HETEROGENEOUS PHOTO-FENTON-LIKE DEGRADATION OF EVANS BLUE USING Cu₃V₂(OH)₂O₇·2H₂O

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Degradation of a non-biodegradable azo-dye (Evans blue) has been carried out by the heterogeneous photo-Fenton like processes using copper pyrovanadate ($Cu_3V_2(OH)_2O_7 \cdot 2H_2O$) as a catalyst. This catalyst was prepared by wet chemical method. These catalysts were characterized by different techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Brunauer–Emmett–Teller (BET) surface area analysis. The effect of various parameters such as initial pH, concentration of dye, amount of catalyst, amount of H_2O_2 and light intensity on the reaction rate has also been studied. The various parameters like chemical oxygen demand (COD), conductance, pH, TDS, salinity and dissolved oxygen (DO) in the reaction mixture has been determined before and after treatment. The rate of photo-Fenton degradation of this dye followed pseudo-first order kinetics. A tentative mechanism involving ˙OH radicals as an oxidant for degradation of dye has been proposed.

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Introduction

Azo dyes, characterized by the presence of one or more azo groups (-N=N-) bound to aromatic rings, are the largest and most important class of synthetic organic dyes. It has been estimated that more than 50 % of all dyes in common use are azo dyes because of their chemical stability and versatility.[1] About 10-15 % of the synthetic textile dyes used are lost in waste streams during manufacturing or processing operations.[2] Azo dyes are not biodegradable by aerobic treatment processes.[3] In addition, under anaerobic condition, they give potentially carcinogenic aromatic amines, which cause long term health concerns.[4]
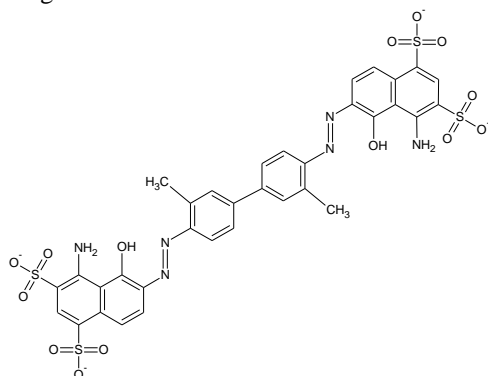
Figure 1. Structure of Evans blue

Evans Blue or T-1824, is an azo dye (Figure 1), which has a very high affinity for serum albumin. Because of this, it can be useful in physiology in estimating the proportion of body water contained in blood plasma.

Several methods have been tried from time to time for the treatment of effluents from dyeing industries, out of which, most common are chemical precipitation and biological methods. In order to develop an efficient method for converting such dyestuffs into harmless products, advanced oxidation processes (AOPs) have been widely applied in recent years, which are characterized by the generation of highly oxidative hydroxyl radicals (˙OH) in the homogeneous or heterogeneous phase.[5]

Heterogeneous Fenton-like catalysts, such as iron oxides[6,7] and transition metal oxides,[8-10] have recently been reported. Costa et al.[11] introduced Co, Mn, and Ni into the magnetite structure to prepare some two-metal composite heterogeneous Fenton like catalysts $Fe_{3-x}Mn_xO_4$, $Fe_{3-x}Co_xO_4$ and $Fe_{3-x}Ni_xO_4$. It was found that the Co and Mn, but not Ni, resulted in a significant increase in the degradation of the organic pollutants. This enhanced activity was attributed to the coupling of the redox pairs of Fe^{3+}/Fe^{2+} and Co^{2+}/Co^{3+}(Mn^{2+}/Mn^{3+}), which resulted in more efficient regeneration of the Fenton active species Fe^{2+}.

Mixed vanadium–chromium oxides present a wide range of interesting properties like excellent catalytic properties,[12-20] potential candidates for anodes in lithium-ion batteries,[21] etc. Zinc pyrovanadate ($Zn_3(OH)_2V_2O_7 \cdot 2H_2O$)[22] and copper pyrovanadate ($Cu_3V_2(OH)_2O_7 \cdot 2H_2O$)[23] have been prepared by hydrothermal[24] and the coprecipitation techniques.[25] But till date copper pyrovanadate ($Cu_3V_2(OH)_2O_7 \cdot 2H_2O$) has not been used quite commonly as heterogeneous photo-Fenton like catalyst.

