

## Degradation of trypan blue dye using copper pyrovanadate as heterogeneous photo-Fenton like catalyst

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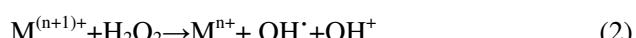
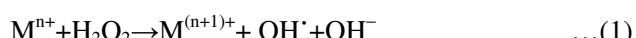
The photo-Fenton like degradation of trypan blue dye has been studied by using copper pyrovanadate catalyst. Catalyst has been prepared by wet chemical method and characterized by X-ray diffraction, scanning electron microscopy, Barrett-Emmett-Teller (BET), thermal gravimetric analysis and FT-IR techniques. The effects of different reaction parameters have been assessed.  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$  etc. ions have been identified as final mineralization products. Chemical Oxygen Demand of the reaction mixture before and after exposure has been determined. A tentative mechanism for the degradation of trypan blue has also been proposed. Involvement of  $\text{OH}^\cdot$  radical as a main oxidant has been confirmed using its scavengers. The photodegradation efficiency after 2 hour of illumination is found to be 72.41%. The results indicate that copper pyrovanadate acts as an effective catalyst for the heterogeneous photo-Fenton degradation of trypan blue.

**Keywords:** Chemical oxygen demand, Copper pyrovanadate, Barrett-Emmett-Teller, Heterogeneous, Photo-Fenton like, Trypan blue.

The textile industry is one of the largest consumers of molecular dyes in the world, many of which are polluting the environment<sup>1-5</sup>. It has been estimated that more than 50% of all dyes in common use are azo dyes because of their chemical stability and versatility<sup>6</sup>. About 10-15% of the synthetic textile dyes used are lost in waste streams during manufacturing or processing operations<sup>7</sup>. The effluents are colored which not only created environmental and aesthetic problems, but also posed a great potential toxic threat to ecological and human health as most of these dyes are toxic and carcinogenic<sup>8</sup>. Azo dyes are not biodegradable by aerobic treatment processes<sup>9</sup>. Trypan blue is also an azo dye and the name trypan blue is given because it can kill trypanosomes, the parasites that cause sleeping sickness. Trypan blue is also known as diamine blue and niagara blue. Structure of trypan blue dye is given in Fig. 1.

In the last few years, advanced oxidation processes (AOP's) have emerged as efficient technologies for the destruction of various classes of biorecalcitrant pollutants in water. The characteristic feature of AOP's is the generation of  $\text{OH}^\cdot$  radical as the main

oxidizing species. Fenton method is one of the frequently used advanced oxidation process, as it offers various advantages of green chemistry like low cost and formation of ecofriendly end products  $\text{H}_2\text{O}$  and  $\text{O}_2$  from  $\text{H}_2\text{O}_2$ . In Fenton chemistry too, hydroxyl radical ( $\text{OH}^\cdot$ ) is thought to be a main oxidizing species leading to nonselective degradation of organics. Equations (1) and (2) are regarded as the two key steps in the decomposition of  $\text{H}_2\text{O}_2$  with Eq. (2) representing the rate determining step<sup>10,11</sup>.



M = Fe, V (Refs. 12-15) etc.

However, the homogeneous Fenton process has significant disadvantages: (i) iron ions have to be separated from the system at the end of the process by precipitation, which makes the process expensive. (ii) the process requires narrow pH range (pH 2-3) and (iii) iron ions may be deactivated due to complexation with some iron complexing reagents such as phosphate anions and intermediate oxidation products<sup>12</sup>.

