

Optimization of Photo Catalytic Activity of ZnO Nano Composites by Surface Modification with Cu metal using Facile Hydrothermal Approach

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ABSTRACT

ZnO nano particles and Cu modified ZnO nano composites have been prepared by simple, facile hydrothermal approach. The novelty of this work was the use of aqueous methanolic solution (50:50 ratio) as the solvent of reaction, while zinc chloride was used as the precursor of ZnO NPs and Cu- modified ZnO nano composites. XRD results revealed that the synthesized ZnO and Cu-modified ZnO nano composites were of nano size and XRD patterns matched with JCPDS Card 35-1451, confirming the synthesis of ZnO nanoparticles. The FT-IR results confirmed the synthesis of target materials and also the adsorption of Cu metal on ZnO surface. The UV visible spectroscopic analysis indicated that the optical properties improved as the concentration of Cu metal increased on ZnO surface. SEM analysis explored the spherical shape of synthesized nano composites. The EDX graph showed the elemental composition of prepared materials that composed of Zn, O and Cu and no other impurity was found. The Tartrazine Yellow Azo Dye was degraded to investigate the photo catalytic activity which was optimized under sunlight with increasing the Cu metal concentration on surface of ZnO.

Keywords: ZnO Nano Composites, Cu Modification, Hydrothermal, Photo catalysis, Dye removal, Tartrazine Yellow

1. Introduction

Synthetic dyes can be used in a number of items, including meats, fabrics, leather goods, and furniture. These dyes are widely used on a daily basis. However, because of their frequent use, up to 12% of these dyes are discarded during the dyeing period, and about 20% of this waste is released into environment (mainly into water supply) [1]. Numerous dyes are discharged into environments through water waste, especially in the food, chemical, and textile industries. Many of these dyes can cause cancer when they come into contact with humans [2]. As a results, modern water waste treatment processes are still being developed. Several scientific trials are being conducted to degrade these toxic organic dyes using the least risky methods to overcome the hazards of these organic dyes to the environment [3].

Dye degradation is a chemical reaction that breaks down large dye molecules into smaller ones. Water, carbon dioxide, and mineral byproducts are the end products, which give the initial dye its hue. Not many of the dye molecules are used throughout the dyeing process. A proportion of these dye molecules can be found in the water waste that the industry produces [4].

Since certain organic materials are immune to light, acids, bases, and oxygen, they survive in the atmosphere. The material's color becomes irreversible [5]. For environmental purification, heterogeneous photo-catalysis is a commonly accepted process. A UV lamp is used in the standard experimental setup for dye, Photo Catalytic Degradation Activity (PCDA) to provide energy for the formation of oxidizing radicals. The addition of light to a metal oxide semiconductor causes electrons to move from the valence band to the conduction band, resulting in photo catalysis [6].

The developed electron-hole pairs will react with oxygen and water molecules to produce superoxide anions and hydroxide radicals [7], which will be used to

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oxidize and reduce a variety of industrial dye compounds. As a light source interacts with the surface of semiconductor materials, as photo catalysts, photo catalysis process occurs [8]. At least two simultaneous reactions, oxidation from photogenerated holes and reduction from photo generated electrons, must occur during this process. Since the photo catalyst does not alter, the two processes must be precisely synchronized. Water electrochemical photo catalysis at a semiconductor electrode was first performed by several researchers in 1972 [9]. Following the discovery that ZnO aids in the decomposition of cyanide in water, interest in the material's environmental applications increased [10].

ZnO is an excellent photocatalyst for a number of factors, including its widespread availability, low cost, and chemical stability [11]. Photo catalysis may be used to decompose toxins and improve the consistency of the atmosphere's air in a real-world environment. As a result, photo catalysis can be used in the construction industry to improve indoor air quality [12]. Because of its photochemical stability, non-toxicity, and low cost, ZnO has been extensively studied as a photo-catalyst for the decomposition of organic compounds [13]. The aim of this study was to look into the decomposition of toxic organic dyes and the de-colorization processes of colored waste materials from the food industry that contained organic dyes. Tartrazine dye, which has a wide range of applications in the food and pharmaceutical industries, was chosen as the organic pollutant. The toxic concentration of Tartrazine in humans has been estimated to be 7.5 mg/kg [12].

Tartrazine Yellow Azo Dye (TYAD) is a synthetic pigment or dye, and cosmetic pigment that is commonly used. It is a nitrous derivative that has been related to allergic reactions including asthma and urticarial [14], as well as mutagenesis and carcinogenesis reactions thanks to its turn into the aromatic amine sulfanilic acid after being metabolized by the gastrointestinal microflora [15]. The second most frequently used food coloring agent is TYAD [6]. It is used in soft drinks, chips, cookies, jam, pickles, candy, sugar, gelatin, and baked goods, among other things. TYAD is a bright yellow azo dye that is more durable than natural food dyes while still being less expensive. Other names for this dye include FD&C Yellow No. 5 and E 102 Europe.

TYAD can also be used in liquid soaps, lotions, hand sanitizers, perfumes, nail polish, and shampoos. TYAD is used in a number of drugs, giving them a yellow or orange color. Antacids, supplements, cough syrups, and lotions all contain it. TYAD is also used in inks, crayons, stamp dyes, and glues, among other things

[16]. TYAD intolerance is referred to as a TYAD allergy. It triggers allergic reactions in a limited percentage of the population, the mechanism of which is still unknown. Despite the fact that some reports suggest TYAD and related additives cause hyperactivity in children, the FDA dismissed these arguments due to a lack of adequate evidence. Rather than a direct reaction to TYAD, symptoms of TYAD allergy normally occur as an improvement in reaction to other allergens [8].

Individuals that are sensitive to this dye respond in a variety of ways. TYAD's resistance is characterized by skin rashes, hives, and nasal congestion. TYAD has been linked to the development of asthma in some people. According to research, TYAD may cause problems with the gastrointestinal tract, the central nervous system, and the respiratory system, but all of these side effects are uncommon and unproven. Some researchers suggest that TYAD induces thyroid tumors and lymphomas, but the data is insufficient to support this claim [17]. The findings from numerous research on the impact of TYAD intolerance indicate that TYAD's harmful effects are pharmacological rather than immunological. As a result, sensitization after ingestion is very rare. TYAD extensive cross-reactivity with other azo dyes and natural additives complicates study of this field [18]. Allergen tolerance is the mainstay in TYAD allergy treatment. Foods containing TYAD should be avoided by TYAD intolerant people. In allergic individuals, dietary adjustment is achieved by teaching parents and guardians about the detection and avoidance of additives [19]. When prevention is not an option, allergen toxicity should be managed according to the severity and nature of the allergic reaction.

There is no need for treatment if infection symptoms are mild and self-limiting. Nose sprays and corticosteroids can be used to treat allergic rhinitis and some skin conditions [20]. Antihistamines and bronchodilators are used to relieve asthma symptoms. Inhaling beta agonists can also assist with asthma symptoms including wheezing. Moderate allergic responses should be treated with oral steroids. Because of their success and widespread supply, azo dyes like TYAD have been an essential part of the food industry.

Numerous experiments on TYAD toxicity have provided inconsistent findings, leading to the conclusion that TYAD's negative effects are arbitrary. Wherever susceptibility has been observed, it has been determined to be general azo dye sensitivity rather than TYAD sensitivity in isolation. According to the FDA's Committee on Hypersensitivity to Food Constituents, only around 1 in 10,000 individuals are hypersensitive

enough to experience hives after swallowing TYAD. It was also determined that there is inadequate proof to prove TYAD's function in asthma attacks. The FDA, on the other hand, ordered suppliers to mark the compound as Yellow No. 5 on food ingredient labels so that TYAD-sensitive people would prevent it. In this research study, the Cu modified ZnO Nano Composites (NCs) are synthesized by simple, facile hydrothermal approach.

To optimize the PCA of synthesized Cu-modified ZnO NCs, Cu concentration was increased and the effect was determined. The PCA of Cu modified ZnO NCs was also investigated under different conditions; effect of pH, time, and concentration of metal on the surface of used photo catalyst for degradation of TYD. The surface-related mechanism is mainly governed by the chemisorbed oxygen adsorption and desorption at the ZnO surface, which is used in gas sensing applications. Where the surface area of nanocrystalline films is high, this process becomes more prevalent. PCA is aided by oxygen molecules in grain boundaries in the bulk-related phase. The bulk-related method, on the other hand, is believed to be quicker than the surface-related process.

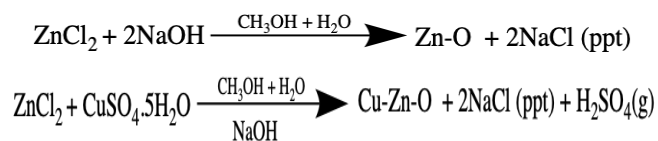
2. Experimental

2.1. Chemicals & Reagents Used

Chemicals used in both approaches were of analytical grade; Zinc Chloride; $ZnCl_2$ (Merck Chemicals GmbH, Germany), Copper Sulfate Pentahydrate; $CuSO_4 \cdot 5H_2O$ (Riedel de Haen Honeywell Research Chemicals, Germany), Sodium Hydroxide; $NaOH$ (Fischer Chemicals AG., Switzerland), Methanol; $MeOH$ (Fischer Chemicals AG., Switzerland) and RO Water (CCL Pharmaceuticals, Lahore, Pakistan)

2.2. Proposed Reaction Schemes

The chemicals & reagents used for both schemes were same, hence following reactions (ionic) occurred.



For the hydrothermal growth of Pure ZnO & Cu Modified ZnO NCs, novelty of this work is the use of Aqueous Methanolic Solution (AMS), and in a typical reaction process, 90mL-100mL (as per ZnO ratio in final products) of 0.04 M $ZnCl_2$, and 2.5 mL-10.0 mL of 0.04 M $CuSO_4 \cdot 5H_2O$ were dissolved in AMS and stirred for 20 min. After stirring, normally 200mL of 0.08 M NaOH solution was added in the solution to maintain the pH= 5.7 of the prepared solution.

The final solution was vigorously stirred for 120 min and consequently transferred to Teflon lined autoclave which was then sealed and heated up to an appropriate low temperature for a certain time. After terminating the reaction, the autoclave was allowed to cool at room temperature and the obtained products were washed several times with AMS, sequentially and dried at an appropriate temperature. Then, calcination was done at 450 °C for four hours. After calcination, the products were ground. The synthesized products were investigated in terms of their morphological, structural, and optical properties. Finally, the prepared NCs were used for characterization (**Fig. 1**).

