Degradation and mineralization of victoria blue B dye in a slurry photoreactor using advanced oxidation process

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Photocatalysed degradation of victoria blue B (VBB) dye has been studied in aqueous suspension of zinc oxide using visible spectrophotometric analysis technique. Effect of Fenton like system was also studied. Complete aromatic ring destruction was ascertained by UV spectroscopic analysis. Decrease in COD and increase in CO2 and NO3- concentration indicated mineralization of dye. Zinc oxide proved potentially efficient photocatalyst for proposed visible and solar light system. However, power law model showed intricacy of degradation process.

Keywords: Degradation, Mineralization, Photocatalysis, Visible light, Zinc oxide

Introduction

Large-scale production and extensive applications of synthetic dyes cause considerable environmental pollution. About 15% of total world production of dyes is released as textile effluents. Dyes are difficult to decompose biologically and chemically. Physicochemical processes only transfer pollutant from one phase to another. Therefore, a new contamination requires further treatments. Heterogeneous photocatalytic degradation lead to complete destruction of a wide range of organic substrate. Photocatalytic degradation of eosin Y, pararosaniln and remazol red F3B and acridine orange dyes have been studied with ZnO.

This study presents ZnO/Vis-mediated degradation of victoria blue B (VBB), which has irritating effect on eyes and respiratory system. Mineralization of dye was studied by using UV-Vis spectral analysis, COD, CO2 and NO3- estimation.

Experimental

VBB dye was obtained from Sigma-Aldrich Chemical Company. Photocatalyst ZnO (purity 99%, surface area 10 m²/g) was obtained from Merck Company (New Delhi, India). H2O2 (30% aq), FeCl3, FeSO4, NaCl and Na2CO3 were of analytical grade and used without further purification. All solutions were prepared in distilled water.

Photocatalytic and photolytic experiments were carried out in a slurry type batch reactor (Fig. 1) having a pyrex vessel (ht, 7.5 cm; diam, 6 cm), which is equipped with magnetic stirrer surrounded by thermostatic water circulation arrangement to maintain temperature (30±0.3°C). Irradiation was carried out using 500 W halogen lamp surrounded by aluminium reflectors to avoid irradiation loss. During photocatalytic experiment, after
stirring for 10 min, slurry composed of dye solution and catalyst was placed in dark for ½ h in order to establish equilibrium between adsorption and desorption phenomenon of dye molecule on photocatalyst surface. Then slurry containing aqueous dye solution and ZnO was stirred magnetically to ensure complete suspension of catalyst particle while exposing to visible light. At specific time intervals, aliquot (3 ml) was withdrawn and centrifuged for 2 min at 3500 rpm to remove ZnO particles from aliquot to assess extent of decolourisation photometrically. Changes in absorption spectra were recorded at 580 nm on double-beam UV-Vis spectrophotometer. Intensity of visible radiation was measured by a digital lux-meter. pH was constantly monitored. COD, CO₂ and NO₃⁻ ion estimation were performed. Performance efficiency was calculated as

\[
\text{% efficiency} = \frac{C_0 - C}{C_0} \times 100 \quad \text{...(1)}
\]

\[
X_{\text{COD or CO}_2} = \frac{C}{C_0} \quad \text{...(2)}
\]

where C and C₀ are initial and final dye concentration or COD or CO₂ for reaction time t.

**Results and Discussion**

**Kinetics of Photo degradation**

Langmuir-Hinshelwood pseudo-first order kinetics \((-dC/dt = kt)\) is used to model photo degradation of dye, where C is initial dye concentration at time t. Integrating this equation for limits from \((0, C_0)\) to \((t, C)\) gives

\[
\ln \left( \frac{C_0}{C} \right) = kt
\]

\[
(3)
\]

**Catalyst Screening**

Initial reaction rates were found to be directly proportional to catalyst concentration in static, slurry, or dynamic reactors. Experiments were performed at different ZnO concentrations, keeping other parameters constant. Rate constant of VBB increased from \(2.95 \times 10^{-4}\) s⁻¹ to \(8.71 \times 10^{-4}\) s⁻¹ with increase in catalyst loading from 50 mg/100 ml to 350 mg/100 ml, attributed to increment in active sites available for reaction on catalyst surface, which enhance rate of radical formation of hydroxyl radicals and superoxide radicals. Further increase in catalyst amount (350-600 mg/100ml) showed a drastic reduction in rate constant (Fig. 2). Results on catalyst loading for dye degradation are in agreement with reported studies.

