Heterogeneous photo-Fenton-like catalysts \(\text{Cu}_2\text{V}_2\text{O}_7\) and \(\text{Cr}_2\text{V}_4\text{O}_{13}\) for an efficient removal of azo dye in water

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Heterogeneous photo-Fenton-like catalysts $\text{Cu}_2\text{V}_2\text{O}_7$ and $\text{Cr}_2\text{V}_4\text{O}_{13}$ for an efficient removal of azo dye in water

Sangeeta Kalal$^1$, Arpita Pandey$^1$, Rakshit Ameta$^2$ and Pinki B. Punjabi$^1$*

Abstract: This work deals with the degradation of non-biodegradable azo-dye (Evans blue) by the heterogeneous photo-Fenton-like process using copper pyrovanadate ($\text{Cu}_2\text{V}_2\text{O}_7$) and chromium tetravanadate ($\text{Cr}_2\text{V}_4\text{O}_{13}$) as catalysts, which have been prepared by wet chemical method. These catalysts were characterized by different techniques such as scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and Brunauer–Emmett–Teller surface area analysis. The effect of various parameters such as initial pH, concentration of dye, amount of catalyst, amount of $\text{H}_2\text{O}_2$, and light intensity on the reaction rate has also been studied. Photodegradation efficiency was found 77.78 and 79% for copper pyrovanadate ($\text{Cu}_2\text{V}_2\text{O}_7$) and chromium tetravanadate ($\text{Cr}_2\text{V}_4\text{O}_{13}$), respectively. A tentative mechanism involving OH radicals as an oxidant for the degradation of dye has also been proposed. The observations revealed that the rate of photo-Fenton-like degradation of dye follows pseudo-first-order kinetics.

Subjects: Chemistry; Environmental Chemistry; Physical Sciences

Keywords: copper pyrovanadate; chromium tetravanadate; heterogeneous; photo-Fenton-like process

PUBLIC INTEREST STATEMENT

Today it is very important to remove dyes from industrial or domestic sewage systems before discharging into nearby water resources. 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 ($\cdot\text{OH}$) in the homogeneous or heterogeneous phase. Moreover, there are some drawbacks in the utilization of homogeneous Fenton or Fenton-like reagents (Fe$^{2+}$, Cu$^{2+}$ and $\text{H}_2\text{O}_2$). In order to solve this problem, researchers have tried to make them heterogeneous in nature.

But till date, copper pyrovanadate ($\text{Cu}_2\text{V}_2\text{O}_7$) and chromium tetravanadate ($\text{Cr}_2\text{V}_4\text{O}_{13}$) have not been used as heterogeneous photo-Fenton-like catalyst. Hence, in the present study, we focused on the optimization of the degradation of an azo dye i.e. Evans blue, using copper pyrovanadate ($\text{Cu}_2\text{V}_2\text{O}_7$) and chromium tetravanadate ($\text{Cr}_2\text{V}_4\text{O}_{13}$) as heterogeneous photo-Fenton-like catalysts.
1. 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 (Neamtu, Siminiceanu, Yediler, & Kettrup, 2002). About 10–15% of the used synthetic textile dyes are lost in waste streams during manufacturing or processing operations (Gomathi Devi, Girish Kumar, Mohan Reddy, & Munikrishnappa, 2009). Azo dyes are not biodegradable by aerobic treatment processes (Pagga & Brown, 1986). In addition, under anaerobic condition, they are reduced to potentially carcinogenic aromatic amines, which cause long-term health concerns (Brown & Hamberger, 1987). Evan’s blue, (Figure 1) is an azo dye, which has a very high affinity for serum albumin. Due to this fact, it is useful in physiology for estimating the proportion of body water contained in blood plasma.

Several methods have been undertaken from time to time for the treatment of dye effluents, out of which chemical precipitation and biological methods are more common. 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 (Farias, Rossetti, Albizzati, & Alfano, 2007).

