

## COPPER AND COBALT Co-MODIFIED NITROGEN DOPED TITANIA NANO PHOTOCATALYSTS FOR DEGRADATION OF ERICHROME BLACK-T

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Highly efficient copper and cobalt co-modified nitrogen doped titania (TiON/Cu/Co) nano photocatalysts were synthesized using a modified sol-gel method. The azo dye, Erichrome black- T (EBT) was used as model pollutant to examine the photocatalytic activity of these synthesized nano photocatalysts under solar light irradiation. The synthesized photocatalysts consist of single phase quasispherical nanoparticles that exhibited homogeneous distribution of dopants. These catalysts enhanced the optical properties with synthesis methodology adopted. The morphology and structure of the synthesized materials were analyzed by X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). The composition and distribution of the dopants were investigated by Rutherford Backscattering spectrometry (RBS). The optical properties were observed with Diffuse Reflectance Spectroscopy (DRS). At lower cobalt ions concentration in the doped samples, the TiON/Cu/Co responded with extraordinary photocatalytic properties. The photocatalytic degradation efficiency of TiON/Cu/Co was found 95.5% in 100 min duration. The kinetic study of the degradation data followed the pseudo-first order model for all the three catalysts.

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### 1. Introduction

The dyes are unavoidable to human being and their utilization in industry is widespread. More than 50% of the total production of dyes is used in the textile industry and about 15% is used in paper and leather industries [1]. In the dyeing process, 15% of the total dye production becomes an industrial waste [2]. The waste produced from the industries enters into water bodies and aquatic systems. The aquatic eco-system is disturbed due to the deficiency of oxygen and light transmission. Additionally, the waste water containing dyes enters into drinking water resources and hazardously influences the life of human being. Consequently, this destruction can be controlled by removing these dyes from water resources up to a tolerable level [3, 4].

Different techniques like Flocculation, Osmosis, Adsorption and others have already been used conventionally for the removal of dyes from textile waste water, but such techniques have some drawbacks. A currently adopted procedure for the remediation of such kind of impurities from waste water is photocatalytic process. Now this process appears as a promising technology regarding the complete mineralization of organic pollutants from waste water [5, 6]. By the application of such process, the degradation of organic pollutants under solar light may be an ideal technique for the treatment of waste water. On the other hand, till now there is no leading approach to produce a constructive catalyst that can be successfully utilized for the treatment of water. The ambition of this research work is to develop an extremely capable photocatalyst driven by solar light based on a nano scale for the treatment of waste water.

During the previous decades, the titanium dioxide has been investigated as an emerging photocatalyst for environmental remediation and used for the production of hydrogen because of its cut-rate, chemical steadiness, non-toxicity, and elevated power of oxidation for the generation of holes. On the other hand, there are some restrictions concerning its band gap which lies in the UV region (3.2 eV) and its high recombination ratio of photo-induced electrons ( $e^-$ ) and holes ( $h^+$ ) produced when irradiated under ultraviolet light. For the removal of these flaws a choice of modifications [7-16] has been introduced since from the pioneer work in 1972 by Fujishima and Honda's [17]. Amongst the anionic doping of  $TiO_2$ , Asahi et al and others [18, 19] suggested that nitrogen is the main appropriate dopants for the modification of titania, by reason of its analogous dimension and electro negativity regarding oxygen which accordingly decreases the width of its band gap. On the other hand, doping anionic materials show little quantum efficiency and lasting instability regarding photocatalyst [20, 21]. In current studies, copper used as a dopant for titanium dioxide has been experienced for an effective photo reduction of  $CO_2$ , enhanced properties as a photocatalyst [22-26], enhanced properties as a gas sensing material and for the production of hydrogen. For improved optical properties it might be more suitable for tailoring the band gap of  $TiON/Cu$  by various transition metals. Presently due to mixed valance states, cobalt becomes an outstanding and relatively low-cost nominee and consequently might be a valuable attendant for copper.

In this research work, we have reported the photocatalytic activity of doped  $TiO_2$  catalysts synthesized via sol-gel method. The synthesized catalysts were used to study the degradation of Erichrome black- T (EBT), as a model organic pollutant which is widely used in textile dyeing process.