3. Results and Discussion

Characterization of prepared ZnO / Cu-ZnO NCs

The synthesized Pure ZnO NPs & Cu modified ZnO NCs were extensively characterized in terms of their morphological, structural, optical, compositional and electrical properties. To analyze the internal molecular structures of synthesized pure ZnO and Cu Modified ZnO NCs, Compact FT-IR spectrometer Alpha-II by Bruker, Germany, was used and transmittance spectra were studied in range $450cm^{-1} - 4000cm^{-1}$. UV Vis spectrometer is a tool used for investigating electronic transitions and determining the electronic bonding in a molecule. To analyze the internal molecular vibrations and UV band gap of synthesized pure ZnO and Cu Modified ZnO NCs, Varian Cary 100 UV-VIS Spectrophotometer by Agilent Technologies, California was used and absorbance spectra were studied in the range 600nm-200nm. The Bruker D8 Advance XRD instrument was used for the analysis of all prepared samples in the diffraction angle range of $20^\circ \leq 2\theta \leq 60^\circ$, with monochromatic Cu K radiation ($\lambda = 1.5406 \text{ \AA}$) source. Nova NanoSEM 450 field-emission scanning electron microscope (FE-SEM) was used to study topography, morphology and local chemical and phase composition from nanometers to millimeters. The EDX coupled with FE-SEM was used to investigate the elemental compositions of prepared samples.

Photo Catalytic Degradation of TYAD pollutant

The aim of the present work was to enhance the PCA of synthesized ZnO NCs by surface modification with Cu metal on ZnO. The selected organic dye pollutant was TYAD, which is present in waste materials of food & Cosmetics industries. The second main objective of this study was to investigate the effectiveness of degradation of TYAD using the photo catalytic process by using ZnO/ Cu modified ZnO NCs as photo catalyst, UV light (254nm) room-light as the irradiation sources. The

degradation of TYAD was analyzed by using the UV-Vis spectrophotometer.

A dye solution of 10ppmL^{-1} concentration was prepared by mixing the dye powder in water. From this solution, 25 mL of solution was taken in 9 different flasks. The Pure ZnO & Cu modified ZnO NCs synthesized by the hydrothermal approach were used as a catalyst. 5mg of each synthesized catalyst was added in each 25mL flask containing the dye solution. The solutions were mixed by stirring for about 5-10 minutes. These samples were placed in different irradiation sources which were; UV light-254nm, sunlight, in absence of light (Dark). The activity was performed for about 120 minutes. The degradation performance was analyzed after equal time intervals. For studying the kinetics of the dye degradation reactions, 4 mL of dye solution is collected in regular time intervals, after which the UV-vis spectra & absorbance were recorded at 426-nm. The concentration of the TYAD solution is determined by UV-vis spectroscopy. The absorbance is converted to concentration using a calibration curve. All UV-vis spectra are collected using Agilent Cary 100 UV-Vis Spectrophotometer, California (All experiments are

performed at the natural pH of the dye solutions). Percentage degradation of dye was calculated using the relation (Equation 1);

$$\% \text{ Degradation} = [(A_0 - A_t)/A_0] \times 100 = (C_0 - C_t/C_0) \times 100$$

Where, A_0 is absorbance of dye at the initial stage, C_0 is the initial concentration of dye before irradiation and C_t is the concentration of dye after irradiation, and A_t is the absorbance of dye at time “t”,

The pure ZnO & Cu modified ZnO ($\text{Zn}_{1-x}\text{Cu}_x\text{O}$, $x=2.5\%$, 5.0% , 7.5% , & 10.0%) NCs were synthesized by the hydrothermal approach. All the same chemicals, reagents and salts were used in both approaches. The physical appearance was analyzed by its color and nature of powder (**Table 1**). The synthesized products were extensively characterized by various analytical techniques. Photo-catalytic degradation of organic dye using Pure ZnO & Cu modified ZnO NCs as catalyst was studied using UV-Visible Spectroscopy.

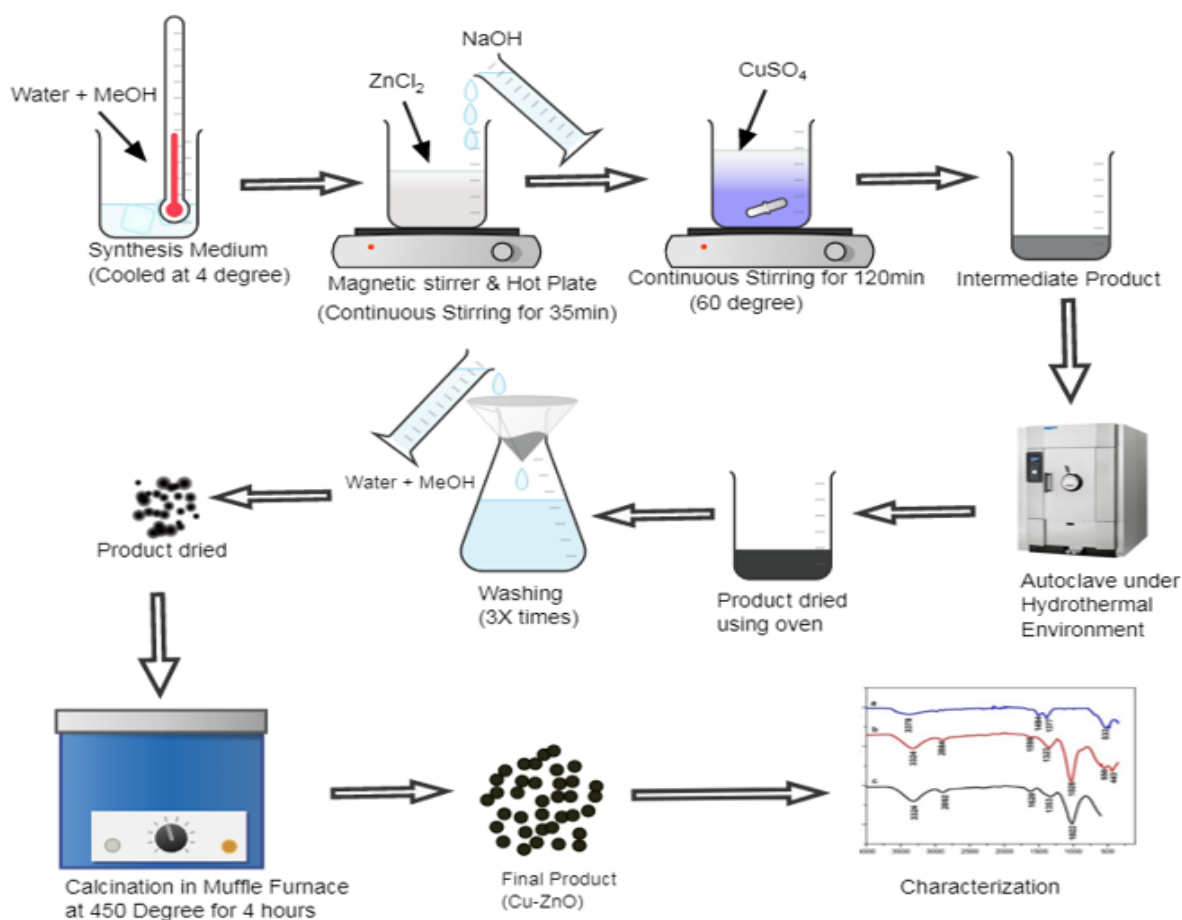
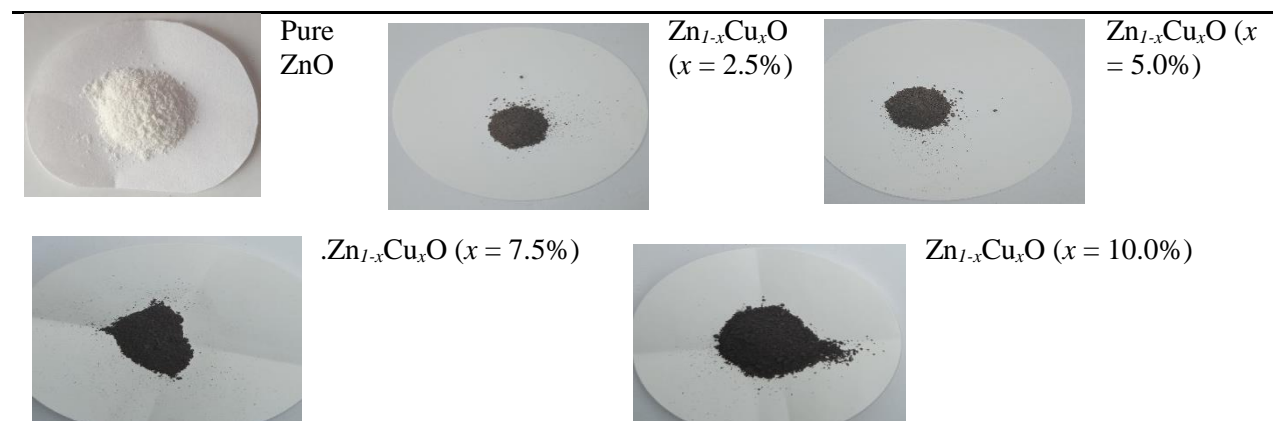


Fig. 1: Synthesis of Cu Modified ZnO NCs by Hydrothermal Approach

Table 1: Physical Appearance of synthesized Pure ZnO/Cu modified ZnO NCs

XRD Analysis

To examine the crystallinity and crystal quality of the as-synthesized ZnO NCs, XRD technique was used and the pattern is reported in **Fig. 2**. Several well-defined diffraction reflections are observed which are well matched with the pure wurtzite hexagonal phase.

The Bruker D8 Advance XRD instrument was used for analysis of all prepared samples in the diffraction angle range $20^\circ \leq 2\theta \leq 60^\circ$, with monochromatic Cu K radiation ($\lambda = 1.5406 \text{ \AA}$) source. The lattice parameters for synthesized ZnO and Cu doped ZnO NCs were calculated using the Scherrer formula. The crystallite sizes of the ZnO nanoparticles (D) can be obtained using Scherrer Equation (2);

$$D = \frac{k\lambda}{B_{hkl} \cos\theta}$$

Where, D is the thickness of (hkl) crystal plane, k is the wavelength of the incident X-ray (1.5406 \AA) for Cu K α , k is a constant equal to 0.94, B_{hkl} is the peak width at half-maximum intensity, and θ is the peak position.

The lattice constant “a” for the planes was calculated using the formula (Eq. 3);

$$a = \frac{\lambda}{\sqrt{3}\sin\theta}$$

The lattice constant “c” for the planes was calculated using the formula (Eq. 4);

$$c = \frac{\lambda}{\sin\theta}$$

The calculated lattice parameters, average crystallite size calculated by Scherrer formula and Scherrer constant values are reported in tabular form (**Table 2**). These results confirmed the hexagonal structure and nano size of synthesized NCs. These results are compared with JCPDS data and the results are found similar to JCPDS Card No.: 36-1451 which is XRD pattern of ZnO. These results also confirmed that by the addition of Cu metal into ZnO, there is no effect or distortion on the hexagonal structure of ZnO.

FTIR Analysis

The targeted NCs were synthesized by two different approaches. The quality and effectiveness of both approaches were determined from the results achieved by characterization of synthesized products. The quality and chemical composition of synthesized pure ZnO & Cu doped ZnO NCs were examined by FTIR Spectroscopy. FT-IR Spectrophotometer Alpha-P by Bruker Germany was used in the range of $4000\text{-}450 \text{ cm}^{-1}$ at room temperature. All the synthesized products were examined in same conditions and parameters.