Use of heterogeneous Fenton-like catalysts, such as iron oxides (Pignatello, Oliveros, & MacKay, 2006; Shin, Yoon, & Jang, 2008) and transition metal oxides (Ghouch, Abou Assi, & Tuqan, 2010; Giordano et al., 2007; Heckert, Seal, & Self, 2008) have recently been reported. Costa, Leis, Oliveira, Fabris, & Ardisson, 2003 introduced Co, Mn, and Ni into the magnetite structure to prepare some two-metal composite heterogeneous Fenton-like catalysts Fe$_{3-x}$Mn$_x$O$_4$, Fe$_{3-x}$Co$_x$O$_4$, and Fe$_{3-x}$Ni$_x$O$_4$. 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$^{3+}$. Some novel Fe-containing catalysts, such as FeVO$_4$ (Deng et al., 2008), Fe$_2$V$_4$O$_{13}$ (Zhang et al., 2009) and Fe$_2$(MoO$_4$)$_2$ (Tian et al., 2013) have been reported, where the cationic iron and the anions combined with the catalyst could synergistically activate H$_2$O$_2$ towards the oxidation of pollutants and thus, greatly enhance the wastewater treatment efficiency. Some researchers have reported different ions loaded pillared bentonite as heterogeneous catalyst for photo-Fenton-like oxidation of textile organic pollutants (Chanderia, Kumar, Sharma, Ameta, & Punjabi, 2012; Ya-Ping, Cheng-Guang, Ran, Feng, & Guang-Nan, 2014).

Mixed vanadium–chromium oxide compounds present a wide range of interesting properties; for instance, they have excellent catalytic properties (Pradier et al., 2000; Wittgen et al., 1982), and recently, they were shown to be potential candidates for anodes in lithium-ion batteries (Soudan, Pereira-Ramos, Farcy, Gregoire, & Baffier, 2000) also. But till date, copper pyrovanadate (Cu$_2$V$_2$O$_7$) and chromium tetravanadate (Cr$_2$V$_4$O$_{13}$) have not been used as heterogeneous photo-Fenton-like catalyst.

Hence, in the present study, we focused on the optimization of the degradation of an azo dye i.e. Evans blue, using copper pyrovanadate (Cu$_2$V$_2$O$_7$) and chromium tetravanadate (Cr$_2$V$_4$O$_{13}$) as heterogeneous photo-Fenton-like catalysts.

Figure 1. Structure of Evans blue.
2. Experimental

2.1. Preparation of Catalysts

Cu$_2$V$_2$O$_7$ was prepared by wet chemical process. Copper nitrate ($0.1 \text{ m L}^{-1}$) in water was quickly poured into an aqueous solution of NH$_4$VO$_3$ ($0.2 \text{ m L}^{-1}$) 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 isolated by filtration, washed several times with pure water and methanol, and dried at room temperature overnight. Then, the powder was kept in muffle furnace at 700 °C for 5 h.

Cr$_2$V$_4$O$_{13}$ powder was synthesized by simple aqueous process. In a typical synthesis, aqueous solutions of Cr(NO$_3$)$_3$·9H$_2$O and NH$_4$VO$_3$ stock solution were mixed together with the molar ratio of 1:1. The mixture was stirred for 1 h at room temperature. The resulting precipitates were collected and washed with deionized water and anhydrous ethanol for three times separately, then dried at 30 °C in air. This powder was kept in muffle furnace at 300 °C for 24 h.

2.2. Experimental Process

For the photo-Fenton degradation, stock solution of dyes ($1.0 \times 10^{-3} \text{ M}$) has been prepared. A reaction mixture containing dye ($\approx 10^{-5} \text{ M}$), 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 using standard 0.1 N sulfuric 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. The rate constant was measured using Equation 1. A plot of $2 + \log A$ vs. time was found linear, which confirms pseudo-first-order kinetics. Typical runs are shown in Figure 2.

$$k = 2.303 \times \text{Slope}$$

(1)

X-ray powder diffraction (XRD) measurements were performed on a BrukerD8 Advance X-ray diffractometer using Cu Kα radiation ($\lambda = 0.154 \text{ nm}$). 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$^{-1}$.

Figure 2. Typical runs.
Scanning electron microscopy (SEM) studies were performed using a Bruker AXS microscope equipped with energy dispersive X-ray fluorescence spectral analysis for element composition and Robinson secondary electron and backscattered electron 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. The chemical oxygen demand (COD) of reaction mixture before and after treatment has been determined by redox method.