## 2. Experimental

### Catalyst preparation

The copper and cobalt co-modified nitrogen doped titania nanoparticles ( $TiON/Cu/Co$ ) were synthesized by using a sol gel method in single step technique. For this purpose the chemicals used were consist of titanium tetraisopropoxide (TTIP) (Aldrich, 97%), Cobalt nitrate (Aldrich, 99.9%), Copper nitrate hexahydrate (Aldrich, 99.9%), Acetic acid (Aldrich, 99.7%), Ammonium nitrate (Aldrich, 99.5%), anhydrous ethanol (Aldrich, 99.5%) and deionized water. During synthesis process, a solution of 0.043g Cobalt (II) nitrate and 0.2g of Copper nitrate were mixed in a mixture of Ethanol, Acetic acid and water with a ratio 7:2:1 at a temperature of  $10^\circ C$ . After that 18.5 ml of TTIP was added drop wise into the above solution at energetic stirring. After that the solution was placed for 24 hours in a dark place for nucleation process. When this process was completed, the solution was placed in an oven at  $70^\circ C$  for 6 hours for ageing and gelation. After this process, the dry gel obtained was crushed into powder. Then the powder was calcined at  $420^\circ C$  for 3 hours in a tube furnace. Similar scheme was adopted for the synthesis of all the three catalysts  $TiON$ ,  $TiON/Cu$  and  $TiON/Cu/Co$ .

### Characterization

The synthesized samples were analyzed with the help of X-ray diffractometer with wide angle (Philips X'Pert PRO 3040/60), by the application of  $Cu-K\alpha$  radiation. The TEM analysis of synthesized samples was performed in model Titan G<sup>2</sup> 80-300 FEI Company (FEI Company, Hillsboro, OR). The spatial frequency (lattice d-spacing) of the synthesized samples was calculated by the Fast-Fourier transforms (FFTs) of HRTEM micrographs and consequently crystal structure of samples was determined. The elemental analysis and distribution of dopant of the nanoparticles was measured by Rutherford Backscattering Spectrometry (RBS). The Perkin-Elmer Lambda 950 UV/VIS/NIR spectrophotometer was used to measure the optical properties.

A comprehensive procedure for measurement of photocatalytic activity of the synthesized samples for removal of dye EBT was adopted. All the three photocatalysts i.e.,  $TiON$ ,  $TiON/Cu$  and  $TiON/Cu/Co$  were used in this photo-reduction experiment. The experiment was carried out in 500 ml cylindrical pyrex glass cylinder. A 100 ppm solution of EBT was prepared in double distilled water. Each time 100 ml dye solution was taken and 0.1 g/L of synthesized sample was put in dye solution. The degradation reaction was carried out under visible (solar) light. The zero time reading was obtained from the suspension kept in dark for each catalyst. After each 10 min time interval, 3 ml of the sample was collected and centrifuged at 4000 rpm, followed by filtering through 0.45  $\mu m$  nylon filter. For comparative study,  $TiON$ ,  $TiON/Cu$  and  $TiON/Cu/Co$  were also used for degradation of EBT separately under the same conditions. A controlled experiment was also conceded for the confirmation, that reaction is neither thermal nor photochemical, but it is a photocatalytic reaction. The residue concentration of EBT was determined by measuring its absorbance using UV-Visible spectrophotometer.

### 3. Results and discussion

#### XRD analysis

The morphology and crystal structure of the synthesized samples were studied by XRD patterns of TiON, TiON/Cu, TiON/Cu/Co are shown in Fig. (1a). From the XRD analysis it is confirmed that the characteristic peaks are for the anatase TiO<sub>2</sub> and are devoid of any additional phase of impurity. This shows that the dopants are well dispersed and occupy either interstitial position in TiO<sub>2</sub> crystal structure. All the XRD patterns were indexed to the anatase in phase of TiO<sub>2</sub>, consistent with JCPDS No. 02-0387. Due to metallic doping, there is an increased in the crystal behavior of the synthesized catalysts shows that metallic doping induced crystallization at normal temperature [27]. This behavior also suggests that anatase phase of the synthesized samples would have an enhanced photocatalytic influence than titania in amorphous form [28]. On the basis of the peaks with full width at half maxima in the XRD patterns, the average sizes of the crystallites calculated on the basis of Scherrer's formula [29] were 12, 15, and 10 nm for the synthesized samples TiON, TiON/Cu and TiON/Cu/Co, respectively. It was found that no distinct change in the parameters of lattice and cell volume was found after doping the TiO<sub>2</sub> with nitrogen. It is due to the equivalent ionic radii of oxygen and nitrogen. But when Cu is doped, a slight shift in XRD peaks towards left of copper doped titania can be observed, for the reason that radius of ionic Cu<sup>2+</sup> (0.72 Å) is to some extent larger than the ionic radius of Ti<sup>4+</sup> (0.68 Å), due to which it creates a strain in the titania lattice.

#### TEM and FFT studies

Fig. (1b) shows a representative TEM micrograph of the catalyst TiON/Cu/Co. It can be observed that the morphology of the particles is quasispherical, and having an average size of the particles in the range of 12 nm, which was directly measured from the scale of the image.