In the products synthesized by hydrothermal approach, several well-defined peaks at $550\text{-}565 \text{ cm}^{-1}$, $1425\text{-}1435 \text{ cm}^{-1}$, $1450\text{-}1465 \text{ cm}^{-1}$ and $3425\text{-}3465 \text{ cm}^{-1}$ have been observed in the obtained FTIR spectra (**Fig. 3**). The sharp peak in the range of $550\text{-}565 \text{ cm}^{-1}$ confirms the growth of metal oxide group (MO_x) i.e. ZnO. The second broad peak in the range of $1425\text{-}1435 \text{ cm}^{-1}$ shows the presence of -OH group due to the use of water

(H-OH) in the synthesis medium. The third sharp peak in the range of $1450\text{-}1465\text{ cm}^{-1}$ confirms the presence of C-H group (or CH_3 group) which may come from MeOH (CH_3OH) used in synthesis medium in equal ratio to water.

The fourth broad peak obtained in the range of $3425\text{-}3465\text{ cm}^{-1}$ is attributed to the surface adsorbed water and hydroxyl groups. In addition to the observed peaks, no other peak related to any functional group was detected in the spectrum which reveals that the synthesized nano composites are pure ZnO & Cu-doped ZnO without any significant impurities.

Table 1: Calculated XRD Results of ZnO & Cu-modified ZnO NCs.

Sr.	Product Name	Synthesis Approach	Wavelength Cu-K α	Unit Cell values	Calculated Density (g/cm 3)	Average Crystallite
1	ZnO	Hydrothermal	1.541874 Å	a = 3.2493 c = 5.2057 I/IC = 6.77	5.678	338 Å or 33.8 nm
2	Zn $_{1-x}$ Cu $_x$ O (x=2.5%)	Hydrothermal	1.541874 Å	a = 3.2493 c = 5.2071 I/IC = 7.16	5.5682	1732 Å or 173.2 nm

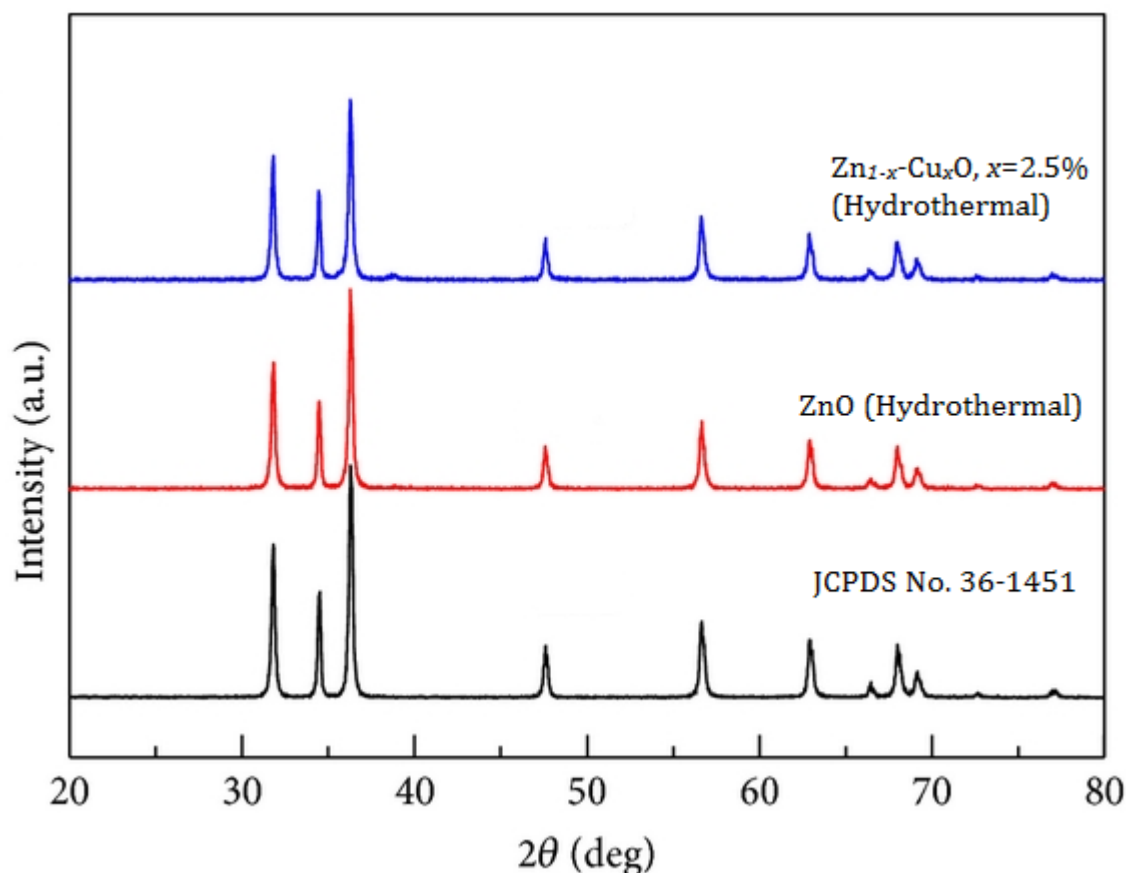


Fig. 2: XRD Patterns of synthesized products

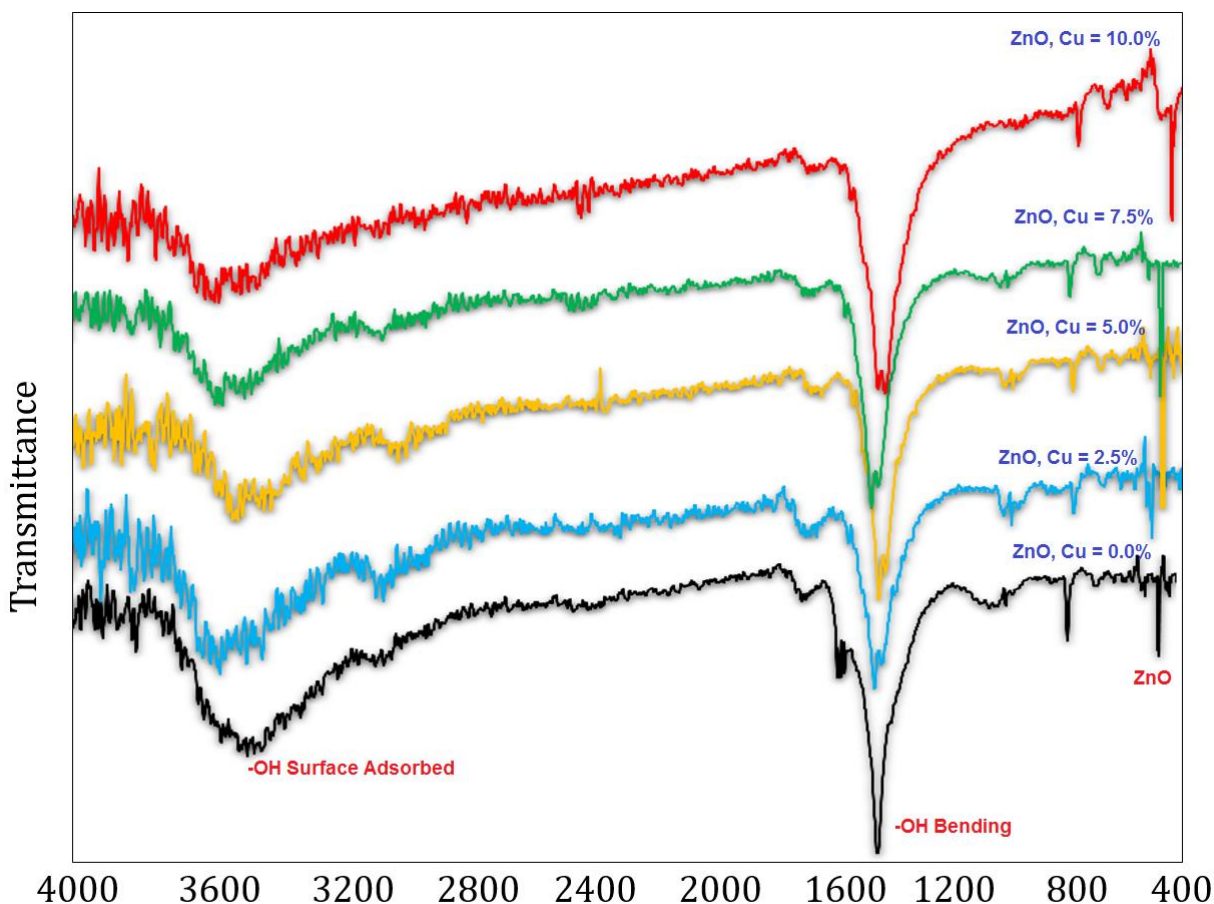


Fig. 3: IR Spectra of synthesized products

UV-Visible Spectroscopic Analysis

To evaluate the optical properties, the Pure ZnO & Cu modified ZnO NCs synthesized by both approaches, were examined by using a UV-visible (UV-Vis) spectrophotometer after dispersion in DMSO by means of ultrasounds for about 1 hour at room-temperature. The effectiveness of both approaches were also evaluated on the basis of results obtained by UV-Visible Spectroscopic analysis. **Fig. 4** illustrates the typical UV-Visible spectrum of Pure ZnO & Cu modified ZnO NCs synthesized by hydrothermal approach and their well-defined absorption peaks in the range of 372nm-412 nm are clearly visible (**Table 3**).

In **Fig. 4**, the peak “a” illustrates the typical UV-Visible spectrum of Pure ZnO NCs synthesized by hydrothermal approach and well-defined absorption peak at 372 nm is clearly visible which is characteristic responsive peak of ZnO and its evidence is available in literature.

The peak “b” illustrates the typical UV-Visible spectrum of $Zn_{1-x}Cu_xO$ ($x=2.5\%$) NCs synthesized by hydrothermal approach and well-defined absorption

peak at 379 nm is clearly visible which is characteristic peak of Cu modified ZnO NCs. This visible peak at 379 nm showed the red shift in wavelength from 372 nm to 379 nm due to incorporation of Cu metal on surface of ZnO NCs. This red shift change represents the change in optical properties of ZnO NCs and may help the change in energy band gap (EBG).

The peak “c” illustrates the typical UV-Visible spectrum of $Zn_{1-x}Cu_xO$ ($x=5.0\%$) NCs synthesized by hydrothermal approach and a well-defined absorption peak at 389 nm is clearly visible which is characteristic peak of Cu modified ZnO NCs. This visible peak at 379 nm showed the red shift in wavelength from 372nm to 389 nm due to incorporation of Cu metal on surface of ZnO NCs. As the concentration of Cu metal increased, the change in red shift is also increased. This red shift change represents the change in optical properties of ZnO NCs and may favor the change in EBG.

The peak “d” illustrates the typical UV-Visible spectrum of $Zn_{1-x}Cu_xO$ ($x=7.5\%$) NCs synthesized by hydrothermal approach and a well-defined absorption peak at 397 nm is clearly visible which is characteristic

peak of Cu modified ZnO NCs. This visible peak at 397 nm showed the red shift in wavelength from 372nm to 397 nm due to incorporation of Cu metal in the structure of ZnO NCs. As the concentration of Cu metal increased, the change in red shift is also increased. This red shift change represents the change in optical properties of ZnO NCs and may favor the change in EBG.