3. Results and Discussion

3.1. Characterization Results

The morphology and structure of the as-synthesized products after annealing was examined by SEM (Figure 3). SEM micrographs of Cu₂V₂O₇ (Figure 3(a)) shows that particles are nearly spherical, while Figure 3(b) shows that the nanoparticles are dispersed equally with the diameter of ~100 nm for Cr₂V₄O₁₃. After annealing at 300 °C, the nanoparticles become metamorphic due to the stress produced during the crystallization process, which indicates that further reaction of crystal structure transformation takes place. The specific surface areas of the catalysts were measured by means of conventional Brunauer–Emmett–Teller method. Results showed that the average specific surface area was 17.6 and 17.7 m² g⁻¹ at 105 °C for Cu₂V₂O₇ and Cr₂V₄O₁₃ particle, respectively.

The catalysts were further characterized with Fourier transform infrared spectroscopy (FTIR) (Figure 4). In Figure 4(a), Cu–O bonding has been confirmed by a band at 592 cm⁻¹. The intense absorption at 789 cm⁻¹ is due to the asymmetric vibrations of V–O–Cu and V–O–V, and the weak absorption at 1402 cm⁻¹ has been assigned to the vibration of V–O bond (Orel, Anzlovar, & Drazic, 1999). In Figure 4(b), the absorption band with the maxima at 896 cm⁻¹ corresponds to the V–O stretching bond (Filipek, Walczak, & Tabero, 1998; Šurca & Orel, 1999). The band at 798 cm⁻¹ corresponds to the V–O–V stretching bond, and bands at 653, 536, and 464 cm⁻¹ correspond to the Cr–O bond (Music et al., 1999). Strong bands below 1000 cm⁻¹ further confirm the composition of chromium–vanadium oxides.

Stabilities of the catalysts were checked by atomic absorption spectroscopy using ECTL 4129A atomic absorption spectrophotometer. Even after one month, leaching of copper, chromium, and vanadium ions from the catalysts was found to be negligible. Thus, catalysts were found to possess good stability for its use as heterogeneous photo-Fenton-like reagents under visible range.

XRD diffraction patterns of the samples were recorded on 18 KW X-ray diffractometer using Cu Kα radiation. Diffraction patterns were recorded over the 2θ range from 10° to 90° with a step size of 0.05°. From the diffraction peaks (Figure 5), it was observed that the synthesized sample (Cu₂V₂O₇) showed orthorhombic structure having cell parameters a = 20.67 Å, b = 8.76 Å, c = 6.45 Å and match
with (JCPDS No. 73-1032). Figure 6 illustrates the indexed XRD pattern of \( \text{Cr}_2\text{V}_4\text{O}_{13} \). All the Bragg reflections have been indexed in monoclinic structure in the hexagonal setting \([Z = 4 \text{ and } P_{21}C \text{ (space group)}]\). The obtained value of the cell parameters for \( \text{Cr}_2\text{V}_4\text{O}_{13} \): \( a = 8.2320 \text{ Å} \), \( b = 9.3003 \text{ Å} \), \( c = 14.5430 \text{ Å} \) and angles \( \alpha = \gamma = 90 \), \( \beta = 102.613 \) are in very good agreement with reported standard...
values of Cr$_2$V$_4$O$_{13}$ [phase (JCPDS card No. 00-049-1645, $a = 8.287$ Å, $b = 9.300$ Å, $c = 7.530$ Å, $eta = a = 8.265$ Å, $b = 9.2997$ Å, $c = 14.5215$ Å and $\alpha = \gamma = 90$ and $\beta = 102.618$.])]. The crystallite size ($t$) of the peak appeared at $2\theta = 13^\circ$, was calculated by using Scherrer’s formula: $t = \frac{0.9}{\lambda} \frac{\beta}{\cos\theta}$ where $\lambda$ is the wavelength of X-rays used (1.5406 Å), $\beta$ is the full width at half maximum (FWHM) and $\theta$ is the angle of diffraction. The particle sizes of Cu$_2$V$_2$O$_7$ and Cr$_2$V$_4$O$_{13}$ were 28.6 and 70.7 nm, respectively.