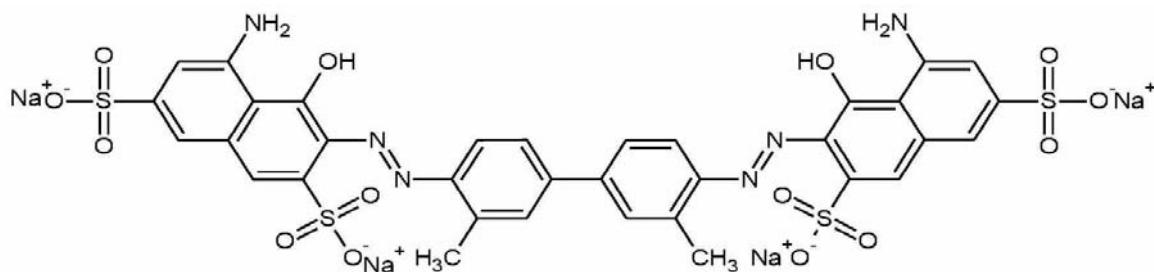


Fig. 1 — Structure of trypan blue dye

To overcome the disadvantages of homogeneous Fenton type processes, heterogeneous Fenton and Fenton like catalysts have recently received much attention. Heterogeneous Fenton-like catalysts, such as iron oxides<sup>16,17</sup> and other transition metal oxides<sup>18-20</sup> have recently been reported. Zhang *et al.*<sup>13</sup> used iron tetrapolyvanadate  $\text{Fe}_2\text{V}_4\text{O}_{13}$  as a multi-metal heterogeneous Fenton like catalyst for the degradation of organic pollutants.

It has been reported<sup>21,22</sup> that copper plays a similar role as iron in producing hydroxyl radicals on reaction with hydrogen peroxide (Eq. 5). This is usually referred to as a Fenton like process. The more important is that the Fenton like reaction does not very much depend on *pH* so that it acts efficiently at a higher *pH* also. However, its catalytic efficiency is not as good as iron in the acidic medium. Moreover, since copper is a highly toxic heavy metal ion, it is not suitable to be used as homogeneous catalyst in the liquid medium.



In order to tackle this problem, researchers have tried to load metal ions like copper ions onto porous solid support by various techniques such as impregnation<sup>23</sup>, coprecipitation<sup>24</sup> etc. for their use as heterogeneous catalyst. Punjabi *et al.*<sup>25</sup> also studied the degradation of coomasie brilliant blue R-250 by using copper modified iron oxide as heterogeneous photo-Fenton reagent. Punjabi *et al.*<sup>26</sup> also reported the degradation of bismark brown-R using copper loaded neutral alumina as heterogeneous photo-

Fenton like reagent. Pradhan *et al.*<sup>27</sup> reported the photo-Fenton degradation of phenolic compounds (phenol, 2-chloro-4-nitrophenol and 4-chloro-2-nitrophenol) in aqueous solution using mesoporous  $\text{Cu}/\text{Al}_2\text{O}_3$ -MCM-41 nanocomposite as a heterogeneous photo-Fentonlike catalyst. Yip *et al.*<sup>28</sup> developed chemical-vapor-deposited copper on acid-activated bentonite clay and used as heterogeneous catalyst for the photo-Fenton like oxidation of textile organic pollutants. Degradation of sunset Yellow FCF using copper loaded bentonite and  $\text{H}_2\text{O}_2$  as photo-Fenton like reagent has been reported by Chanderia *et al.*<sup>29</sup>.

Although mixed oxides based on vanadium have been studied for their many technological applications like lithium rechargeable battery<sup>30</sup> and heterogeneous catalyses<sup>31</sup>, but negligible attention has been paid on the use of copper pyrovanadate as visible light responsive heterogeneous photo-Fenton like catalyst for the degradation of dyes.

In the present work, copper pyrovanadate, a novel visible light sensitive photo-Fenton like catalyst has been prepared by wet chemical method. It has been used for the degradation of trypan blue dye in presence of  $\text{H}_2\text{O}_2$ / visible light.