The Fast Fourier Transform (FFT) of the representative sample of TiON/Cu/Co nanoparticles consists in the form of six resolved concentric rings as shown in Fig. (1c). These specified rings are presented at specific spatial frequencies in the image of FFT. The radii of these rings (R<sub>1</sub>-R<sub>6</sub>) are determined through the measurement of the diameter of each ring, and then dividing it by 2, and then taking the resultant numbers reciprocal. After then the d-spacing values can be obtained from the pattern of diffraction. The numbers labeled on diffraction rings of the representative sample represent the subsequent planes of the TiON/Cu/Co: (R1): (101); (R2): (004); (R3): (200); (R4): (211); (R5): (220); and (R6): (105).

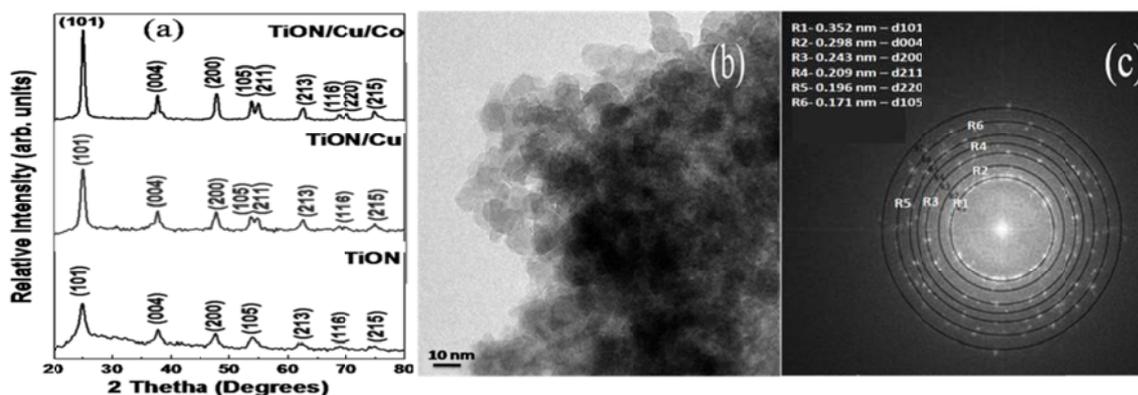


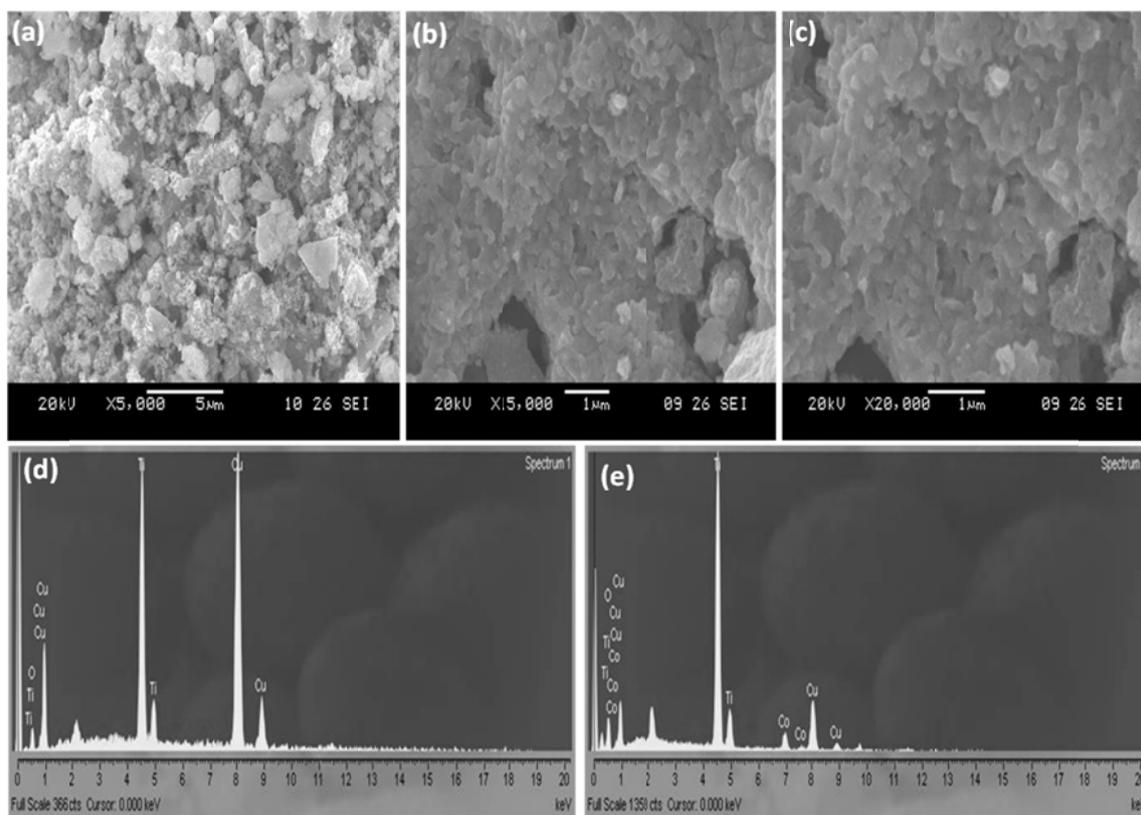
Fig 1: (a) XRD Patterns of TiON, TiON/Cu, TiON/Cu/Co (b) A representative TEM image and (c) FFT analysis of TiON/CuO/Co nanoparticles.