**Effect of Electron Acceptors and Hole Scavengers**

Hydrogen peroxide (\(H_2O_2\)) and \(K_2S_2O_8\) can play a crucial role in photo degradation of dyes (Fig. 3). At optimal \(H_2O_2\) concentration \((7.0 \times 10^{-6}\) mol dm⁻³), decolourisation rate of VBB was \(2.5 \times 10^{-4}\) mol dm⁻³ s⁻¹. \(H_2O_2\) inhibits electron-hole recombination by accepting photogenerated electron from conduction band of semiconductor and promotes charge separation and also it forms OH⁻ radicals. \(K_2S_2O_8\) can also trap
photogenerated conduction band resulting into formation of sulphate ion (SO$_4^{2-}$), a strong oxidising agent (standard reduction potential = 2.6 eV)$^{22}$. It can trap photogenerated electrons or generates hydroxyl radicals. At optimal concentration of K$_2$S$_2$O$_8$, degradation rate of VBB was 2.5 x 10$^{-4}$ mol dm$^{-3}$ s$^{-1}$. With increase in concentration of Cl$^{-}$ and CO$_3^{2-}$ from 1.0 x 10$^{-6}$ mol dm$^{-3}$ to 13.0 x 10$^{-6}$ mol dm$^{-3}$, photo degradation rate reduced significantly from 1.3 x 10$^{-7}$ mol dm$^{-3}$ s$^{-1}$ to 0.8 x 10$^{-4}$ mol dm$^{-3}$ s$^{-1}$(Cl$^{-}$) and 0.7 x 10$^{-7}$ mol dm$^{-3}$ s$^{-1}$(CO$_3^{2-}$), respectively (Fig. 3). Inhibition undoubtedly describes their ability to act, as hydroxyl radical’s scavenger (OH$^-$)$^{10,11,13}$.

**Effect of FeCl$_3$**

Under chosen reaction condition, both FeCl$_3$/Vis and FeCl$_3$/ZnO/Vis systems are capable in decolourisation of VBB dye (Fig. 4) at slow rate. In FeCl$_3$, catalysed reaction, photo-sensitization of ion complex (Fe$^{3+}$/OH$^-$) results in formation of hydroxyl radicals and Fe$^{2+}$, which reacts with dissolved oxygen to form superoxide radicals O$_2^-$ and Fe$^{3+}$ ions$^{23}$. In ZnO/FeCl$_3$/Vis addition of FeCl$_3$ caused an increase in decolourisation rate (2.9 x 10$^{-7}$ mol dm$^{-3}$ s$^{-1}$) up to concentration 7.0 x 10$^{-6}$ mol dm$^{-3}$. Photoactivation of surface adsorbed complex ion (Fe$^{3+}$/OH$^-$) results in formation of Fe$^{2+}$/OH species, which inject electrons to conduction band of ZnO. Increased rate of decolourisation in case of FeCl$_3$ is explicable due to rapid scavenging of conduction band electrons by molecular oxygen leading to formation of superoxide and hydroperoxide radicals$^{23}$. Higher concentration of FeCl$_3$, eliminates adsorption of cationic dye on ZnO surface and also inhibits reaction rate by reducing production of hydroxyl radicals$^{24}$.