The peak “e” illustrates the typical UV-Visible spectrum of $Zn_{1-x}Cu_xO$ ($x=10.0\%$) NCs synthesized by hydrothermal approach and a well-defined absorption peak at 412 nm is clearly visible which is characteristic

peak of Cu modified ZnO NCs. This visible peak at 412 nm showed the red shift in wavelength from 372 nm to 412 nm due to incorporation of Cu metal in the structure of ZnO NCs. As the concentration of Cu metal increased, the change in red shift is also increased. This red shift change represents the change in optical properties of ZnO NCs and may favor the change in EBG.

The red shift in wavelength appeared from 372nm to 412nm as the concentration of Cu metal is increased from 0.0% to 10.0% (Fig 5).

Table 2: UV-Visible Analysis Results of Pure ZnO & Cu modified ZnO NCs synthesized by Hydrothermal Approach

Sr. No.	Product Name	λ_{max} (nm)
1	Pure ZnO	372
2	$Zn_{1-x}Cu_xO$ ($x = 2.5\%$)	379
3	$Zn_{1-x}Cu_xO$ ($x = 5.0\%$)	389
4	$Zn_{1-x}Cu_xO$ ($x = 7.5\%$)	397
5	$Zn_{1-x}Cu_xO$ ($x = 10.0\%$)	412

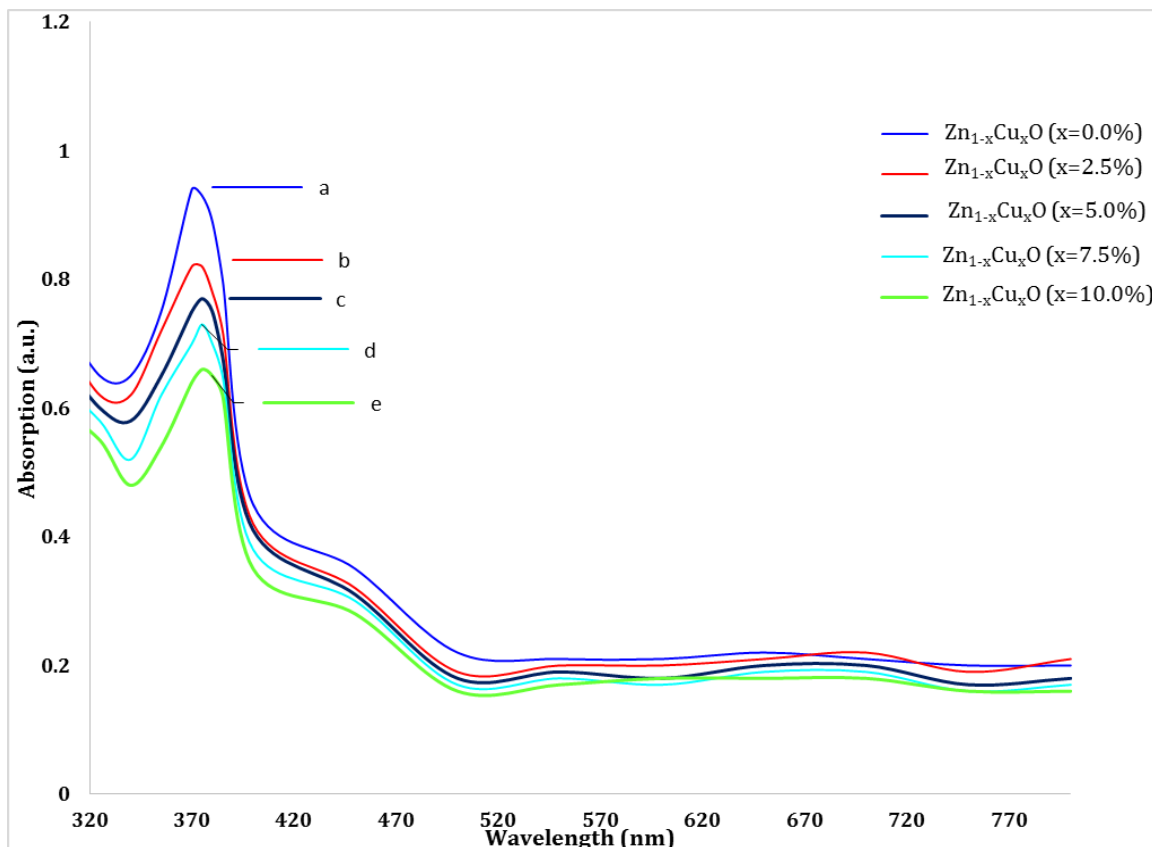


Fig. 4: UV-Visible Spectrum of all prepared samples ranging from 412nm to 372nm

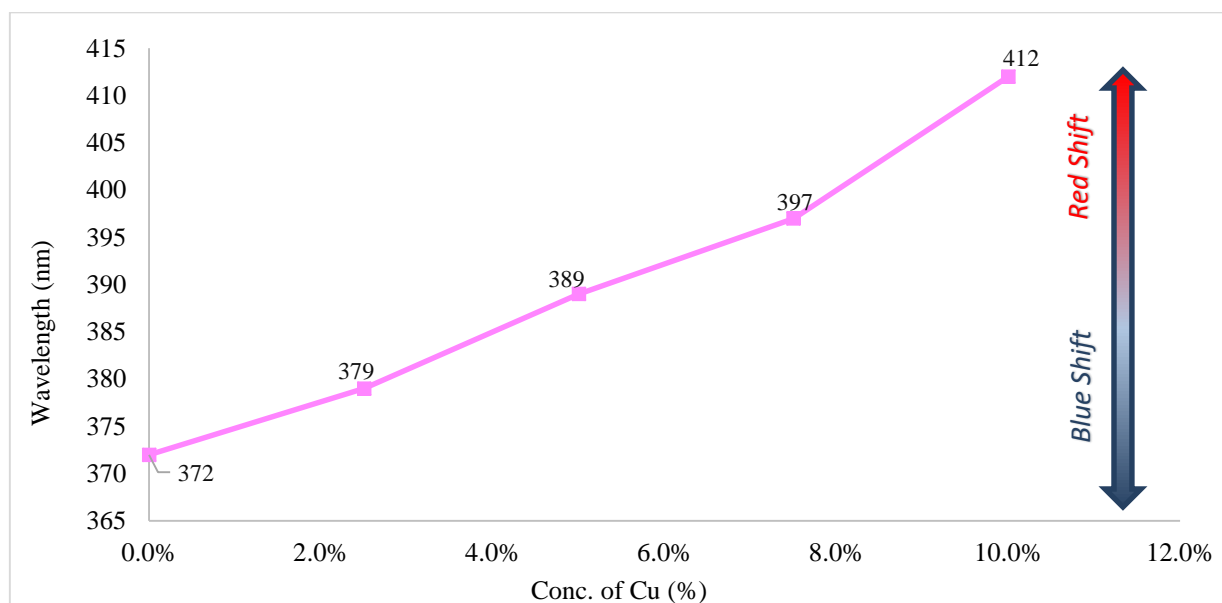


Fig. 5: Effect of Cu metal on Wavelength for Pure ZnO & Cu modified ZnO NCs synthesized by hydrothermal Approach

SEM Analysis

For crystal morphology and grain size observation for all the synthesized samples, SEM was used. The SEM images of pure ZnO and Cu-ZnO NCs synthesized by hydrothermal approach are shown in **Fig. 6**. These images indicate that the shape and morphology of ZnO NCs change with increasing Cu concentration. The influence of Cu-metal on the ZnO NCs homogeneity and morphology is very much in-line with the findings of Saad *et al.* (samples with Cu 1-3 wt% by co-precipitation method) who reported this could be due to increasing substitution of different Cu ions with Zn sites.

The image for pure ZnO (**Fig. 6-a**) shows the grown NCs with relatively uniform size distribution with the somehow larger size. This could be an indication of the formation of secondary NCs through the aggregation of the primary NCs. In the Cu-modified ZnO NCs, the NCs seem to be more and more agglomerated with the increase of Cu content; therefore, it is difficult to say something about the average grain size from the less-resolved SEM images (**Fig. 6 b-e**).

EDX analysis of synthesized pure ZnO/Cu Modified ZnO NCs

To authenticate the existence of dopant on ZnO, EDX analysis was carried out. The EDX is a chemical micro-analysis technique used together with SEM. Typical EDX images of the Pure ZnO NCs (**Fig. 7**) and 5.0% (wt.%) Cu modified ZnO NCs (**Fig. 8**) synthesized by Hydrothermal Approach are illustrated.

The elemental composition of samples prepared by both approaches has been reported in **Table 4**. It can be seen in images of products prepared by both approaches that Cu content in the samples is almost equal to the nominal value. It is valuable to note that the NCs synthesized by the hydrothermal approach are composed of Zn, Cu, and O only.

The main objective of this study was to investigate the effectiveness of degradation of TYAD using the photocatalytic process by using ZnO/ Cu modified ZnO NCs as photo catalyst, while UV light (254nm), sunlight, and darkness were used as the irradiation sources. In heterogeneous catalysis, the color of the sample turned colorless on completion of dye degradation (**Fig. 9**). This study also was conducted to compare the percentage degradation of TYAD at different conditions which are pH of dye solution, exposure time, presence and absence of irradiation sources and real and surface modified photo catalyst. The degradation of TYAD was analyzed by using UV-Vis spectrophotometer. The results showed that the photocatalytic degradation of TYAD proved to be effective under solar radiation by using ZnO as photo catalyst. The optimum photocatalytic degradation occurred at optimum pH of TYAD, in presence of used photo catalyst and complete time of radiation. The optimum weight of ZnO was 10 mg, and the optimum pH of TYAD solution was 6.

The most effective condition for photocatalytic degradation of TYAD was degradation with ZnO catalyst and solar radiation. The radiation time was 1 hour with (93.91±0.57) % degradation. The formation of OH⁻ required both the presence of the catalyst and solar radiation.