#### SEM and EDX analysis

The morphology of synthesized samples TiON, TiON/Cu and TiON/Cu/Co was evaluated by SEM as presented in Fig. 2a-c respectively. It is clear from the figures that all the synthesized samples are highly porous in nature and their porosity increases by the introduction of dopants in the TiON. It can also be seen in all the micrographs that the particle size is decreased by the introduction of dopants. It can be observed that the particle size data is in accordance with XRD finding. It was found that the surface of the catalysts can be modulated through metal oxides, by enhancing the active site dispersion. The composition of the

synthesized samples is determined by the energy dispersive X-ray utility of SEM.

The EDX analysis of the samples TiON/Cu and TiON/Cu/Co are shown in **Fig. 2d,e** confirming the elemental compositions as used in the experimental procedure.



*Fig. 2. SEM of (a) TiO/N (b) TiON/Cu (c) TiON/Cu/Co, EDX analysis of (d) TiON/Cu (e) TiON/Cu/Co*

### RBS Analysis

The composition and dopants distribution of the synthesized samples was analyzed by RBS analysis. For this function, a beam of 2.0 MeV  $\text{He}^{2+}$ , 20 nA and 20  $\mu\text{C}$  with 5mm in diameter was produced by Tandem Pelletron Accelerator (5UDH-2, National Electrostatic Corporation, USA). The samples of synthesized catalysts were placed on a goniometer with high precision ( $0.01^\circ$ ) five-axis in a vacuum chamber. In this regard the orientation of samples with respect to the  $\text{He}^{2+}$  beam could be controlled precisely. The particles found during backscattering were collected by detector with Si Surface Barrier (SSB). The angle for detection was  $170^\circ$  and its resolution energy was about 25 keV. The RBS recorded calibrated spectra was analyzed using the computer Code Software “SIMNRA” (version 6.02) [30, 31]. To overcome the detection problem for nitrogen detection, a precise experiment was conducted, using 3.60 MeV  $\text{He}^{2+}$  ion beams, which regards the nuclear resonance energy of nitrogen.

RBS analysis was carried out for detailed composition and dopants distribution in the synthesized samples, as shown in Fig. (3). In the RBS spectra, all elements were detected except nitrogen because of its low concentration in the samples. For detecting nitrogen, specific experiment was performed using resonance nuclear energy of nitrogen i.e.  $\text{He}^{2+}$  ion beam energy of 3.6 MeV. In each sample, around 0.32% atomic, nitrogen was detected. For stoichiometric of the nano photocatalysts, the experimental data is simulated, and the resultant simulated curve showed a good agreement with that of experimental observations. We concluded that all dopants are homogeneously distributed into  $\text{TiO}_2$  across the pellet because of synthesis procedure adopted for design of the photocatalysts.