Hence, in the present study, the focus was on the optimization of the degradation of an azo dye, Evans blue, in presence of copper pyrovanadate ($Cu_3V_2(OH)_2O_7 \cdot 2H_2O$) as heterogeneous photo-Fenton like catalyst.

Experimental

Synthesis of Catalyst

($Cu_3V_2(OH)_2O_7 \cdot 2H_2O$) was prepared by wet chemical process.[26] Copper nitrate aqueous solution (0.1 M L^{-1}) was quickly poured into an aqueous solution of NH_4VO_3 (0.2 M L^{-1}) maintained at 75 °C under continuous stirring.

A yellow precipitate was formed. On further stirring for 1 h, the color of the precipitate was changed to green. It was then separated by filtration, washed several times with pure water and methanol and dried at room temperature overnight.

Characterization

X-ray powder diffraction (XRD) measurements were performed on a BrukerD8 Advance X-ray diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm). Infrared (IR) spectra were recorded using a Perkin-Elmer FTIR-1730 spectrometer with KBr disks at room temperature in the range of 4000–400 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. Stability of the catalyst was checked by atomic absorption spectroscopy using ETCL4129A atomic absorption spectrophotometer.

Procedure

For the photo-Fenton degradation, stock solution of dye (10^{-3} M) was prepared. A reaction mixture containing dye ($\approx 10^{-5}$ *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 was used to cut off thermal radiations. *p*H of the solution was measured by a digital *p*H meter (Systronics Model 335) and it 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).

It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of Evans blue dye decreases with increasing time of exposure. A plot of 2 + log A versus time was linear following pseudo-first order kinetics.

The rate constant was measured using following expression:

$$k = 2.303 \times \text{Slope} \qquad \ldots \qquad (1)$$
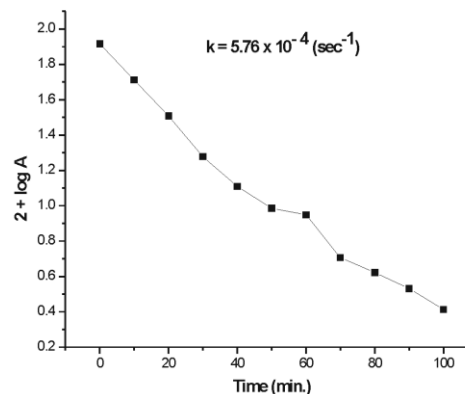
A typical run has been presented (Figure 2)

Figure 2. Typical run

The chemical oxygen demand of reaction mixture before and after treatment has been determined by redox method using ferrous ammonium sulphate and $KMnO_4$. The photodegradation efficiency of the catalyst was calculated from the following expression:

$$\eta = \frac{COD_{before} - COD_{after}}{COD_{before}} \times 100 \qquad (2)$$

where

η = photodegradation efficiency (%),

COD_{before} = COD of dye solution before illumination, and

COD_{after} = COD of dye solution after illumination

Other quality parameters i.e. dissolved oxygen, conductivity, salinity and total dissolved solids were measured using water analyzer (Systronics Model 371).

Results and discussion

Characterization results

Scanning electron microscopy (SEM) image of ($Cu_3V_2(OH)_2O_7 \cdot 2H_2O$) has been shown in Figure 3. The basic structure of catalyst (volborthite) is a sheet-like structure with copper oxide/hydroxide layers held together by the pyrovanadate groups. These layers are stacked by layers of water. It can also be seen from the SEM result that in addition to the larger particles, the surface contains some smaller particles as small as 20 µm or even smaller.

Figure 3. SEM image of catalyst

The specific surface area of the catalyst was measured by means of conventional BET method. Results showed that the average specific surface area of $(Cu_3V_2(OH)_2O_7 \cdot 2H_2O)$ particle was 17.6 $m^2 g^{-1}$ at 105 °C.