To investigate its optical response to the visible light irradiation, the diffuse reflectance UV–vis absorption of Cu$_2$V$_2$O$_7$ and Cr$_2$V$_4$O$_{13}$ catalysts in a wavelength between 400 and 800 nm was measured, and the spectra are presented in Figure 7. Band gap of both the compounds were found to be 2.17 and 2.76 eV for Cu$_2$V$_2$O$_7$ and Cr$_2$V$_4$O$_{13}$, respectively. Both the catalysts were found effective in visible range, but the reaction rate was higher for chromium tetravanadate than copper pyrovanadate.

3.2. 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 8(a)). It was observed that with an increase in pH, rate of reaction increases and after attaining the maximum value at pH 6.0 and 7.0 for Cu$_2$V$_2$O$_7$ and Cr$_2$V$_4$O$_{13}$, respectively, the rate decreases with further increase in 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 and (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$^+/Cr^{3+}$ and V$^{4+}$ ions with hydrogen peroxide.
(ii) by the photochemical reaction of Cu$^{2+}/Cr^{6+}$ and V$^{5+}$ ions and water.

The increase in pH of the medium favors 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 and 7.0 for Cu$_2$V$_2$O$_7$ and Cr$_2$V$_4$O$_{13}$, respectively. At this point, both these steps are favored equally so that the rate of reaction becomes maximum. However, the retardation of the reaction above pH 6.0 and 7.0 suggests the dominance of step (i) over step (ii).

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 and 7.0, the number of OH ions further 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 in dye concentration on the rate of photo-Fenton degradation has been observed in the range from $0.40 \times 10^{-5}$ to $1.8 \times 10^{-5}$ M (Figure 8(b)). This may be explained on the basis that initially, on increasing the concentration of dye, the reaction rate increases as more dye molecules are available for degradation. But further increase in concentration beyond $1.0 \times 10^{-5}$ and $0.80 \times 10^{-5}$ M for Cu$_2$V$_2$O$_7$ and Cr$_2$V$_4$O$_{13}$, respectively, 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 and 0.05 g of Cu$_2$V$_2$O$_7$ and Cr$_2$V$_4$O$_{13}$ catalyst, respectively, but rate decreases on increasing the amount of the catalysts above 0.06 and 0.05 g (Figure 8(c)). On increasing the amount of catalyst, the rate of reaction increases to a certain amount of catalyst (0.06 and 0.05 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 catalysts, the surface area of catalysts increases and as a consequence, a rise in the rate of reaction has been observed. But after a certain amount of the catalysts (0.06 and 0.05 g), an 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 (Litter, 1999). As a result, less number of hydroxyl radical are formed and rate of reaction is retarded.

The effect of variation in the amount of H$_2$O$_2$ on the photo-Fenton degradation of Evans blue has also been investigated in the range from 0.15 to 0.50 mL (Figure 8(d)). It has been observed that initially on increasing H$_2$O$_2$, upto 0.35 and 0.30 mL for Cu$_2$V$_2$O$_7$ and Cr$_2$V$_4$O$_{13}$, respectively, the rate of degradation increases due to availability of hydroxyl radicals by decomposition of more hydrogen peroxide molecules. However, beyond 0.35 and 030 mL, the rate of photo-Fenton degradation decreases. Since propagation step in the oxidative cycle will be hindered by excess of H$_2$O$_2$, which
scavenges the \( \cdot \text{OH} \) radicals in solution. As a result, less hydroxyl radicals are available resulting in a decrease in the rate of degradation of Evans blue.

Effect of light intensity on the rate dye degradation was also investigated in the range of 20–70.0 mWcm\(^{-2}\). It was observed that on increasing light intensity, the rate of reaction also increases and maximum rate was attained at 70.0 mWcm\(^{-2}\) (Figure 8(e)). 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.

The COD of reaction mixture before and after treatment has been determined by redox method using ferrous ammonium sulfate and KMnO\(_4\). The photodegradation efficiency of the catalyst was calculated from the following expression:
\[ \eta = \frac{\text{COD}_{\text{Before}} - \text{COD}_{\text{After}}}{\text{COD}_{\text{Before}}} \times 100 \]

\( \eta \) = Photodegradation efficiency (%), \( \text{COD}_{\text{Before}} \) = COD of dye solution before illumination, \( \text{COD}_{\text{After}} \) = COD of dye solution after illumination. The photodegradation efficiency was found 77.78% and 79% for \( \text{Cu}_2\text{V}_2\text{O}_7 \) and \( \text{Cr}_2\text{V}_4\text{O}_{13} \), respectively after 2 h of illumination.