## Experimental Section

### Preparation of catalyst

Copper pyrovanadate,  $\text{Cu}_3\text{V}_2(\text{OH})_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  was synthesized by simple wet chemical method. For the synthesis, aqueous solutions of  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  and  $\text{NH}_4\text{VO}_3$  were mixed together with the Cu/V molar ratio of 1:2. The mixture was stirred for 1 h at room temperature in air. The resulting green colored precipitate was collected and washed with deionized water many times and finally with anhydrous ethanol. The precipitate was air dried for 12 h.

### Characterization

X-ray powder diffraction (XRD) measurements were performed on a BrukerD8 Advance X-ray

diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.154\text{nm}$ ). The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-Pyris-1 thermogravimetric analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$ . Infrared (IR) spectrum was recorded using a Perkin-Elmer FTIR-1730 spectrometer with KBr disks at room temperature in the range of  $4000\text{-}400\text{ cm}^{-1}$ . Scanning electron microscopy (SEM) studies were performed using a Bruker AXS microscope equipped with energy dispersive X-ray (EDX) fluorescence spectral analysis for element composition and Robinson secondary electron (SE) and backscattered electron (BSE) detectors for imaging. The surface area of the sample was determined by nitrogen adsorption/desorption analysis. The instrument utilized for nitrogen sorption analysis was a Micromeritics (Gemini 2370), USA surface area analyzer. Before each experiment, the sample (0.2 g) was degassed at  $105^\circ\text{C}$  for 24 h. Stability of the catalyst was checked by atomic absorption spectroscopy using ETCL4129A atomic absorption spectrophotometer.

For the photo-Fenton degradation, stock solution of trypan blue dye ( $1.0 \times 10^{-3}\text{M}$ ) has been prepared. A reaction mixture containing dye ( $1.0 \times 10^{-5}\text{ M}$ ), catalyst and hydrogen peroxide, was exposed to light for a certain period of time. A 200 W tungsten lamp (Philips) was used for irradiation purpose. The intensity of light at various distances was measured by "Suryamapi" [CEL Model 201]. A water filter has been used to cut off thermal radiations. pH of the solution was measured by a digital pH meter [Systronics Model 335]. pH of the solution was adjusted by using standard 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The progress of the degradation was monitored by measuring the absorbance of the reaction mixture at regular time intervals using UV visible spectrophotometer (Systronics Model 106).

## Results and Discussion

### Characterization of catalyst

#### Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) of  $\text{Cu}_3\text{V}_2(\text{OH})_2\text{O}_7\cdot 2\text{H}_2\text{O}$  calcined at  $750^\circ\text{C}$  is shown in Fig. 2a. The basic structure of catalyst (copper pyrovanadate) is a sheet-like structure with copper oxide/hydroxide layers that are held together by the pyrovanadate groups and then these layers are stacked

by layers of water (similar to Volborthite). Based on the SEM images, porosity of the surface is evident and it seems that the particles have not grown with uniform size. The particles size of  $\text{Cu}_3\text{V}_2(\text{OH})_2\text{O}_7\cdot 2\text{H}_2\text{O}$  that were propagated on the surface seems to be in the range of  $50\text{-}200\text{ }\mu\text{m}$ . The EDX analysis was performed for further confirmation of the obtained product composition. Figure 2b shows EDX spectrum which indicates the existence of V (23.35%), Cu (48.94%) and O (25.74%) elements in the prepared catalyst.

#### BET analysis

The specific surface area of the catalyst was measured by means of conventional BET method. Results showed that the average specific surface area of  $\text{Cu}_3\text{V}_2(\text{OH})_2\text{O}_7\cdot 2\text{H}_2\text{O}$  particle was  $17.6\text{ m}^2/\text{g}$  at  $105^\circ\text{C}$ . This value may be attributed to the enhanced crystalline grain size calcined at  $750^\circ\text{C}$ .

