Copper pyrovanadate as an effective photo-Fenton-like catalyst for degradation of methylene blue

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Received 9 February 2015; revised and accepted 31 July 2015

Visible light-based photo-Fenton-like catalytic performance of Cu\textsubscript{3}V\textsubscript{2}(OH)\textsubscript{3}O\textsubscript{2}.2H\textsubscript{2}O is investigated using methylene blue as the target pollutant. Specific surface area, structure, and particle size distribution of the catalysts and its components are investigated by techniques such as standard Brunauer-Emmett-Teller isotherms, X-ray diffraction, scanning electron microscope and energy dispersive X-ray spectroscopy Under optimized conditions in the Cu\textsubscript{3}V\textsubscript{2}(OH)\textsubscript{3}O\textsubscript{2}.2H\textsubscript{2}O–H\textsubscript{2}O\textsubscript{2}–visible light system, the degradation efficiency and the pseudo first-order rate constant are found to be 69.07\% and 4.23×10\textsuperscript{-4} \text{s}\textsuperscript{-1} respectively. The new bifunctional material is found to be a promising material for use as a Fenton-like catalyst for the degradation of organic contaminant in waste water. Copper and vanadium leaching from the catalyst is almost negligible, which demonstrates the stability of the catalyst; the catalyst is very stable and can be reused for at least four cycles when operated under near neutral pH.

Keywords: Catalysts, Photocatalysts, Degradation, Dye degradation, Methylene blue

It is known that water-soluble organic dyes are biorecalcitrant compounds existing in a wide concentration range in effluents from the textile and photographic industries.\textsuperscript{1,2} Dyes have high carbon content and contribute to nearly 95\% of the solution color even at a very low concentration (1 mg L\textsuperscript{-1}).\textsuperscript{3,4} Therefore, it is very important to remove dyes from industrial or domestic sewage systems before discharging into nearby water resources. Of the various pollutant dyes, methylene blue is considered as a particularly hazardous pollutant due to its non-biodegradability and toxicity even at low concentrations.

Since most of the dyes are non-biodegradable, the conventional techniques to remove dye pollutants from effluents require a secondary process for complete destruction of dyes. The limitations of conventional waste water treatment methods can be overcome by the application of advanced oxidation processes,\textsuperscript{5,6} such as ozonation,\textsuperscript{7} photo-Fenton process,\textsuperscript{8} photoelectrocatalytic degradation\textsuperscript{9,10} and adsorption\textsuperscript{11,12}.

Homogeneous photo-Fenton reaction is an effective AOP method for treatment of waste waters due to its high efficiency, simplicity of operation and low cost. However, the classic Fe\textsuperscript{2+} based Fenton system requires operation at pH < 3.0 to prevent the precipitation of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} so that a large excess of Fe salts is not recycled. As a result, a large amount of chemical sludge is produced.\textsuperscript{13} To overcome these limitations, some efforts have been made to develop heterogeneous catalysts for photo-Fenton-like reactions.

Some novel Fe-containing catalysts such as FeVO\textsubscript{4},\textsuperscript{14} Fe\textsubscript{2}V\textsubscript{2}O\textsubscript{13},\textsuperscript{15} and Fe\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} have been reported, where the cationic iron and the anions combined with the catalyst and synergistically activated H\textsubscript{2}O\textsubscript{2} towards oxidation of pollutants, thus greatly enhancing the waste water treatment efficiency.\textsuperscript{16} Recent literature reports that copper may play a similar role as iron, reacting with hydrogen peroxide to produce hydroxyl radical.\textsuperscript{17,18}

Copper is still not widely used in the liquid oxidation process due to its severe toxicity to marine life. Moreover, there are some drawbacks in the utilization of homogeneous Fenton or Fenton-like reagents (Fe\textsuperscript{2+}, Cu\textsuperscript{2+} and H\textsubscript{2}O\textsubscript{2}). In order to solve this problem, researchers have tried to load metal ions like copper ions onto porous solid support by various techniques such as impregnation,\textsuperscript{19} coprecipitation\textsuperscript{20} etc. to make them heterogeneous in nature.