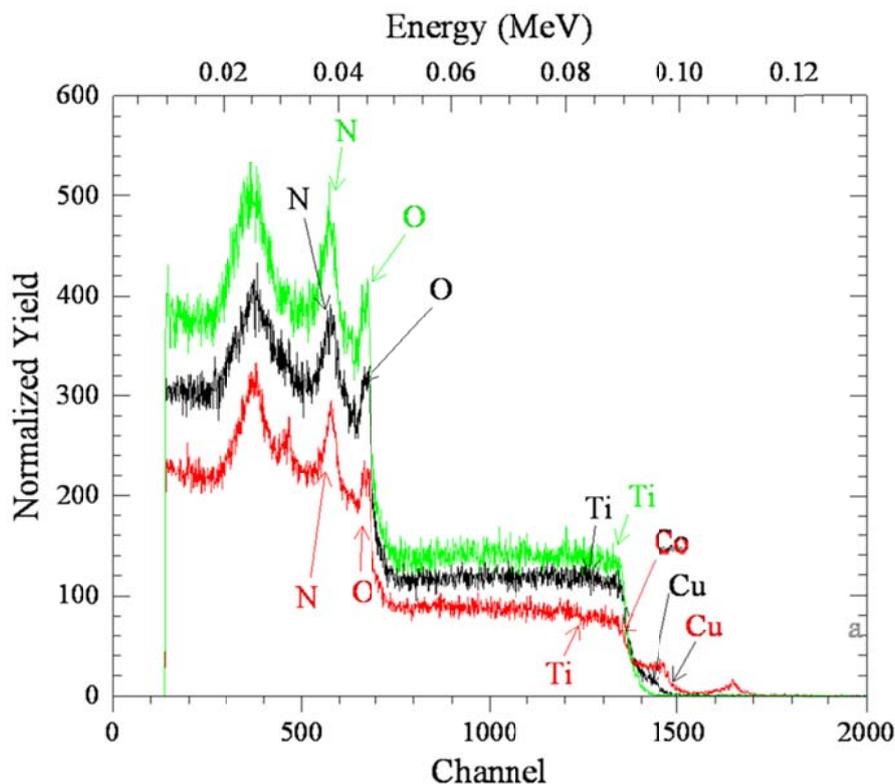


Fig. 3 RBS analysis of TiON, TiON/Cu and TiON/Cu/Co

### Optical properties (DRS)

The optical properties of TiON, TiON/Cu and TiON/Cu/Co nanoparticles were evaluated by measuring the DRS. The optical absorbance in term of Kubelka–Munk function was estimated using the equation given below.

$$F(R) = \frac{(1-R)^2}{2(R)}$$

Where, R is the diffuse reflectance [32]. For TiON nanoparticles in Fig. (4), a characteristic red shift was observed that could be ascribed to the nitrogen dopant [33]. The TiON/Cu/Co nanoparticles showed enhanced visible-light absorption phenomenon compared to that of other powders. This phenomenon is because of donor levels generated by  $\text{Cu}^{+2}$  and  $\text{Co}^{2+}$  ions into the band gap of titania or might be due to the formation of mixed valance cobalt oxide i.e.  $\text{Co}_3\text{O}_4$ . The  $\text{Co}_3\text{O}_4$  is generally produced from hydrated cobalt in presence of air above  $275^\circ\text{C}$  [34], which is p-type semiconductor. Therefore, the possibility of heterounion of n-type  $\text{TiO}_2$  and p-type  $\text{Co}_3\text{O}_4$  not only enhance the optical properties but also the quantum efficiency. The band gaps of these nanoparticles were calculated by extrapolation of linear region of the plot, with lower band gap value of 1.28 eV for TiON/Cu/Co.

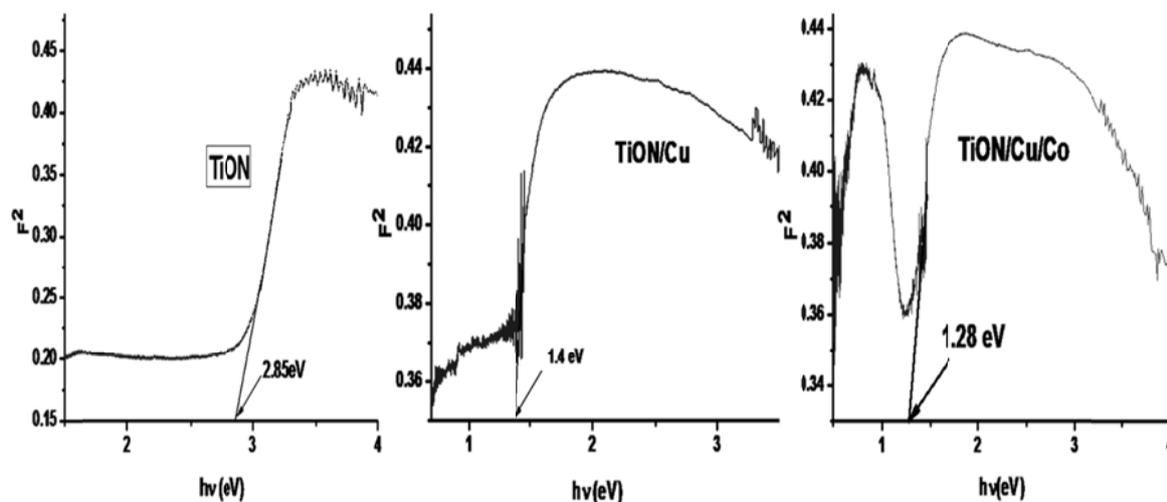


Fig. 4. Band gap of TiON, TiON/Cu and TiON/Cu/Co calculated from the DRS spectra.