### 3.3. 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 \( \text{Cu}_2\text{V}_2\text{O}_7 \) and \( \text{Cr}_2\text{V}_4\text{O}_{13} \), \( \text{H}_2\text{O}_2 \) and light. \( \text{V} \) and \( \text{Cu} \) may simultaneously activate \( \text{H}_2\text{O}_2 \) to give \( \cdot\text{OH} \) radicals.

\[ \text{Cu}^{2+} + \text{H}_2\text{O} \xrightarrow{\text{Visible light}} \text{Cu}^+ + \cdot\text{OH} + \text{H}^+ \]  

(2)

\[ \text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \cdot\text{OH} + \text{HO} \]  

(3)

\[ \text{Cr}^{6+} + \text{H}_2\text{O} \xrightarrow{\text{Visible light}} \text{Cr}^{3+} + \cdot\text{OH} + \text{HO} \]  

(4)

\[ \text{Cr}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Cr}^{6+} + \cdot\text{OH} + \text{HO} \]  

(5)

\[ \text{V}^{5+} + \text{H}_2\text{O} \xrightarrow{\text{Visible light}} \text{V}^{4+} + \cdot\text{OH} + \text{H}^+ \]  

(6)

\[ \text{V}^{4+} + \text{H}_2\text{O}_2 \rightarrow \text{V}^{5+} + \cdot\text{OH} + \text{HO} \]  

(7)

The participation of \( \cdot\text{OH} \) radical as an active oxidizing species was confirmed using hydroxyl radical scavenger, 2-propanol, where the rate of photodegradation was found to be drastically reduced.

\[ [\text{EB}] \xrightarrow{\text{hv}} [\text{EB}]^* \]  

(8)

\[ [\text{EB}]^* \xrightarrow{\text{ISC}} [\text{EB}]^* \]  

(9)

\[ [\text{EB}]^* + \cdot\text{OH} \rightarrow \text{Smaller products} \]  

(10)

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 (Zakharova, Korobov, Shabalov, & Chibisov, 1983) where the rate of reaction was found to be reduced.

### 4. Conclusion

Researches on the heterogeneous photo-Fenton process are expected to grow 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. Efficient heterogeneous photo-Fenton catalysts copper pyrovanadate and chromium tetravanadate were successfully prepared using wet chemical method. The degradation could occur efficiently over a wide pH range of 5.0–8.5. The best operation parameters for the heterogeneous photo-Fenton-like oxidation observed are; pH 6.0; [Evans blue] = 1.0 × 10^{-5} M; amount of catalyst = 0.06 g; \( \text{H}_2\text{O}_2 \) = 0.35 mL; Light intensity = 70 mWcm^{-2}; and pH 7.0; [Evans blue] = 0.8 × 10^{-7}; Catalyst = 0.05 g; \( \text{H}_2\text{O}_2 \) = 0.35 mL; Light Intensity = 70 mWcm^{-2} for \( \text{Cu}_2\text{V}_2\text{O}_7 \) and \( \text{Cr}_2\text{V}_4\text{O}_{13} \), respectively. Under these conditions, 77.78 and
79.0% mineralization of Evans blue in aqueous solution were achieved within a 120 min reaction time. The product analysis confirmed that Evans blue is completely degraded into simple inorganic counter parts like CO$_3$($\bar{\text{aq}}$), SO$_4^{2-}$$\bar{\text{aq}}$,$\text{NO}_3^{-}$ etc. as revealed by their usual tests. The catalysts have shown good stability for the degradation of Evans blue and can here be used. These have great potential as photocatalysts. However, heterogeneous photo-assisted Fenton process for the removal of dye effluent from wastewater is normally done under UV irradiation. The UV source is relatively expensive and consumes large quantities of electrical power, whereas these catalysts will utilize sunlight or visible light irradiation as the light source and work efficiently for the degradation of Evans blue.

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