The degradation of phenolic compounds (phenol, 2-chloro-4-nitrophenol and 4-chloro-2-nitrophenol) in aqueous solution using mesoporous Cu/Al\textsubscript{2}O\textsubscript{3}-MCM-41 nanocomposite as a heterogeneous photo-Fenton like catalyst have been studied.\textsuperscript{21} Copper ion pillared bentonite has been reported as heterogeneous catalyst for photo-Fenton like oxidation of textile organic pollutants.\textsuperscript{22} Catalytic activity of copper modified bentonite supported ferrioxalate has been used for the degradation of direct blue71, acid green 25 and reactive blue 4 dye pollutants in batch photo-Fenton process without requiring pH adjustment.\textsuperscript{23}
Although mixed oxides based on vanadium have been studied for their many technological applications like lithium rechargeable battery\(^{24}\) and heterogeneous catalyses\(^{25}\), 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 based photo-Fenton like catalyst has been prepared by wet chemical method and used for the degradation of methylene blue dye in presence of H\(_2\)O\(_2\)/visible light. Its high catalytic activity may be due to synergistic activation by both copper and vanadium ions.

**Experimental**

\(\text{Cu}_3\text{V}_2(\text{OH})_2\text{O}_7\cdot2\text{H}_2\text{O}\) was prepared by wet chemical process.\(^{26}\) Copper nitrate aqueous solution (0.1 mol L\(^{-1}\)) was quickly poured into an aqueous solution of NH\(_4\)VO\(_3\) (0.2 mol L\(^{-1}\)) maintained at 75 °C under continuous stirring, when a yellow precipitate was formed. On further stirring for 1 h, the color of the precipitate changed to green. The precipitate was then isolated by filtration, washed several times with pure water and methanol and dried at room temperature overnight.

For photo-Fenton-like degradation, stock solution of methylene blue dye (1.0×10\(^{-3}\) mol L\(^{-1}\)) was prepared. A reaction mixture containing dye (1.0×10\(^{-5}\) mol L\(^{-1}\)), 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 a solarimeter (Suryamapi, CEL model 201). A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH-meter [Systronics, model 335] and adjusted with standard 0.1 equiv. L\(^{-1}\) sulphuric acid and 0.1 equiv. L\(^{-1}\) sodium hydroxide solutions. The experiments were conducted thrice in identical conditions and difference in the error between consecutive experiments was found to be less than 2%. The entire photoreactor system was maintained at 25 °C using thermostat. The progress of the dye degradation was monitored by measuring the absorbance of the reaction mixture at regular time intervals using UV visible spectrophotometer (Systronics, model 106).

Phase identification was done by X-ray diffraction (XRD) with a D/MAX-III A, Rigaku diffractometer using Cu-K\(_\alpha\) radiation at 35 kV, 30 mA and 20 =10–80°. Scanning electron microscopy (SEM) was 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. 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\(^{-1}\). 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) surface area analyzer.

The chemical oxygen demand (COD) of reaction mixture before and after treatment was determined by redox method using ferrous ammonium sulphate and potassium permanganate. The photodegradation efficiency of the catalyst was calculated from the expression: \(\eta = [(\text{COD}_{\text{before}} - \text{COD}_{\text{after}})/\text{COD}_{\text{before}}]\)×100, where \(\eta\) = photodegradation efficiency (%), \(\text{COD}_{\text{before}}\) = COD of dye solution before illumination and \(\text{COD}_{\text{after}}\) = 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**

XRD patterns of the synthesized catalyst were recorded. The diffraction peaks showed a monoclinic crystalline structure (Fig. 1) and are in good agreement with JCPDS card No. 46-1443. The crystallite size at 2\(\theta\) = 13°, was calculated by using Scherrer’s formula, \(t = 0.9\lambda/\beta\cos\theta\), 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 average crystallite size of the prepared powder is found to be 82 nm.

**Fig. 1** – XRD pattern of copper pyrovanadate.
SEM image of Cu$_3$V$_2$(OH)$_7$.2H$_2$O calcined at 750 °C is shown in Fig. 2a. The basic structure of catalyst (copper pyrovanadate) is a sheet-like structure with copper oxide/hydroxide layers held together by the pyrovanadate groups. These layers are stacked by layers of water (similar to Volborthite). Based on the SEM images, porosity of the surface is evident and it appears that the particles have not grown with uniform size. The particles size of Cu$_3$V$_2$(OH)$_7$.2H$_2$O that were propagated on the surface seems to be in the range of 50–200 µm. EDX analysis performed for further confirmation of the obtained product composition indicates the existence of V (23.35%), Cu (48.94%) and O (25.74%) in the prepared catalyst.