#### FT-IR spectroscopy

Surface properties, especially surface hydroxyl groups, are very important for the degradation of organic pollutants in heterogeneous catalytic

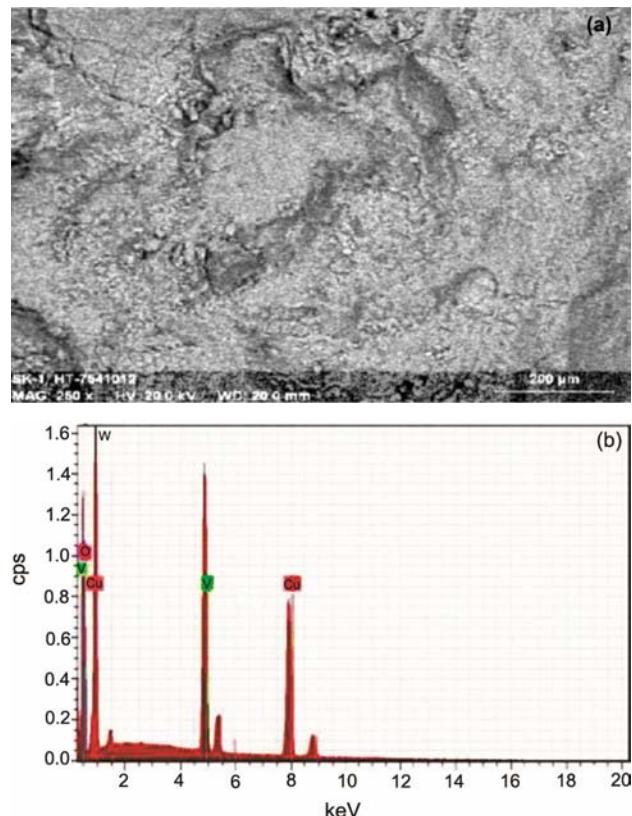


Fig. 2 — (a) SEM image of catalyst (b) EDX of catalyst

reactions. The catalyst was further characterized with FTIR to elucidate the surface OH groups. From FTIR spectrum of heated  $\text{Cu}_3\text{V}_2(\text{OH})_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , the sharp band at  $592\text{ cm}^{-1}$  corresponded to the vibration of the Cu–O bonds in the crystalline lattice of catalyst. The band at  $1508\text{ cm}^{-1}$  was assigned to the bending vibration of adsorbed water. The wide band at  $3500\text{--}3600\text{ cm}^{-1}$  was attributed to the stretching of OH groups of chemisorbed water. This fact suggested that after loss of the water adsorbed on the surface, the catalyst did not suffer from any obvious decomposition and had favorable thermal stability in the temperature range investigated.

#### X-Ray diffraction (XRD)

X-ray powder diffraction (XRD) measurements were performed on a BrukerD8 Advance X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154\text{ nm}$ ). From diffraction peaks (Fig. 3) it is observed that the synthesized catalyst showed monoclinic crystalline structure compared with standard orthorhombic ammonium metavanadate and rhombohedral copper nitrate trihydrate. The crystallite size ( $t$ ) of the peak appeared at  $2\theta = 13^\circ$ , can be calculated by using Scherrer's formula:

$$t = 0.9 \lambda / \beta \cos \theta$$

where  $\lambda$  is the wavelength of X-rays used ( $1.5406\text{ \AA}$ ),  $\beta$  is the full width at half maximum (FWHM) and  $\theta$  is the angle of diffraction. The average crystallite size of prepared catalyst is found to be  $82\text{ nm}$  which is of the order of nano size.