In FT-IR (Figure 4), the band at 1508 cm^{-1} was assigned to the bending vibration of adsorbed water. The wide band at 3500-3600 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 any obvious decomposition and had some favorable thermal stability in the temperature range investigated. Cu-O bonding has been confirmed by a band at 592 cm^{-1}. The absorption band with the maxima at 896 cm^{-1} corresponds to the V-O stretching bond.[27,28] Band at 798 cm^{-1} corresponds to the V-O-V stretching bond.

Figure 4. FT-IR spectrum of catalyst

Stability of the catalyst was checked by atomic absorption spectroscopy using ECTL 4129A 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.

XRD diffraction pattern of the sample was recorded on 18 KW X-Ray diffractometer using Cu Kα radiation. Diffraction pattern was recorded over the 2θ range from 10° to 90° with a step size of 0.05°. Figure 5 shows the XRD pattern of the copper pyrovanadate $(Cu_3V_2(OH)_2O_7 \cdot 2H_2O)$. All the peaks in pattern can be indexed to a pure monoclinic $(Cu_3V_2(OH)_2O_7 \cdot 2H_2O)$ phase, in good agreement with the report of Lafontaine et al.[29] and the JCPDS card No. 46-1443. The crystallite size (t) of the peak can be calculated by using Scherrer's formula: $t = 0.9 \ \lambda / \beta \cos \theta$ where λ is the wavelength of X-rays used (1.5406 Å), β is the full width at half maximum (FWHM) and θ is the angle of diffraction.

Figure 5. XRD pattern of copper pyrovanadate

Effect of various parameters

The effect of pH on the rate of photo-Fenton degradation has been investigated in pH range 5.0 – 8.5 (Figure 6). It has been observed that with an increase in pH, rate of reaction increases and after attaining the maximum value at pH 6.0, the rate decreases with further increase in pH.

Figure 6. Effect of initial pH

It can be anticipated that changes in pH will influence the degradation of the dye in two ways (a) direct involvement of H^+ in the reaction at lower pH (b) mass transport limitations imposed by the precipitation of a passive film on the metal surface at higher pH.

(a) The hydroxyl radicals are generated by two steps:

(i) by the reaction between Cu^+ and V^{4+} ions with hydrogen peroxide,

(ii) by the photochemical reaction of Cu^{2+} and V^{5+} ions and water.

The increase in pH of the medium favours the step (ii) where H^+ ions are formed along with hydroxyl radicals, whereas ^-OH are generated in step (i). Thus, it may be concluded that the step (ii) dominates over step (i) at pH below 6.0. At pH 6.0, both these steps are favoured equally so that the rate of reaction becomes maximum. However, the retardation of the reaction above pH 6.0 suggests the dominance of step (i) over step (ii).

(b) Alternatively, another explanation is also possible. It was observed that the rate of reaction increases on increase in pH of the medium and it was based on the fact that relative number of ^-OH ions increases with increasing pH. As a consequence, the number of $^•OH$ radicals will also increase, resulting in higher rate of degradation of dye. But on increasing the pH beyond 6.0, the number of ^-OH ions also increase and get adsorbed on the catalyst surface making it negatively charged. The approach of the anionic dye molecule towards catalyst surface becomes difficult due to electrostatic repulsion. As a result, the rate of degradation decreases.

The effect of variation of dye concentration on the rate of photo-Fenton degradation has been observed in the range from 0.40 x 10^{-5} M to 1.8 x 10^{-5} M (Figure 7). It has been observed that the rate of degradation increases with increase in concentration of Evans blue up to 1.0 x 10^{-5} M.
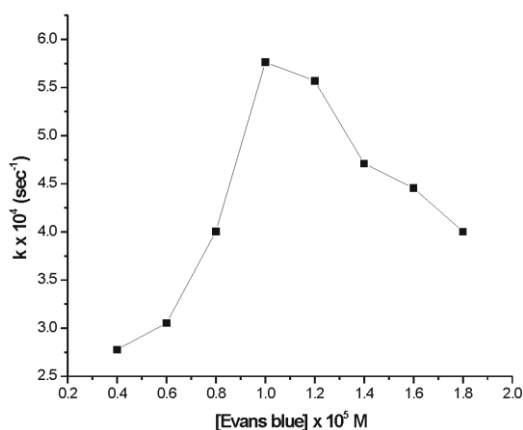