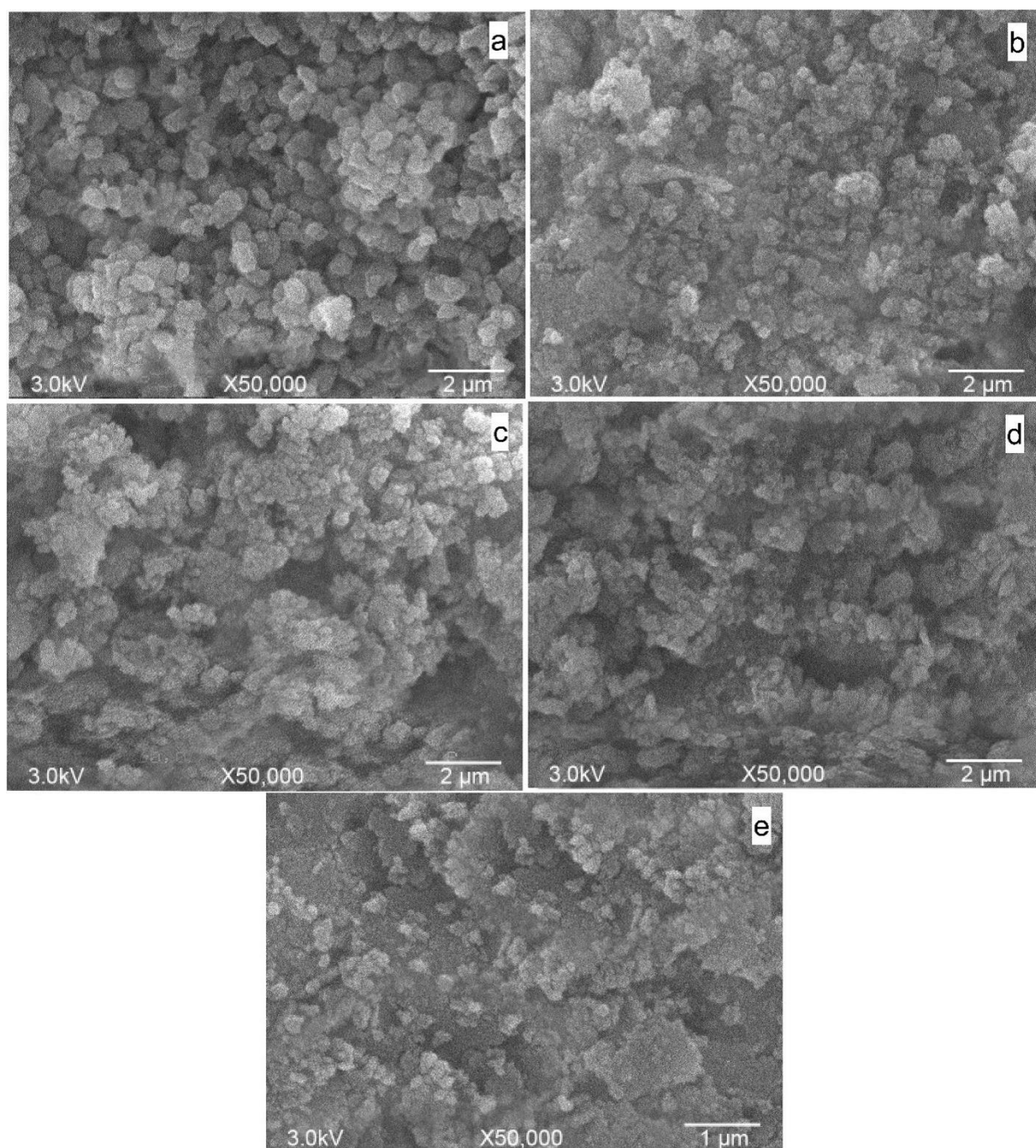


Fig. 6: SEM images of (a) pure ZnO (b) 2.5 wt% (c) 5.0 wt% (d) 7.5 wt% (e) 10 wt% Cu-modified ZnO NCs by hydrothermal approach

PD of TYAD dye under Sunlight as irradiation Source

The sunlight was used as a irradiation source for PD of TYAD and ZnO ; Cu modified ZnO NCs synthesized by Hydrothermal approach were used as photo catalysts. The experiment was performed for about 120 minutes. The degradation of dye was determined by measuring the absorbance with UV-Visible spectrophotometer (Agilent Carry-100 series), and from absorbance, the concentration of dye was determined after equal time

points. The results on each time point are explained in **Tables 5 & 6**.

The concentration of dye was determined from the initial absorbance (A_0) of the dye and the absorbance (A_t) after irradiation. It was seen that since the time of irradiation increased, the concentration of dye decreased and PD performance (%) was increased (**Fig. 10**).

Table 4: Elemental Composition of synthesized NCs calculated by EDX analysis

Sr. No.	Product Name	Synthesis Approach	Elemental Composition
1	ZnO	Hydrothermal	Zn = 51.09 % O =48.91 %
2	Zn _{1-x} Cu _x O (x = 5.0%)	Hydrothermal	Zn =48.65 % O =46.49 % Cu =4.86 %

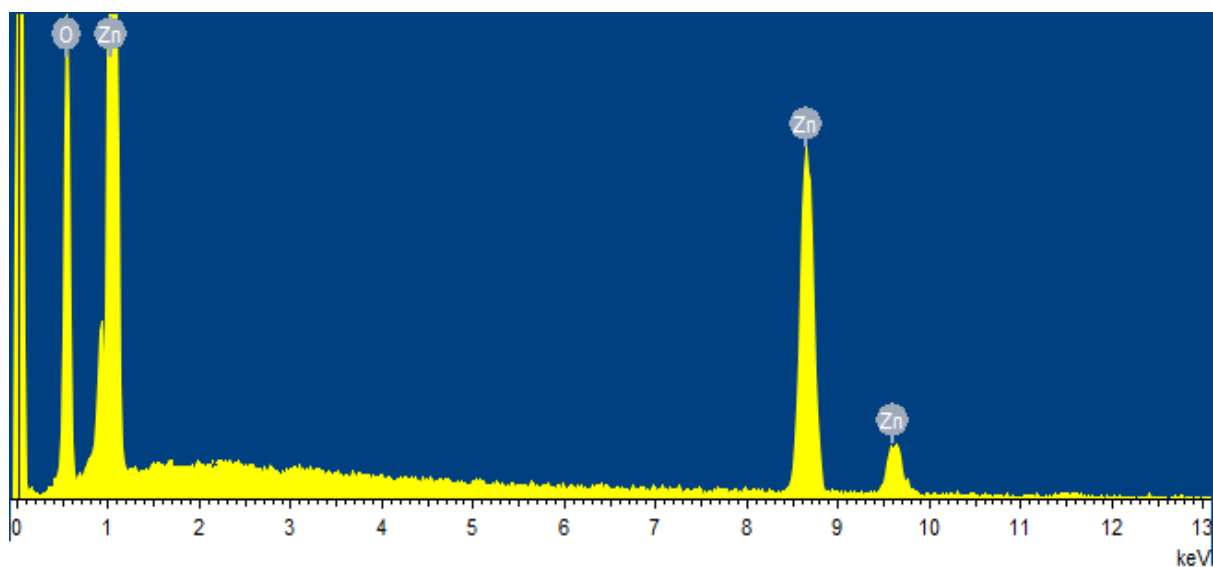


Fig. 7: EDX images of Pure ZnO NPs synthesized by Hydrothermal Approach.

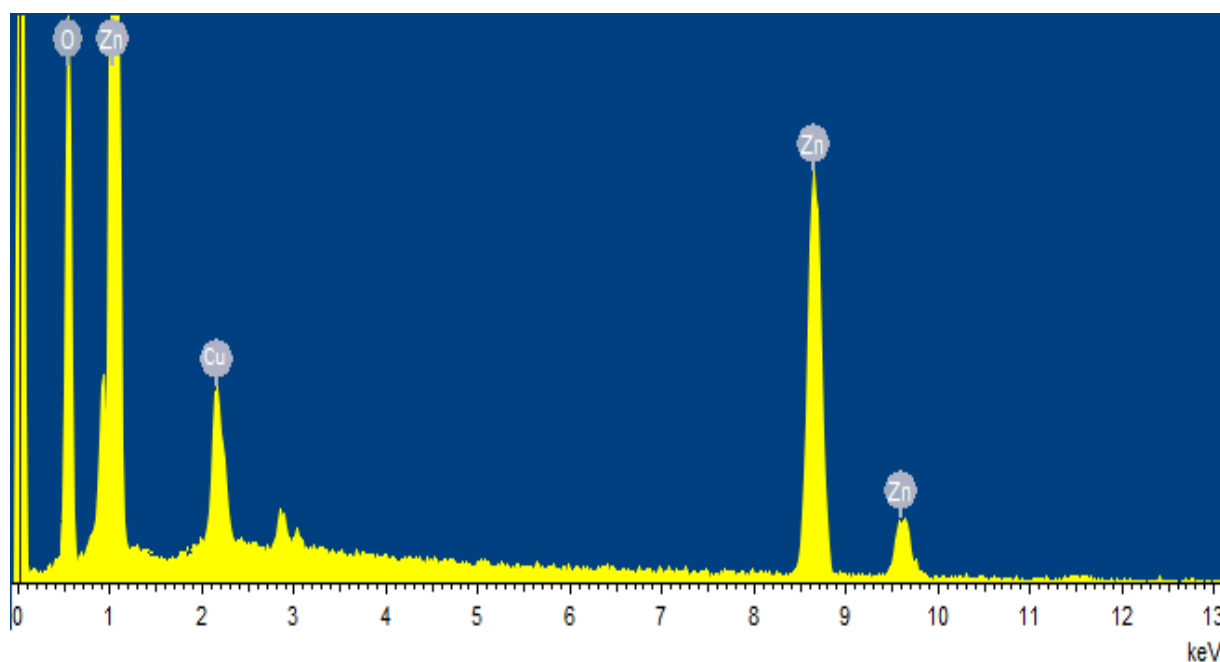


Fig. 8: EDX images of Cu modified ZnO NCs (Cu 5.0% wt) synthesized by Hydrothermal Approach.

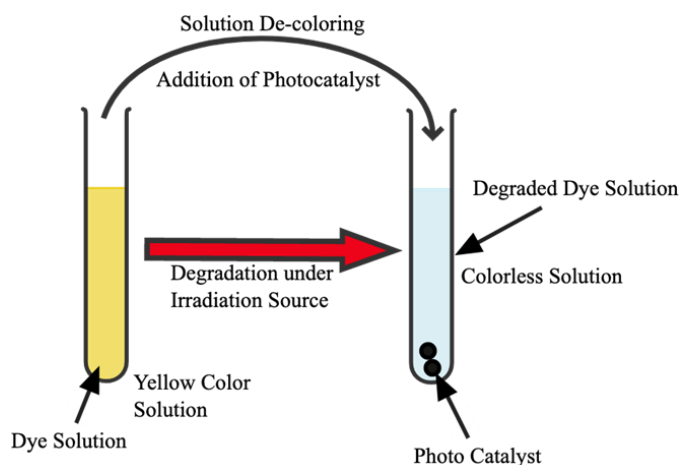


Fig. 9: De-coloration of colored dye solution using synthesized photo catalyst

Under sunlight, the samples synthesized by hydrothermal approach showed their maximum PCDA after a complete process of 120 minutes (**Table 5**). It was seen that the results of pure ZnO NPs are less to all

of other Cu modified ZnO NCs. It was also explored that as the concentration of Cu metal was increased equally, % degradation of TYAD was also increased gradually.

PD of TYAD under UV-254nm as irradiation Source

The UV-254 nm light was used as a irradiation source for PD of TYAD and ZnO, Cu modified ZnO NCs synthesized by Hydrothermal approach were used as photo catalysts. The experiment was performed for about 120 minutes. The degradation of TYAD was determined by measuring the absorbance with UV-Visible spectrophotometer (Agilent Carry-100 series), and from absorbance, the concentration of dye was determined after equal time points.

The results on each time point are explained in Table 6. It was seen that as the time of irradiation increased, the concentration of dye decreased and PD performance (%) was increased (**Fig. 11**).