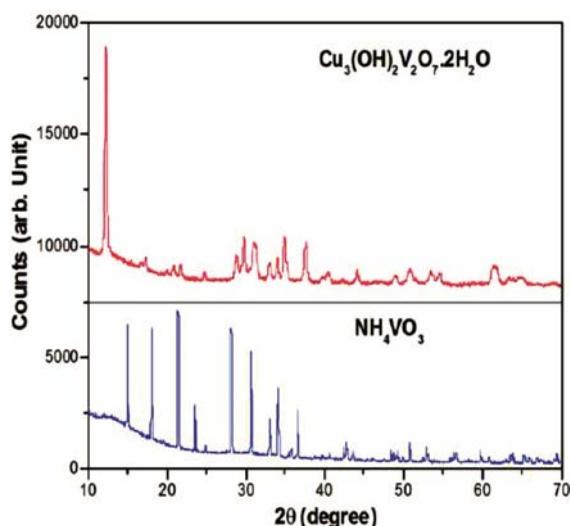


Fig. 3 — XRD images of catalyst and ammonium metavanadate

#### Thermal gravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA-Pyris-1 thermogravimetric analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$ . The sample was kept in  $\text{N}_2$  atmosphere to avoid oxidation during the whole heating process.

In order to investigate the thermal stability of catalyst its TG/DTG was determined. Thermal decomposition process of catalyst was recorded at a heating rate of  $10^\circ\text{C}/\text{min}$  in the air from room temperature to  $800^\circ\text{C}$ . The total weight loss of the catalyst was approximately 77% and the decomposition process can be divided into two distinct steps. From the structural study of copper pyrovanadate<sup>32</sup>, it was suggested that the copper pyrovanadate can be described by the formulation  $\text{Cu}_3\text{V}_2(\text{OH})_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  this formulation was found to be in good agreement with TG curve which presents two breaks at  $270$  and  $330^\circ\text{C}$ , which correspond to two weight loss steps: removal of physically adsorbed water of hydration and the loss of surface hydroxyl group.

#### Atomic absorption spectroscopy (AAS)

Stability of the catalyst was checked by atomic absorption spectroscopy using ETCL4129A atomic absorption spectrophotometer. Even after one month, leaching of copper or vanadium ions from the catalyst was found to be negligible. Thus, catalyst was found to possess good stability for its use as heterogeneous photo-Fenton like reagents under visible range.

#### Photo-Fenton activity

An aliquot of  $3.0\text{ mL}$  was taken out from the reaction mixture at definite time intervals and the absorbance was measured at  $590\text{ nm}$ . It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of trypan blue decreases with increasing time of exposure. A plot of  $2 + \log A$  against time was linear and follows pseudo-first order kinetics. The rate constant was measured with the expression.

$$k = 2.303 \times \text{Slope} \quad \dots (7)$$

Typical run for the degradation of dye under optimum conditions is reported in Table 1.

The chemical oxygen demand of reaction mixture before and after treatment has been determined by redox method using ferrous ammonium sulphate and  $\text{KMnO}_4$ . The photodegradation efficiency of the catalyst was calculated from the following expression:

Table 1 — Typical run for the degradation of dye

Time (min)	Absorbance (A)	2+ log A
0	1.096	2.039
10	0.721	1.875
20	0.322	1.507
30	0.236	1.372
40	0.184	1.264
50	0.102	1.008
60	0.069	0.838
70	0.055	0.544
80	0.024	0.380
90	0.016	0.204
100	0.010	0.0

Rate constant k ( $\text{sec}^{-1}$ ) =  $7.83 \times 10^{-4}$   
 $p\text{H} = 6.5$ , Light intensity =  $70 \text{ mWcm}^{-2}$ , Catalyst = 0.06 g  
[trypan blue] =  $1.6 \times 10^{-5} \text{ M}$ ,  $\text{H}_2\text{O}_2$  = 0.45 mL

$$\eta = \frac{\text{COD}_{\text{before}} - \text{COD}_{\text{after}}}{\text{COD}_{\text{before}}} \times 100$$

$\eta$  = Photodegradation efficiency (%)

COD<sub>before</sub> = COD of dye solution before illumination

COD<sub>after</sub> = COD of dye solution after illumination

#### Effect of pH

The effect of pH on the rate of photo-Fenton degradation has been investigated in pH range 5.0–8.0. It has been observed that with an increase in pH, rate of reaction increases and after attaining the maximum value at pH 6.5, rate decreases with further increase in pH. The increase in rate of degradation on increasing pH may be explained by the fact that larger numbers of hydroxyl ions are available at higher pH values. These  $\cdot\text{OH}$  ions will generate more  $\cdot\text{OH}$  radicals resulting in higher rate of degradation of dye. But on increasing the pH beyond 6.5, the number of  $\cdot\text{OH}$  ions also increase and get adsorbed on the catalyst surface making it negatively charged. Due to this approach of the anionic dye towards catalyst surface becomes difficult. As a result, the rate of degradation decreases.