Figure 7. Effect of dye concentration

This may be explained on the basis that initially, on increasing the concentration of dye, the reaction rate increases as more molecules are available for degradation. But further increase in concentration beyond 1.0 x 10^{-5} M causes retardation of reaction due to increasing number of collision among dye molecules resulting in decrease in number of collision among dye molecule and $^•OH$ radicals. As consequence, the rate of reaction is retarded.

It was observed that rate of degradation increases up to 0.06 g of catalyst, but decreases on increasing the amount further above 0.06 g (Figure 8). On increasing the amount of catalyst, the rate of reaction increases to a certain amount of catalyst (0.06 g). Beyond this point, the rate of reaction decreases with increase in amount of catalyst. This may be explained by the fact that with 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), any increase in the amount of catalyst would also increase the number of vanadium and copper ions and then there is a possibility of short circuiting between Cu^+ and Cu^{2+} & V^{4+} and V^{5+} ions.[30] As a result, less number of hydroxyl radical are formed and rate of reaction is retarded.

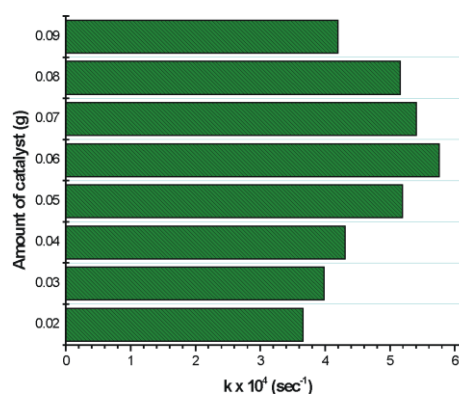**Figure 8**. Effect of amount of catalyst

The effect of variation of amount of H_2O_2 on the photo-Fenton degradation of Evans blue has also been investigated in the range from 0.15 to 0.50 mL (Figure 9). It has been observed that initially upon increasing H_2O_2 from 0.15 mL to 0.35 mL, the rate of degradation increases due to availability of more hydroxyl radicals by decomposition of more hydrogen peroxide molecules.
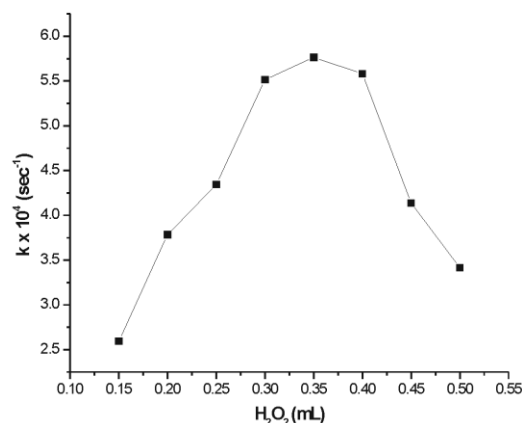

Figure 9. Effect of amount of H_2O_2

However, beyond 0.35 mL, the rate of photo-Fenton degradation decreases. Since propagation step in the oxidative cycle will be hindered by excess of H_2O_2, which

scavenges the ˙OH radicals in solution. As a result, less hydroxyl radicals are available resulting into a decrease in the rate of degradation of Evans blue.