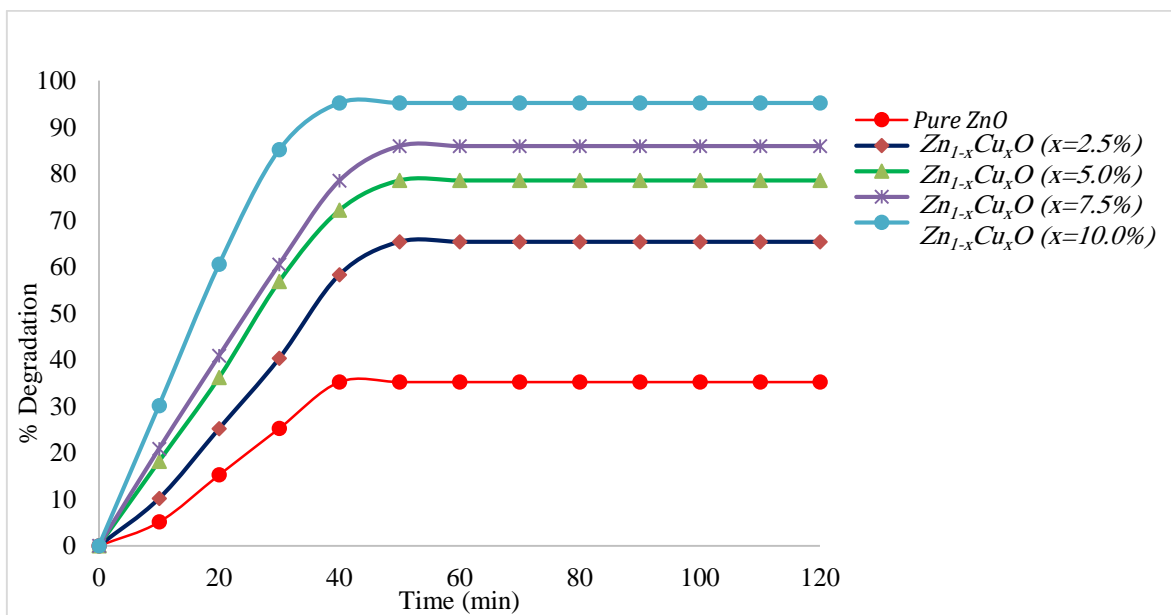


Fig. 10: PD of TYAD by ZnO/Cu modified ZnO NCs (prepared by hydrothermal approach) under sunlight as irradiation source

Table 5: PD (%) of TYAD by Prepared ZnO/Cu-modified ZnO NCs (Prepared by Hydrothermal approach) under sunlight (Irradiation Source)

Sr. No.	Product Name	% Degradation
1	Pure ZnO	35.21
2	Zn _{1-x} Cu _x O (x = 2.5%)	65.36
3	Zn _{1-x} Cu _x O (x = 5.0%)	78.55
4	Zn _{1-x} Cu _x O (x = 7.5%)	85.91
5	Zn _{1-x} Cu _x O (x = 10.0%)	95.22

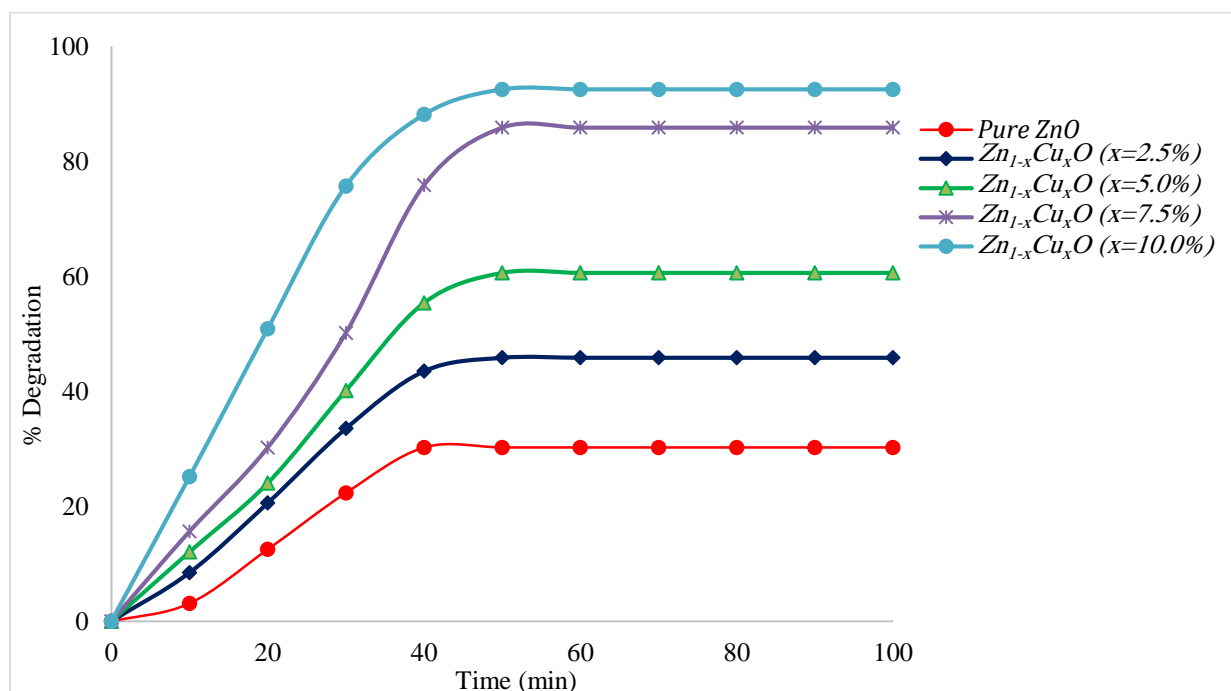


Fig. 11: PD of TYAD by ZnO/Cu modified ZnO NCs (prepared by hydrothermal approach) under UV-254nm as irradiation source

Under UV-254nm light, the samples synthesized by hydrothermal approach showed their maximum PCDA after a complete process of 120 minutes (**Table 6**). It was seen that the results of pure ZnO NPs are less than other Cu doped ZnO NCs. It was also explored that as the concentration of Cu metal increased equally, the degradation percentage of TYAD was also increased gradually.

In absence of an irradiation source for PD of TYAD and ZnO, Cu-modified ZnO NC's synthesized by hydrothermal approach were used as photo catalysts. The experiment was performed for about 120 minutes. The degradation of dye was determined by measuring the absorbance with UV-Visible spectrophotometer (Agilent Carry-100 series), and from absorbance, the concentration of dye was determined after equal time points. The results on each time point are explained in Table 7. It was seen that as the time of reaction increased, the concentration of dye decreased slightly and PD performance (%) was increased very slightly (**Fig. 12**).

In the absence of light, the samples synthesized by the hydrothermal approach showed their maximum PCDA after a complete process of 120 minutes (**Table 7**). It was seen that the results of pure ZnO NPs are less than other Cu modified ZnO NCs. It was also explored that as the concentration of Cu metal was increased equally, the degradation percentage of TYAD was also increased

gradually. But the results in absence of irradiation source are much less than the results in the presence of irradiation source.

Effect of Irradiation Time on PCA of ZnO/ Cu-modified ZnO NCs

It was seen from all the above-achieved results at all provided conditions (sunlight, UV-254nm light, and in absence of irradiation source), as the time of interaction with irradiation source increased, the PD (%) of TYAD also increased and the concentration of dye in prepared solution decreased with the passage of irradiation time intervals (**Table 8, 9, & 10**).

Photo catalytic Degradation Mechanism of Dye

The photo catalytic degradation (PD) mechanisms of TYAD on pure ZnO and Cu modified ZnO NCs under UV-visible light (UV-254nm), sunlight, and darkness (absence of light) as irradiation sources are different from each other. Mainly, the organic dye a macro molecule is degraded and decomposed into its smaller molecules (**Fig. 13**).

A common proposed mechanism is that when the sunlight or UV-Visible light was irradiated on the surface of the used photo catalyst, the photons can excite the electrons in the VB to be moved up to the CB. As a result of this irradiation, the electron and the hole pair (e^- & h^+) are generated (**Fig. 14 & 15**). Both will

Table 6: PD (%) of TYAD by Prepared ZnO/Cu-modified ZnO NCs (Prepared by Hydrothermal approach) under UV-254nm light (Irradiation Source)

Sr. No.	Product Name	% Degradation
1	Pure ZnO	30.22
2	Zn _{1-x} Cu _x O (x = 2.5%)	45.85
3	Zn _{1-x} Cu _x O (x = 5.0%)	60.58
4	Zn _{1-x} Cu _x O (x = 7.5%)	85.85
5	Zn _{1-x} Cu _x O (x = 10.0%)	92.51

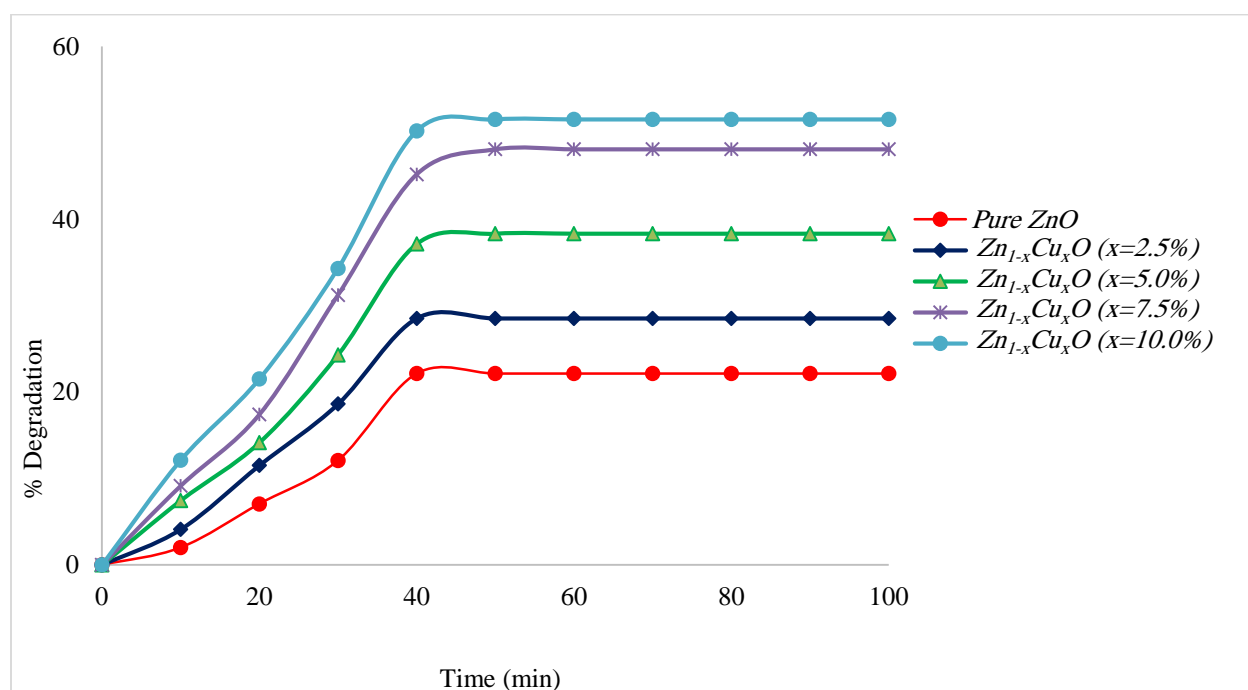


Fig. 12: PD of TYAD by ZnO/Cu modified ZnO NCs (prepared by hydrothermal approach) in absence of irradiation source

