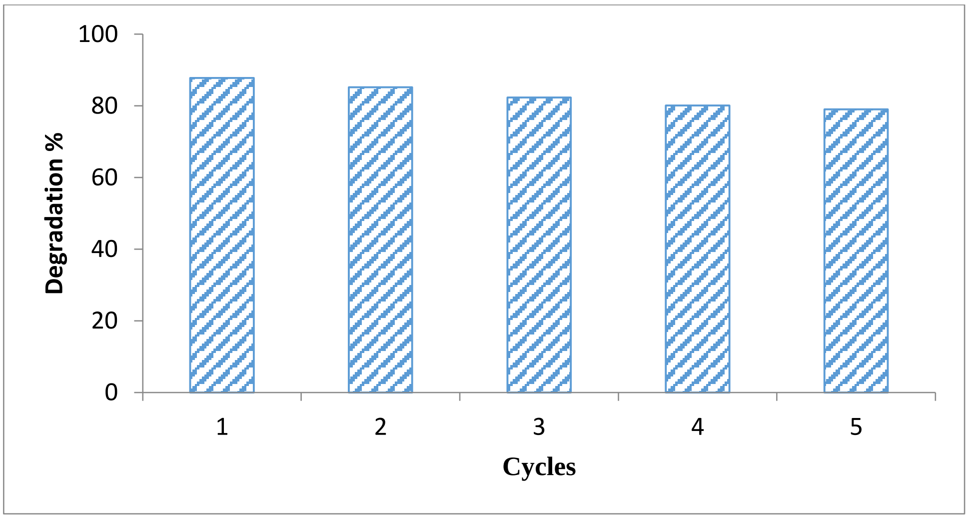

**Figure 10: Recyclability of catalytic degradation of crystal violet pollutant by CCNF**

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