It was observed that on increasing light intensity, the rate of reaction also increases and maximum rate has been found at 70.0 mWcm^{-2} (Figure 10). It may be explained on the basis that as light intensity was increased, the number of photons striking per unit area also increases, resulting into higher rate of degradation.
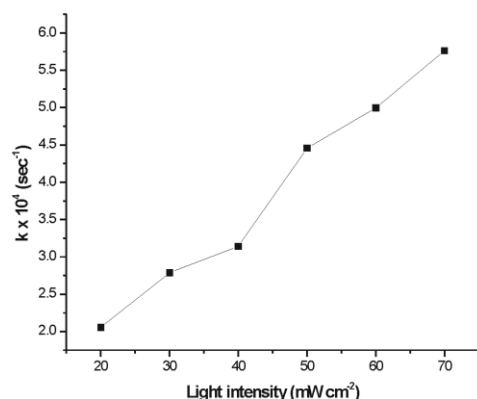

Figure 10. Effect of light intensity

Determination of water quality parameters

Quality of water before and after photo-Fenton degradation has been tested by measuring some parameters. The results are summarized in Table 1.

Table 1. Water quality parameters

Various parameters studied	Before photo-Fenton degradation	After photo-Fenton degradation
COD (mg/L)	27.0	6.0
DO (ppm)	8.1	14.3
Conductivity (µS)	132.0	189.0
Salinity (ppt)	0.10	0.18
TDS (ppm)	63.1	85.5
pH	6.0	6.52

Chemical oxygen demand of dye solution before and after illumination has been determined by redox method. The photodegradation efficiency after 2 hours of illumination has been found to be 77.78 %.

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 concentration of ions in solution. Conductivity parameter has been increased after the treatment because dye has been mineralized into ions like CO_3^{2-}, NO_3^-, SO_4^{2-} etc. Because of this reason, total dissolved solids (TDS) and salinity of the dye solution was also found greater after photo-Fenton degradation of dye.

Before the treatment, pH of reaction mixture was in basic range, but after this degradation, pH becomes neutral because dye particles are mineralized to a significant extent.

Mechanism

On the basis of the experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for the degradation of Evans blue dye in presence of copper pyrovanadate, H_2O_2 and light. V and Cu may simultaneously activate H_2O_2 to give ˙OH radicals.

The participation of ˙OH radical as an active oxidizing species was confirmed by using hydroxyl radical scavengers, e.g. 2-propanol and butylated hydroxy toluene (BHT), where the rate of photodegradation was found to be drastically reduced.

$$[EB] \xrightarrow{\text{h}\nu} {}^1[EB]^* \qquad (3)$$

$$ {}^1[\dot{E}\dot{B}]^* \xrightarrow{\text{ISC}} {}^3[EB]^* \qquad (4)$$

$$ {}^1[EB]^* + {}^{\bullet}OH \longrightarrow \text{Smaller products} \qquad (5)$$

The involvement of singlet state of dye has been confirmed by conducting the reaction in the presence of a small amount of potassium ferrocyanide as triplet state quencher.[31] The rate of reaction was found to be reduced.

Conclusion

Researches on the heterogeneous photo-Fenton process are expected to grow more rapidly in the near future prompted by the increasing amount of released recalcitrant pollutants. Subsequently, the stability of the produced catalyst needs to be examined under various experimental conditions to prevent the adverse effects of transition metals on the receiving environment. An efficient heterogeneous photo-Fenton catalysts copper pyrovanadate ($Cu_3V_2(OH)_2O_7.2H_2O$) was successfully prepared by using wet chemical method.

The degradation could occur efficiently over a wide pH range of 5.0−8.5. Good degradation effeciency of Evans blue in aqueous solution (77.78 %) was achieved with in 2 h reaction time. This catalyst has good stability for the degradation of Evans blue even after 5 cycles, and therefore, has a great potential. At optimal conditions, (pH = 6.0; [Evans blue] = 1.0 x 10^{-5} M; Amount of catalyst = 0.06 g; H_2O_2 = 0.35 mL; Light intensity = 70 mW cm^{-2}), rate of degradation for Evans blue dye was found to be $k = 5.76 \times 10^{-4}$ sec^{-1}.

During heterogeneous photo-Fenton process, ˙OH radicals react with dye and degrade it into smaller products like H_2O, CO_2, NO_3^- ions etc.

Acknowledgements

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