Table 7: PD (%) of TYAD by Prepared ZnO/Cu-doped ZnO NCs (Prepared by hydrothermal approach) under dark (absence of Irradiation Source)

Sr. No.	Product Name	% Degradation
1	Pure ZnO	22.14
2	Zn _{1-x} Cu _x O (x = 2.5%)	28.54
3	Zn _{1-x} Cu _x O (x = 5.0%)	38.35
4	Zn _{1-x} Cu _x O (x = 7.5%)	48.11
5	Zn _{1-x} Cu _x O (x = 10.0%)	51.55

Table 8: PD (%) of TYAD by Prepared ZnO/Cu-modified ZnO NCs (Prepared by Hydrothermal approach) under sunlight (Irradiation Source)

Sr. No.	Time	Pure ZnO	Zn _{1-x} Cu _x O (x = 2.5%)	Zn _{1-x} Cu _x O (x = 5.0%)	Zn _{1-x} Cu _x O (x = 7.5%)	Zn _{1-x} Cu _x O (x = 10.0%)
1	0	0	0	0	0	0
2	10	5.11	10.14	18.12	20.85	30.12
3	20	15.25	25.19	36.15	40.87	60.51
4	30	25.24	40.28	56.82	60.48	85.14
5	40	35.21	58.25	72.12	78.45	95.22
6	50	35.21	65.36	78.55	85.91	95.22
7	60	35.21	65.36	78.55	85.91	95.22
8	70	35.21	65.36	78.55	85.91	95.22
9	80	35.21	65.36	78.55	85.91	95.22
10	90	35.21	65.36	78.55	85.91	95.22
11	100	35.21	65.36	78.55	85.91	95.22
12	110	35.21	65.36	78.55	85.91	95.22
13	120	35.21	65.36	78.55	85.91	95.22

Table 9: PD (%) of TYAD by Prepared ZnO/Cu-modified ZnO NCs (Prepared by Hydrothermal approach) under UV -254nm (Irradiation Source)

Sr. No.	Time	Pure ZnO	Zn _{1-x} Cu _x O (x = 2.5%)	Zn _{1-x} Cu _x O (x = 5.0%)	Zn _{1-x} Cu _x O (x = 7.5%)	Zn _{1-x} Cu _x O (x = 10.0%)
1	0	0	0	0	0	0
2	10	3.12	8.45	12.05	15.61	25.14
3	20	12.51	20.56	24.01	30.21	50.87
4	30	22.32	33.54	40.11	50.14	75.71
5	40	30.22	43.51	55.36	75.88	88.14
6	50	30.22	45.85	60.58	85.85	92.51
7	60	30.22	45.85	60.58	85.85	92.51
8	70	30.22	45.85	60.58	85.85	92.51
9	80	30.22	45.85	60.58	85.85	92.51
10	90	30.22	45.85	60.58	85.85	92.51
11	100	30.22	45.85	60.58	85.85	92.51
12	110	30.22	45.85	60.58	85.85	92.51
13	120	30.22	45.85	60.58	85.85	92.51

Table 10: PD (%) of TYAD by Prepared ZnO/Cu-modified ZnO NCs (Prepared by Hydrothermal approach) under Darkness (Irradiation Source)

Sr. No.	Time	Pure ZnO	Zn _{1-x} Cu _x O (x = 2.5%)	Zn _{1-x} Cu _x O (x = 5.0%)	Zn _{1-x} Cu _x O (x = 7.5%)	Zn _{1-x} Cu _x O (x = 10.0%)
1	0	0	0	0	0	0
2	10	2.66	5.66	9.66	12.36	14.15
3	20	5.98	12.36	16.25	19.66	22.25
4	30	15.45	21.25	28.55	32.15	36.58
5	40	21.33	29.22	36.25	39.15	42.67
6	50	29.55	35.66	42.69	45.15	48.98
7	60	29.55	35.66	42.69	45.15	48.98
8	70	29.55	35.66	42.69	45.15	48.98
9	80	29.55	35.66	42.69	45.15	48.98
10	90	29.55	35.66	42.69	45.15	48.98
11	100	29.55	35.66	42.69	45.15	48.98
12	110	29.55	35.66	42.69	45.15	48.98
13	120	29.55	35.66	42.69	45.15	48.98

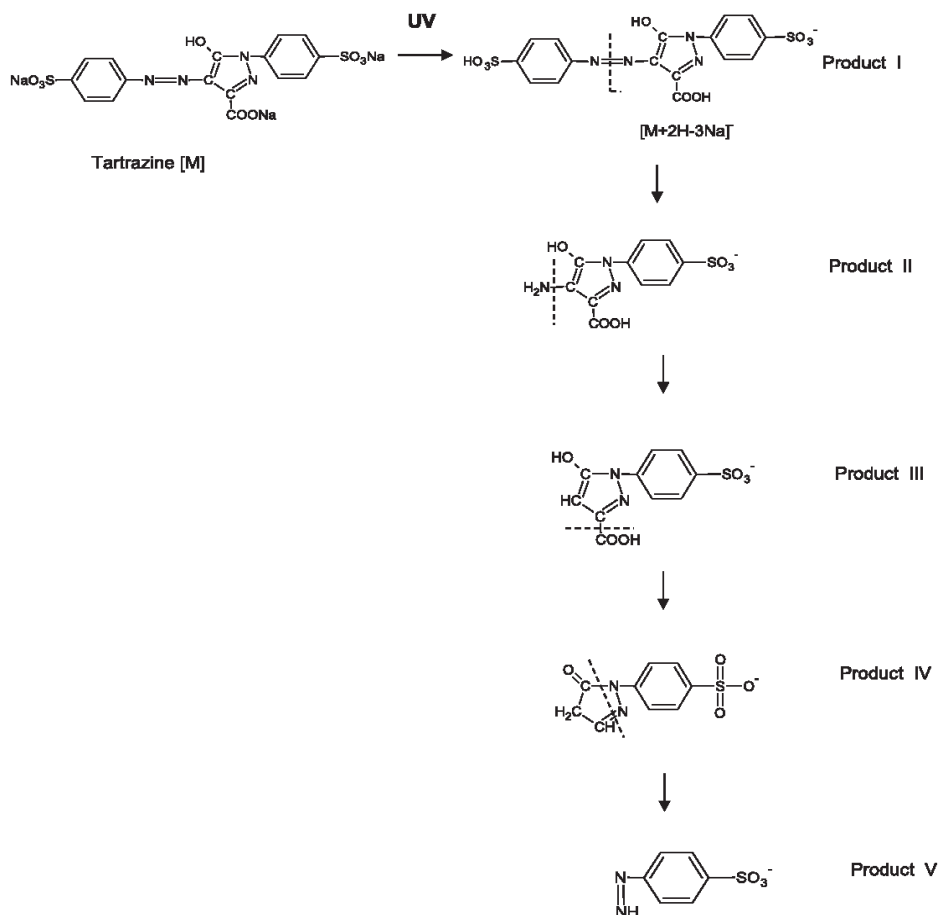
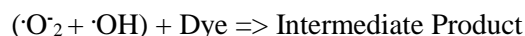
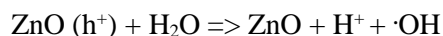
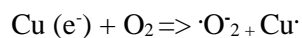
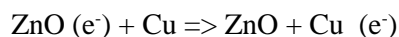
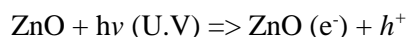


Fig. 13: Degradation mechanism of TYAD solution under UV Light irradiation

interact with water and oxygen on the surface of the ZnO to generate the oxidizing agents including H_2O_2 , $\cdot\text{O}_2$ and $\cdot\text{OH}$, in which $\cdot\text{O}_2$ and $\cdot\text{OH}$ are the strong oxidizing agents. They can degrade the organic compound into H_2O_2 and CO_2 . However, some of the electrons (e^-) lying on the CB is extremely short, the electrons almost immediately release the energy to return to the ground state to re-combine with hole (h^+) originally, and this is one of the most significant limitations of pure ZnO NCs.

Effect of Metal on PD efficiency of ZnO NCs

When the Cu metal is introduced on the structure of ZnO NCs and these Cu-modified ZnO NCs are used as photocatalysts, the ‘‘Schottky Barrier’’ (Potential energy barrier for the electrons formed at a metal-ZnO junction) is formed between Cu metal and ZnO due to energy level of CB of ZnO which is higher than the fermi-level of Cu-ZnO leading to free electrons in CB that can transfer from ZnO to metal, thereby preventing the recombination between electrons and holes [23-24] on the surface of ZnO NCs (Fig. 16 & 17). The electrons on metal can produce the $\cdot\text{O}_2$ free radical, while the holes in the VB can react with H_2O_2 to produce $\cdot\text{OH}$ radical. These free radicals can degrade the organic compounds to CO_2 and H_2O ; the mechanism can be explained by:



From the results, it has been shown that photocatalytic activity of pure ZnO NC's is weaker than that of Cu modified ZnO NC's. The fact is that pure ZnO NC's absorb weakly in the visible light region, meanwhile, the Cu modified ZnO NC's showed significantly enhanced photo catalytic activity, because under sunlight and visible light irradiation, electrons can be formed in metallic NCs via Surface Plasma Resonance (SPR) effect which may lead to strong absorption light in the visible region.

However the Schottky Barrier, formed at the metal-semiconductor interface, can hinder the transfer of electrons from metal NC's to ZnO NC's.

Till now, many research works have proven that electrons can overcome the Schottky Barrier at Cu-ZnO interface because of its strong electron, oscillating collectively on SPR excitation region.

Therefore, electrons can transfer from metal to CB of ZnO. Then, they are scavenged by the adsorbed oxygen molecules to yield superoxide radical anions ($\cdot\text{O}_2$) to degrade the dye molecules.

Meanwhile, the photo generated holes could transfer to the photo catalyst's surface and directly oxidize the organic pollutants, resulting in an improved PCDA in the visible light region [25].