#### Effect of concentration of dye

The effect of variation of concentration of dye on the rate of photo-Fenton degradation has been observed in the range from  $0.40 \times 10^{-5} \text{ M}$ – $3.20 \times 10^{-5} \text{ M}$ . It has been observed that the rate of degradation increases with increasing concentration of trypan blue up to  $1.60 \times 10^{-5} \text{ M}$ . Further increase in concentration beyond  $1.60 \times 10^{-5} \text{ M}$  decreases the rate of degradation.

This may be explained on the basis that initially, on increasing the concentration of dye, the reaction rate increases as more molecules of dye are available for degradation. But further increase in concentration beyond  $1.60 \times 10^{-5} \text{ M}$  causes retardation of reaction due to number of collisions among dye molecules increase whereas, collisions among dye and  $\cdot\text{OH}$  radicals decrease. As a consequence, rate of reaction is retarded.

#### Effect of amount of catalyst

The effect of variation of amount of catalyst has also been observed on the rate of photo-Fenton degradation. It has been observed that with increase in the amount of catalyst, the rate of photo-Fenton reaction increases to a certain amount of catalyst (0.06 g), which may be regarded as a saturation point. Beyond this point, the rate of reaction decreases with increase in amount of catalyst. This may be explained by the fact that with the increase in the amount of catalyst, the surface area of catalyst will increase. Hence, the rise in the rate of reaction has been observed. But after a certain limiting amount of catalyst (0.06 g), if the amount of catalyst was further increased, it would also increase the number of iron and copper ions and then there is a possibility of short circuiting between vanadium (III) and vanadium (V) & copper (I) & copper (II) ions<sup>33,34</sup>. As a result, less number of hydroxyl radicals are formed and reaction rate is retarded.

#### Effect of amount of $\text{H}_2\text{O}_2$

The effect of variation of amount of  $\text{H}_2\text{O}_2$  on the photo-Fenton degradation of trypan blue has also been investigated in the range from 0.20 to 0.55 mL. It has been observed that on increasing amount of  $\text{H}_2\text{O}_2$ , the  $\cdot\text{OH}$  radical concentration increases and hence, rate of degradation of dye also increases. However, beyond 0.45 mL the rate of photo-Fenton degradation decreases. It may be attributed to the fact that  $\cdot\text{OH}$  radicals react with increasing amount of  $\text{H}_2\text{O}_2$ . The reaction generates hydroperoxy radicals ( $\text{HO}_2^\cdot$ ) which are less powerful oxidizing agent as compared to  $\cdot\text{OH}$  radical. As a result, a decrease in rate of reaction has been observed beyond 0.45 mL of  $\text{H}_2\text{O}_2$ .

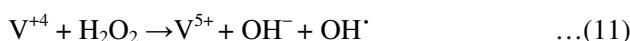
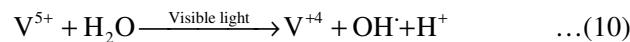
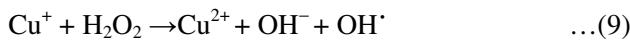
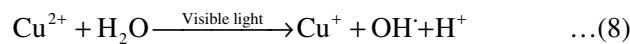
#### Effect of light intensity

The effect of intensity of light has also been observed on the rate of reaction. The data indicate that as light intensity increases, the rate of reaction also increases and maximum rate has been found at

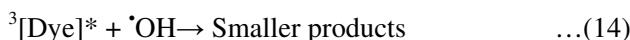
70.0 mWcm<sup>-2</sup>. It may be explained on the basis that as light intensity was increased, the number of photons striking per unit area also increase, resulting into higher rate of degradation. Further increase in the light intensity beyond 70.0 mWcm<sup>-2</sup> results in a decrease in the rate of reaction. It may be probably due to thermal side reactions.