### Photocatalytic degradation efficiency

The efficiency of photocatalytic degradation of EBT aqueous solution with TiON, TiON/Cu and TiON/Cu/Co under visible light (solar light) is depicted in Fig. (5). An extraordinary decrease in absorbance of EBT solution was observed after 10 minutes treatment of TiON/Cu/Co. Moreover, up to 95.5% degradation of EBT was attained after 100 minutes treatment. A degradation trend was also observed with TiON and TiON/Cu but the efficiency was lower than TiON/Cu/Co. The phenomenon of enhancement in activity of TiON/Cu/Co is because of the combined effects i.e. increased optical absorbance in the visible region creating extra electron-hole pairs, surface area enhancement, and increased quantum efficiency because of the  $\text{Co}_3\text{O}_4\text{-TiO}_2$  heterounion. When visible light strike upon catalyst,  $e^-$  -  $h^+$  pair is generated, electrons in conduction band are trapped by  $\text{Co}^{3+}$  ( $\text{Co}_3\text{O}_4$  or  $\text{Co}_2\text{O}_3$ ) and adsorbed oxygen on the surface. Later on, in dark, these electrons are out back to the conduction band, accepted by oxygen and at the end produce OH free radicals. These free radicals degrade EBT. The kinetic studies reveal that all the three samples follow the pseudo-first order kinetic model as shown in Fig (6). The degradation efficiency comparison of all the three samples for the dye EBT (100 ppm) is shown in Table 1.

Table: 1. Comparison of degradation efficiency of catalysts TiON, TiON/Cu, TiON/Cu/Co.

Time (min)	% Degradation		
	TiON	TiON/Cu	TiON/Cu/Co
10	38.3	42.2	48.5
20	48.12	50.6	57.3
30	55.0	58.3	66.0
40	63.1	66.1	72.1
50	66.7	73.2	79.8
60	71.2	76.9	85.0
100	<b>76.4</b>	<b>86.4</b>	<b>95.5</b>

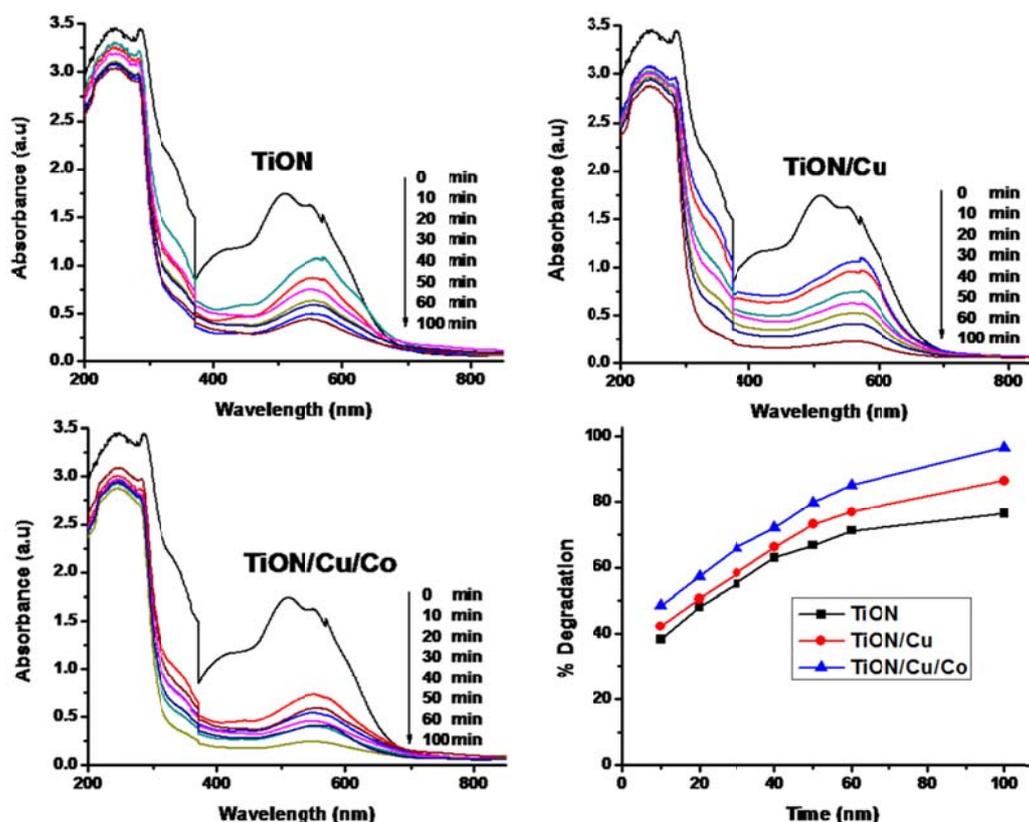


Fig 5. UV-Vis spectral variations of EBT aqueous solution (100ppm) during solar irradiation and % degradation by Catalyst TiON, TiON/Cu and TiON/Cu/Co