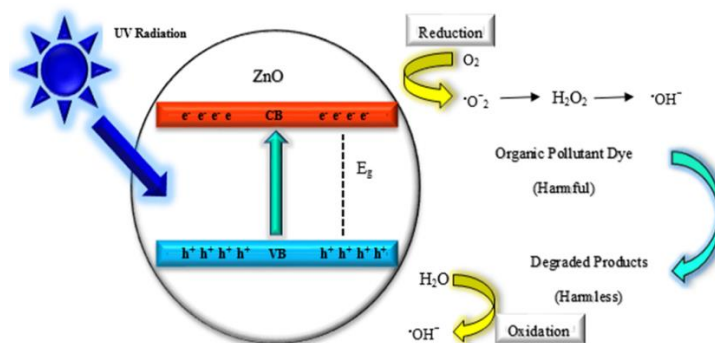


Fig. 14: PD of dye using ZnO NCs as photo catalyst under UV-254nm light as irradiation source

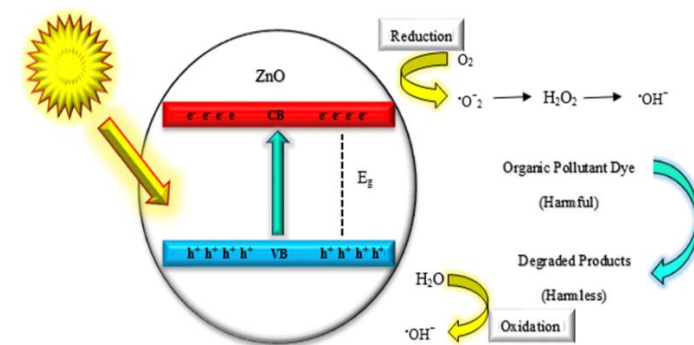


Fig. 15: PD of dye using ZnO NCs as photo catalyst under sunlight as irradiation source

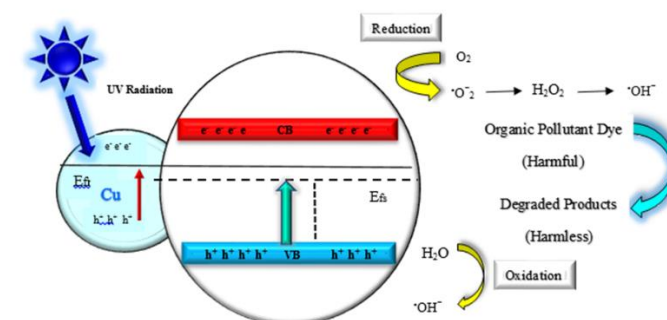


Fig. 16: Effect of Cu metal on PCDA of ZnO NCs under UV-254nm light irradiation source

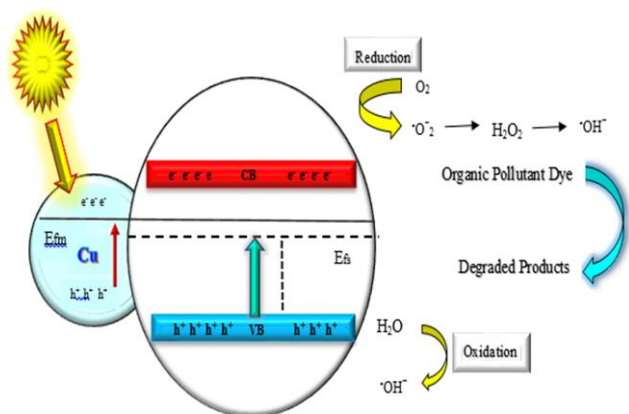


Fig. 17: Effect of Cu metal on PCDA of ZnO NCs under sunlight irradiation source

Effect of pH on PD of Dye

Generally, the pH value of dye solution (and pollutant solutions) is an important factor for well-designed reactions processes. It has a great influence not only on the functional groups and surface charges of adsorbents, but also on the structure and ionization degree of pollutant molecules and ionization degree of pollutant molecules or dye molecules.

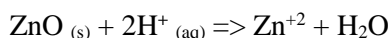
In this study, the effect of initial solution pH on the degradation of dye was investigated. The degradation performance was evaluated at two pH values from 5.0 to 6.0 under fixed other conditions (dosage catalyst, time, concentration of dye solution). The pH gave a critical impact on the degradation performance of dye.

When pH increased from 5.0 to 6.0, the degradation efficiency increased significantly from 95% to ~100% .

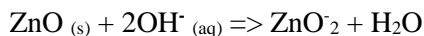
when the ZnO/Cu- modified ZnO NCs synthesized by hydrothermal approach were used as catalyst (**Table 11**).

The pH 6.0 of dye solution was found to be the optimum pH at which the used photo catalysts showed their maximum degradation (**Table 12**). The Zn_{1-x}Cu_xO (x = 10.0%) NCs synthesized by hydrothermal approach showed about 99.96% degradation of dye (under sunlight) which was increased about 6.0% as compared to the natural pH of dye solution. The pH revealed a significant effect on the degradation of dye in the presence of photo catalyst.

The observed optimum pH for the efficient degradation of dye on ZnO and Cu/ZnO is 6.0. At lower pH than 6.0, the degradation efficiency is low because degradation ceased due to the dissolution of ZnO in an acidic medium, as follows.



At higher pH than 6.0, the degradation is low to the dissolution of ZnO in basic medium based on the following equation.



Meanwhile, the surface charge property of NCs which depends on the pH point of zero charge, is also the reason affecting the adsorption properties of dye molecules on the surface of photocatalyst. Hence, at pH 6.0 the catalysis surface will adsorb efficiently the organic anions of dye and lead to significantly enhance the degradation of dye on ZnO, and Cu-ZnO NCs.

Table 11: PD (%) of TYAD by Prepared ZnO/Cu-modified ZnO NCs (Prepared by hydrothermal approach) under Sunlight (Irradiation Source) at optimum pH 6.0

Sr. No.	Product Name	% Degradation
1	Pure ZnO	35.21
2	Zn _{1-x} Cu _x O (x = 2.5%)	65.36
3	Zn _{1-x} Cu _x O (x = 5.0%)	78.55
4	Zn _{1-x} Cu _x O (x = 7.5%)	85.91
5	Zn _{1-x} Cu _x O (x = 10.0%)	99.96

Table 12: PD of TYAD by ZnO/Cu modified ZnO NCs (synthesized by hydrothermal approach) Photo catalyst at Optimum pH 6.0 under

Sr. No.	Time	Pure ZnO	Zn _{1-x} Cu _x O (x = 2.5%)	Zn _{1-x} Cu _x O (x = 5.0%)	Zn _{1-x} Cu _x O (x = 7.5%)	Zn _{1-x} Cu _x O (x = 10.0%)
1	0	0	0	0	0	0
2	10	5.11	10.14	18.12	20.85	30.12
3	20	15.25	25.19	36.15	40.87	60.51
4	30	25.24	40.28	56.82	60.48	85.14
5	40	35.21	58.25	72.12	78.45	95.22
6	50	35.21	65.36	78.55	85.91	99.96
7	60	35.21	65.36	78.55	85.91	99.96
8	70	35.21	65.36	78.55	85.91	99.96
9	80	35.21	65.36	78.55	85.91	99.96
10	90	35.21	65.36	78.55	85.91	99.96
11	100	35.21	65.36	78.55	85.91	99.96
12	110	35.21	65.36	78.55	85.91	99.96
13	120	35.21	65.36	78.55	85.91	99.96

4. Conclusions

ZnO nano particles and Cu modified ZnO NCs have been successfully prepared by hydrothermal approach. The XRD results confirmed the crystalline structure and also Cu modification on crystalline structure of ZnO. The UV-Vis spectroscopy results revealed the optical properties of ZnO NPs & Cu-ZnO NCs. They also conclude that the by increasing the Cu- metal concentration on ZnO crystal surface, the optical properties enhanced and improved. The FT-IR results confirmed the synthesis of target materials and also he modification with Cu metal on ZnO surface. The crystal structure and size were determined by XRD analysis which were found in limits even after modification with Cu metal. The surface morphology of the synthesized products was confined by SEM analysis which indicated the spherical nature of synthesized Pure ZnO NPs & Cu modified ZnO NCs. The EDX graph confirmed the elemental composition of prepared materials and showed the cu modification on ZnO wurtzite structure.

The photo catalytic degradation activity of synthesized ZnO & Cu-modified ZnO NCs was found to be optimized under sunlight by increasing the Cu metal concentration into ZnO. The PCA was also enhanced when degradation was performed at optimum pH 6.0 of dye solution. It has been found that by surface modification of ZnO with Cu metal, there is no change in the chemical properties of ZnO crystal lattice. Rather, by increasing the concentration of Cu metal on the surface, the PCA of ZnO Crystal was found to be enhanced and optimized.

Conflict of Interest

All authors declared no conflict of interest during the whole project

References

- [1]. Khataee, A. R., and Masoud B. Kasiri. J. Mol. Catal.: Chem. 328.1-2 (2010): 8-26.

- [2]. Ullah, Ruh, and Joydeep Dutta. *J. Hazard. mater.* 156.1-3 (2008): 194-200.
- [3]. Vidhu, V. K., and Daizy Philip. *Micron* 56 (2014): 54-62.
- [4]. Omidvar, Afshan, Babak Jaleh, and Mahmoud Nasrollahzadeh. *J. colloid interf. sci.* 496 (2017): 44-50.
- [5]. Sharma, Dharendra Kumar, et al. *Mater. Today: Proceedings* (2020).
- [6]. Assassi, Mirvet, et al. *Acta Periodica Technologica* 52 (2021): 133-145.
- [7]. Kumar, Nishant, et al. *Analytical Methods* 9.33 (2017): 4776-4782.
- [8]. Uribe-López, M. C., et al. *J. Photochem. Photobio. A: Chem.* 404 (2021): 112866.
- [9]. Serpone, N, and A. V. Emeline. *The journal of physical chemistry letters* 3.5 (2012): 673-677.
- [10]. Belver, Carolina, et al. *Nanoscale Materials in Water Purification*. Elsevier, 2019. 581-651.
- [11]. Fazal-ur-Rehman, M., and Iqra Qayyum. *J. Med. Chem. Sci.* 3.4 (2020): 399-407.
- [12]. Saravanan, R., Francisco Gracia, and A. Stephen. *Nanocomposites for visible light-induced photocatalysis*. Springer, Cham, 2017. 19-40.
- [13]. Yarahmadi, Mohadeseh, et al. *Journal of Alloys and Compounds* 853 (2021): 157000.
- [14]. Yusuf, Abdussamad Ahmad, and M. Fazal-ur-Rehman. *Science & Technology* 4 (2018): 90-96.
- [15]. Alcantara-Cobos, A., et al. *Microporous and Mesoporous Materials* 302 (2020): 110212.
- [16]. Tan, Yong Nian, Chung Leng Wong, and Abdul Rahman Mohamed. *International Scholarly Research Notices* 2011 (2011).
- [17]. Callister, William D., and David G. Rethwisch. *Materials science and engineering*. Vol. 5. New York: John wiley & sons, 2011.
- [18]. Tassalit, D., et al. *International Journal of Education and Learning Systems* 1 (2016).
- [19]. Gan, Jin Yee, et al. *Membranes* 10.8 (2020): 175.
- [20]. Balu, Sridharan, et al. *J. Taiwan Instit. Chem. Eng.* 99 (2019): 258-267.
- [21]. Saad, L. Ben, L. Soltane, and F. Sediri. *Russ. J. Physic. Chem. A* 93.13 (2019): 2782-2788.
- [22]. Senobari, Samaneh, and Alireza Nezamzadeh-Ejhi. *J. Mol. Liq.* 261 (2018): 208-217.
- [23]. Dianat, Somayeh. *Iran. J. Catal.* 8.2 (2018): 121-132.
- [24]. Mirsalari, Seyyedeh Atefeh, and Alireza Nezamzadeh-Ejhi. *Separation and Purification Technology* 250 (2020): 117235.
- [25]. Senobari, Samaneh, and Alireza Nezamzadeh-Ejhi. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 196 (2018): 334-343.