The catalyst was further characterized with Fourier transformer infrared spectroscopy (FTIR) to elucidate the surface OH group. Cu–O bonding is confirmed by a band at 592 cm$^{-1}$ in FT-IR of the catalyst. 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 suggests that after the loss of water adsorbed on the surface, the catalyst did not suffer from any obvious decomposition and had favorable thermal stability in the temperature range investigated. Cu$_3$V$_2$(OH)$_7$.2H$_2$O has more OH groups than FeO-H$_2$O$_2$ and CuO-H$_2$O$_2$, and this fact is in agreement with the FTIR results. Thus, Cu$_3$V$_2$(OH)$_7$.2H$_2$O may exhibit higher catalytic activities for pollutants removal. The surface OH group content for Cu$_3$V$_2$(OH)$_7$.2H$_2$O, FeO-H$_2$O$_2$ and CuO-H$_2$O$_2$ were calculated to be 3.8, 2.5 and 2.1%, respectively.

The specific surface area of the catalyst measured by BET method showed that the average specific surface area of Cu$_3$V$_2$(OH)$_7$.2H$_2$O particle was 17.6 m$^2$ g$^{-1}$ at 105 °C. This value may be attributed to the enhanced crystalline grain size calcined at 750 °C.

To investigate the photo-Fenton activity, aliquots of 3.0 mL were taken out from the reaction mixture at definite time intervals and the absorbance was measured at 665 nm. It was observed that the absorbance of the dye solution decreased with increasing time, which indicates the decrease in concentration of methylene blue with exposure time. A plot of 2+log $A$ against time was linear and follows pseudo-first order kinetics (Supplementary data, Fig. S1). The the pseudo first-order rate constant was found to be 4.23×10$^{-4}$ s$^{-1}$.

Catalyst powder was separated with centrifugation after use and washed with plenty of water. The washed slurry was dried at 80 °C in an oven for 5 h and it was used again for further degradation, which confirms its reusability. After 30 min reaction time, the activity of copper pyrovandate decreased slightly, by ~5% in the 5th run.

The effect of pH on the reaction was studied. The results show that as pH was increased, the rate of reaction was increased and after attaining the maximum value at pH 6.0, the rate decreases with further increase in pH. An increase in the degradation rate from pH 3.0–6.0 may be explained by the fact that relative concentration of OH$^-$ ions increases as the pH was increased from 3.0 to 6.0, resulting in the generation of more OH$^\cdot$ radicals by the reaction of Cu$^{2+}$ with OH$^-$, Cu$^{3+}$ + OH$^-$ → Cu$^{2+}$ + OH$^\cdot$.

In addition, in acidic medium, the surface of the catalyst is covered with adsorbed H$^+$ ions. Hence, there is coloumbic repulsion between positively charged catalyst surface and cationic dye. This repulsion is responsible for the decrease in rate of degradation on moving from pH 6.0 to 3.0. The optimum rate of degradation of the dye was obtained at pH 6.0. However, a decrease in rate of degradation was observed beyond 6.0 also, which may be due to the fact that dye does not remain in its cationic form, since OH$^-$ ions surround the dye molecules at much higher pH. Hence, there is less attraction between the
neutral charged catalyst surface (due to adsorption of OH\(^{-}\) ions) and approach of dye molecules towards catalyst surface is retarded. As a consequence, the rate of degradation was also decreased.

The effect of variation in concentration of dye on its degradation rate was studied in the range from 0.4×10\(^{-5}\) to 3.2 × 10\(^{-5}\) mol L\(^{-1}\). It has been observed that the rate of degradation increased with increasing concentration of dye up to 2.0×10\(^{-5}\) mol L\(^{-1}\). Further increase in concentration beyond 2.0×10\(^{-5}\) mol L\(^{-1}\) decreased the rate of degradation. Initially, on increasing the concentration of dye the reaction rate increased as more molecules of dye are available for degradation. However, further increase in concentration beyond 2.0×10\(^{-5}\) mol L\(^{-1}\) caused retardation of reaction due to increase in number of collisions between dye molecules, while the collisions between dye and OH\(^{-}\) radicals decreased. As a consequence, there is retardation of the rate of reaction.

The effect of varying amounts of catalyst on the rate of dye degradation was observed in the range of 0.2–0.9 g. With increase in the amount of catalyst, the rate of degradation was increased up to a certain catalyst amount (0.3 g), which may be regarded as the saturation point. Beyond this point, the rate of reaction decreased with increase in amount of catalyst. This may be explained on the basis that an increase in the catalyst amount increases the surface area of catalyst leading to increase in the rate of reaction. Further increase in the amount of catalyst also increases the number of copper ions, which leads to a possibility of short circuiting of cuprous and cupric ions, in which a cyclic process involving a change from Cu\(^{2+}\) to Cu\(^{+}\) ions and vice versa takes place. Due to this, generation of OH\(^{-}\) radicals is decreased.\(^27\) As a result, fewer of hydroxyl radicals are formed and reaction rate is retarded.