#### Mechanism

On the basis of the experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for the degradation of trypan blue dye by heterogeneous photo-Fenton like reagent. Initially, copper (II) and vanadium (V) ions from catalyst react with water in the presence of light and get reduced to copper (I) and vanadium (IV) state along with the formation of hydroxyl radicals. These ions react with hydrogen peroxide without the requirement of photons generating copper (II) and vanadium (IV) ions along with the formation of OH· radicals. Thus vanadium and copper ion synergistically activating H<sub>2</sub>O<sub>2</sub> to generate OH· radicals.



The OH· radical is non selective and strong oxidizing agent with relatively high oxidizing potential, as compared to common oxidizing agents like H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub> etc. These OH· radicals react with dye and degrade it into smaller products like CO<sub>2</sub>, NO<sub>3</sub><sup>-</sup> ions etc. These products have been identified by usual chemical tests.



It has been observed that simple addition of light makes this process cyclic, in which four ·OH radicals are generated from one cupric and vanadium (V) ions. Thus, efficiency of Fenton process is enhanced in presence of light.

Table 2 — Quality parameters of solutions

Various parameters Studied	Before photo-Fenton Degradation	After photo-Fenton Degradation
COD (mg/L)	29	8
DO (ppm)	6.8	10.6
Conductivity (µS)	117	274
Salinity (ppt)	0.28	0.37
TDS (ppm)	104	217
pH	6.5	6.78

#### Quality parameters of water

Quality of water before and after photo-Fenton degradation has been tested by measuring various parameters (Table 2).

Chemical oxygen demand of dye solution before and after illumination has been determined by redox method. COD of dye solution before and after exposure was found to be 29 and 8 mg/L, respectively. The photodegradation efficiency after 2 h of illumination was 72.41 %.

Dissolved oxygen analysis measures the amount of gaseous oxygen dissolved in an aqueous solution. Increase in dissolved oxygen after photo-Fenton degradation indicates mineralization of dye to a significant extent.

Conductivity as a summation parameter is a measure of the level of ion concentration of a solution. Conductivity increased after the photo-Fenton treatment because dye has been mineralized into ions like CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> etc. Also, total dissolved solids (TDS) and salinity of the dye solution increased after photo-Fenton degradation of dye.

Due to the mineralization of the dye during the treatment, pH of reaction mixture becomes almost neutral from the initial slightly acidic value.

#### Conclusion

Heterogeneous photo-Fenton degradation using copper pyrovanadate offers many advantages over conventional methods. It is a low cost method because amount of catalyst required is much less as compared to conventional methods. The process is cyclic in nature and catalyst is also reusable. The method is ecofriendly because the only reagent present in reaction mixture is H<sub>2</sub>O<sub>2</sub>, which ultimately degrades to harmless H<sub>2</sub>O and O<sub>2</sub>. Since the catalyst is coloured, it can very efficiently absorb visible light to start the photo-Fenton degradation of dye. Copper pyrovanadate catalyst has been prepared by wet chemical method. The effects of the amount of

catalyst, hydrogen peroxide, concentration of dye, *pH* of the reaction medium and light intensity have been observed on rate of reactions. At optimal conditions, rate of degradation for trypan blue dye is found to be as  $k = 7.83 \times 10^{-4} \text{ sec}^{-1}$ . During heterogeneous photo-Fenton process,  $\cdot\text{OH}$  radicals react with dye and degrade it into smaller products like  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}_3^-$  ions etc.

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