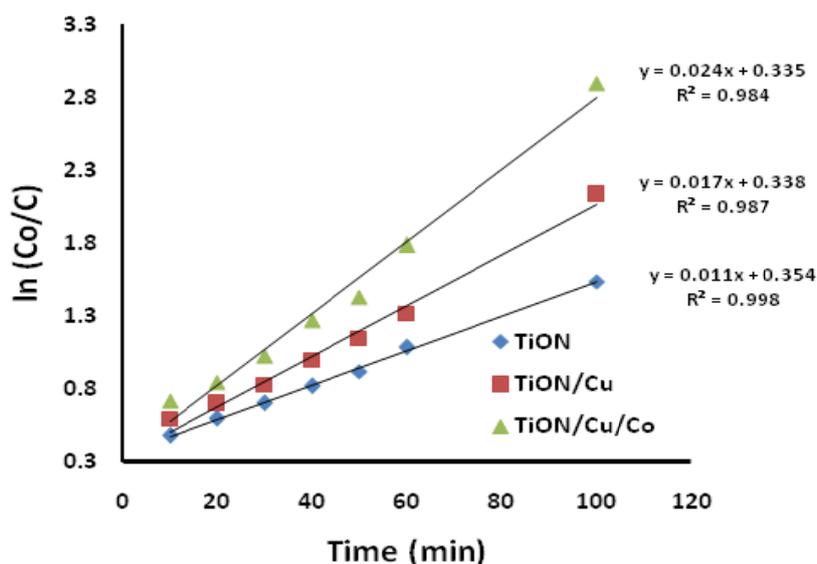


Fig. 6. The pseudo-first order kinetic model of TiON, TiON/Cu and TiON/Cu/Co.

### Effect of initial dye concentration

The effect of initial dye (EBT) concentration from 20 ppm to 100 ppm by the photocatalysts (TiON, TiON/Cu, TiON/Cu/Co) was investigated under solar irradiation. The obtained results are plotted as percentage degradation and kinetics of the dye photo decolorization efficiency under solar light and are shown in Fig. (7). The results mentioned in Table 2 show that the degradation rate of the dye decreases as

the initial dye concentration increases. As the initial dye concentration increase the greater number of dye molecules get absorbed on the surface of catalysts ( TiON, TiON/Cu, TiON/Cu/Co ), which cause a reduction of hydroxyl radicals due to the reduction of active sites for the adsorption. Also due to the short life time (nanoseconds), hydroxyl radicals can only react at the place of their production and the increase in dye concentration from 20 ppm to 100 ppm reduces the degradation efficiency because of the self screening effect of the dye. By increasing the initial dye concentration, the number of molecules of the dye in the solution is enhanced, due to which the majority of the photons from solar irradiation are absorbed by the dye molecules rather than the catalyst surface. As a result, the catalytic efficiency is reduced in all the three catalysts (TiON, TiON/Cu, TiON/Cu/Co) as shown in Table 2.