Variation of H\(_2\)O\(_2\) amount also affects the rate of reaction and therefore, the dye degradation rate was studied in the range from 0.15–0.50 mL of H\(_2\)O\(_2\). On increasing the amount of H\(_2\)O\(_2\) from 0.15 mL to 0.30 mL, the OH\(^{-}\) radical concentration also increases, resulting in an enhancement in rate of degradation of the dye. At high H\(_2\)O\(_2\) concentration, i. e., beyond 0.30 mL, scavenging of hydroxyl radical also takes place due to the H\(_2\)O\(_2\) generating perhydroxyl radical. Perhydroxyl radical is a weaker oxidant as compared to the hydroxyl radical, and therefore the rate of degradation of dye decreases when the amount of H\(_2\)O\(_2\) was increased beyond 0.30 mL.

It was observed that with increasing light intensity, the rate of reaction was also increased and the maximum rate was observed at 70.0 m W cm\(^{-2}\). When light intensity was increased, the number of photons striking per unit area was also increased, resulting in a higher rate of degradation. Further increase in the light intensity beyond 70.0 m W cm\(^{-2}\) results in a decrease in the rate of reaction, which may probably be due to thermal side reactions.

On the basis of the above experimental observations and corroborating with the existing literature, a tentative mechanism has been proposed for the degradation of methylene blue dye in presence of copper pyrovanadate, H\(_2\)O\(_2\) and light. V and Cu may simultaneously activate H\(_2\)O\(_2\) to give OH\(^{-}\) radicals.

\[
\begin{align*}
\text{Cu}^{2+} + \text{H}_2\text{O} & \quad \xrightarrow{\text{visible light}} \text{Cu}^+ + \text{HO}^- + \text{H}^+
\end{align*}
\]
\[
\begin{align*}
\text{Cu}^+ + \text{H}_2\text{O}_2 & \quad \rightarrow \text{Cu}^{2+} + \text{OH}^- + \text{HO}^* \\
\text{V}^{5+} + \text{H}_2\text{O} & \quad \xrightarrow{\text{visible light}} \text{V}^{4+} + \text{HO}^- + \text{H}^+ \\
\text{V}^{4+} + \text{H}_2\text{O}_2 & \quad \rightarrow \text{V}^{5+} + \text{OH}^- + \text{HO}^* 
\end{align*}
\]

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); the rate of photodegradation was found to be drastically reduced.\(^28,29\)

The involvement of singlet state of dye was confirmed by conducting the reaction in the presence of a small amount of potassium ferrocyanide as triplet state quencher.\(^30\) The rate of reaction was found to be unaffected.

Degradation of MB occurred generally by the attack of OH\(^{-}\) radicals, as it is highly reactive electrophilic oxidants. Generally, the sites near the C–S\(^\equiv\)C functional group and the central imino-group are susceptible for attack in photo-Fenton degradation process. MB and most of the degradation intermediates originate from the initial opening of the central aromatic and their subsequent metabolites are slowly oxidized to small molecules such as H\(_2\)O, CO\(_2\), inorganic cations and anions such as SO\(_4^{2-}\) and NH\(_4^+\). End products were confirmed qualitatively by spot tests.

Quality of water before and after photo-Fenton degradation was tested by measuring various parameters. 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 62.4 mg/L and 19.3 mg/L, respectively. The photodegradation efficiency was 69.07% after 2 hours of illumination.

Dissolved oxygen analysis measures the amount of gaseous oxygen dissolved in an aqueous solution. In the present work, increase in dissolved oxygen after photo-Fenton degradation (from 6.8 to 14.4 ppm) 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. As the results show that conductivity is increased after photo-Fenton treatment (from 89.1 to 125 µS) since the dye has been mineralized into ions such as CO$_3^{2-}$, NO$_3^-$, SO$_4^{2-}$ etc. Total dissolved solids (TDS) increased from 46.7 ppm to 154.5 ppm while salinity of the dye solution increased from 0.07 ppt to 0.09 ppt after photo-Fenton degradation of dye. Due to the mineralization of the dye during the treatment, the pH of reaction mixture was almost neutral (6.75) from the initial slightly acidic value (6.0).

Supplementary data
Supplementary data associated with this article, i.e., Fig. S1 is available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_54A(08)1057-1061_SupplData.pdf.

Acknowledgement
One of the authors (SK) is thankful to University Grants Commission, New Delhi, India, for the award of SRF. We are also thankful to UGC-DAE Consortium, Indore, India, for providing FT-IR and XRD data.

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