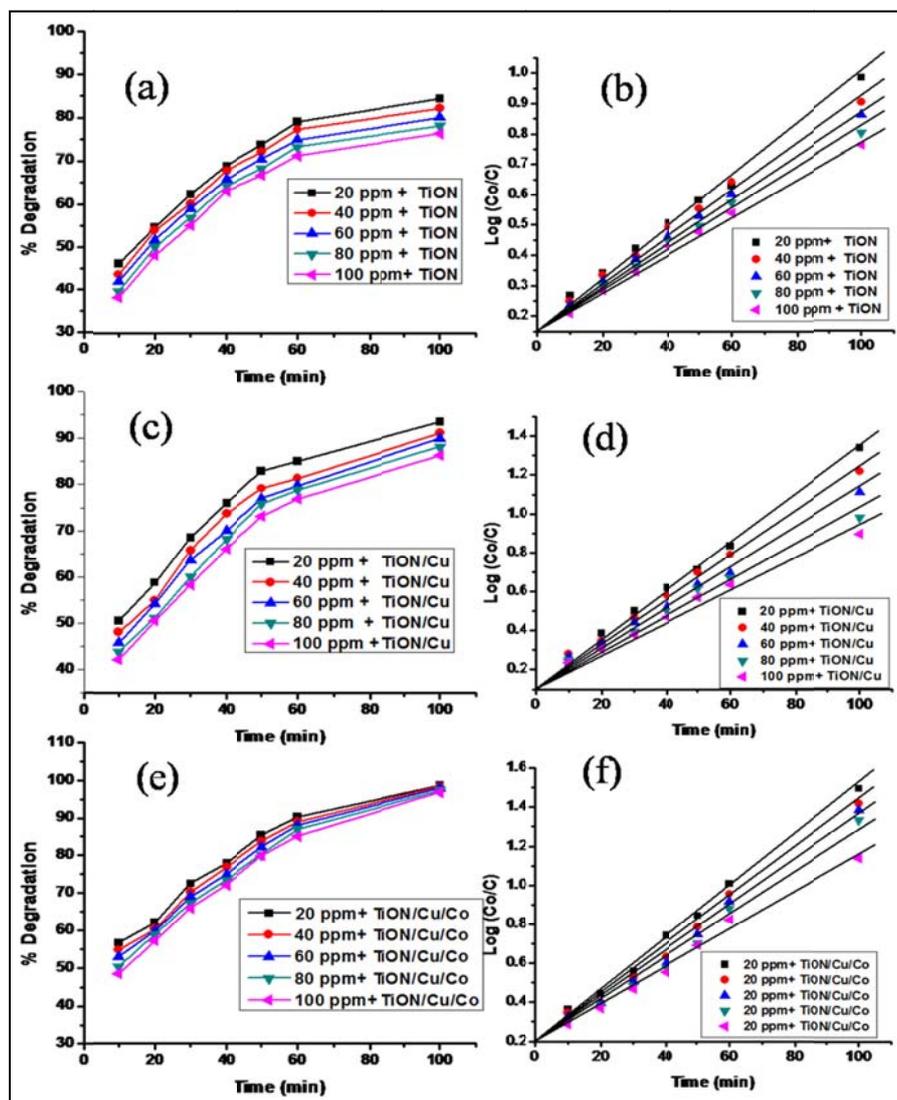


Fig 7. The degradation (%) and kinetics of the samples at different dye concentrations.

Table 2. Reduction in catalytic efficiency of the catalysts with increasing dye concentration.

Time (min)	Catalyst	%Degradation				
		20 ppm	40 ppm	60 ppm	80 ppm	100 ppm
100	TiON	84.5	82.3	80.2	78.2	76.4
100	TiON/Cu	93.6	91.2	90	88.2	86.4
100	TiON/Cu/Co	99.7	98.1	97.7	97.1	95.5

### Effect of Catalyst Concentration

The effect of photocatalyst concentration on the degradation of EBT was studied by applying the different concentrations (0.1 g/L to 1.2 g/L) of the catalysts is shown in Fig. (7). The degradation rate was found to increase by increasing the catalyst dosage from 0.1 g/L to 0.9 g/L and then decreases up to 1.2 g/L in case of catalyst TiON, increases from 0.1 g/L to 0.85g/L and then decreases up to 1.2 g/L in case of TiON/Cu/Co. The optimum values of the catalyst dosage further decreases in case of catalyst TiON/Cu/Co which is 0.7g/L. This is due to the fact that due to introduction of cobalt the band gap decreased upto 1.28 eV which enhances the photocatalytic efficiency. The increase in degradation efficiency upto optimum value of catalyst dosage is due to the increase in active sites and catalyst surface area. The reason that the decrease in degradation after optimum value of catalyst dosage is due to the fact that the turbidity increases by enhancing the catalyst dosage which decreases the penetration of solar light in the suspension [35- 37]. Therefore, it is concluded that due to (i) screening effect the penetration of photon decreases and (ii) increased in catalyst dosage, there is an increase in photon reflectance onto the catalyst. Thus the catalyst dose was fixed to 0.9g/L for TiON, 0.85 g/L for TiON/Cu and 0.7 g/L for TiON/Cu/Co for further investigation.

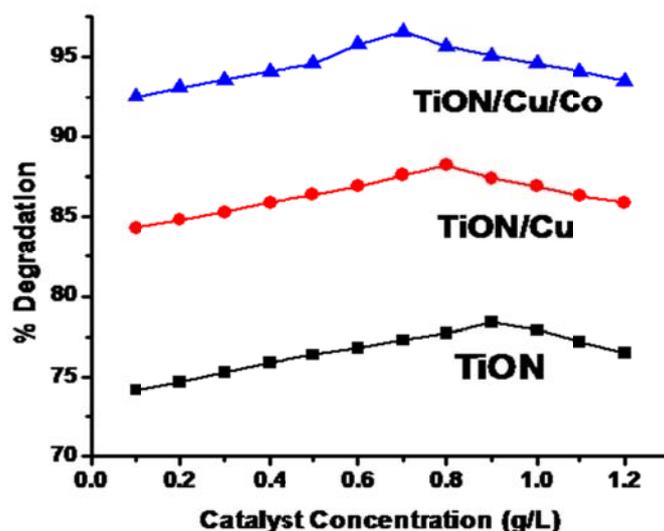


Fig 7. The effect of photocatalyst concentration on the degradation of EBT.

### 4. Conclusion

This study showed that metallic doping in TiON can considerably increase the visible photocatalytic activity of the catalyst. The analysis of the prepared catalysts indicates that the dopants are very well dispersed in the anatase titania matrix. Optical properties enhancement, greater surface area and high quantum efficiency resulted due to adopted methodology and cobalt

modification. The highly efficient Co/Cu/TiON nanoparticle photocatalysts has remarkable activity in the degradation of EBT under visible light illumination. This degradation technique may be a cost effective and alternate to all other conventional techniques used for textile waste water treatment.

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