**Effect of Fe$^{3+}$/H$_2$O$_2$**

Efficiency of Fe$^{3+}$/H$_2$O$_2$ was studied for degradation of VBB in presence of ZnO/Vis process (Fig. 5). Decolourisation rate increased rapidly on addition of [Fe$^{3+}$/H$_2$O$_2$] in molar ratio 3:1. At optimal molar ratio [1:1.4], rate constant was found to be 5.4 x 10$^{-7}$ mol dm$^{-3}$ s$^{-1}$. When Fe$^{3+}$/H$_2$O$_2$/ZnO system was irradiated with visible radiation, production of hydroxyl radicals increased. Dye absorbs visible radiation with high-energy state. Excited dye molecules reduce ferric ion complex to ferrous ion, which react with H$_2$O$_2$ to decompose and produce hydroxyl radical. OH$^-$ radicals also decompose H$_2$O$_2$ to HO$^·$. Synergetic effect of HO$^·$ on ZnO/Vis process also enhances degradation process. At optimal molar ratio of Fe$^{3+}$/H$_2$O$_2$ (1:1) for dye decolourisation, reduction in reaction rate is due to more scavenging of OH$^-$; in absence of ZnO, reaction rate was 2.0 x 10$^{-7}$ mol dm$^{-3}$ s$^{-1}$. Under chosen experimental conditions, Fenton/ZnO/Vis process has been found more efficient than photo-Fenton process for degradation of VBB.

**Effect of pH**

Decolourisation of VBB dye, studied at different pH (3-12), was optimum (5.2 x 10$^{-7}$ mol dm$^{-3}$ s$^{-1}$) at pH 7.4 (Fig. 6). pH without ZnO is about 9$^{24}$. At pH 7-8, negatively charged active sites on catalyst surface are preferentially covered by positively charged dye molecule due to metal-bound OH$^-$. At lower pH, positively charged...
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Active sites on catalyst surface results in low concentration of positively charged dye molecule on catalyst surface. Therefore, with increasing pH, surface concentration of dye molecules and OH\(^-\) radicals increases. However, at lower pH, ZnO gets dissolved forming salts. At higher pH, it forms zincates [Zn(OH)\(_4\)]\(^{2-}\). All these factors are responsible for optimal value of decolourisation rate of VBB at pH 7.4\(^{29,25}\).

**Effect of Solar Light**

VBB was exposed to solar light in aqueous suspension ZnO on sunny days of January 2007 between 12 Noon to 2 PM (Fig. 7). Solar light was efficient for dye degradation. Experiments without ZnO, carried out under sunlight and artificial light, showed no dye loss.

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Fig. 6—Decrease in absorbance of VBB dye with change in pH [VBB conc. = 4.5 x 10\(^{-4}\) mol dm\(^{-3}\), ZnO = 50 mg/100 ml and irradiation intensity = 5600 lux]

Fig. 7—Change in dye concentration under direct sunlight and in presence of artificial visible irradiation [VBB= 4.5 x 10\(^{-4}\) mol dm\(^{-3}\), ZnO = 50 mg/100 ml, irradiation intensity = 5600 lux and pH = 4.1]

Fig. 8—UV-Vis spectra change with respect to different time intervals [VBB conc. = 9.0 x 10\(^{-4}\) mol dm\(^{-3}\), ZnO = 350 mg/100 ml, irradiation intensity = 25600 lux and pH = 7.4]

Fig. 9—COD, CO\(_2\) and NO\(_3\)\(^-\) ion estimations during mineralization process [VVB conc. = 9 x 10\(^{-4}\) mol dm\(^{-3}\), ZnO = 350 mg/100 ml, irradiation intensity = 25600 lux and pH = 7.4]

Fig. 10—Variation of VBB degradation rate vs its concentration [ZnO= 50 mg/100 ml, ZnO = 50 mg/100 ml, irradiation intensity = 5600 lux and pH = 4.1]
Aromatic Ring Destruction and Mineralization of VBB

UV-Vis absorption spectra of VBB were studied at different intervals of irradiation time. Absorbance at 200-400 nm was attributed to $\pi \rightarrow \pi^*$ transition of benzene and naphthalene rings of dye. Absorption peak at 580 nm corresponds to chromophore part of VBB. Bands relating to different molecular parts of VBB decreased with respect to illumination time (Fig. 8), attributed to destruction of aromatic ring and chromophore part of dye. Complete disappearance of bands was observed by illuminating dye solution for 6 h under optimal reaction conditions. With increased irradiation time, COD reduction (50%) was observed (Fig. 9) in 4 h of illumination. Increased CO$_2$ concentration confirmed degradation of VBB. Using ZnO/Vis process, initially for first 4 h, 30% of CO$_2$ formation was detected. A maximum of 42 x 10$^{-3}$ mg dm$^{-3}$/l nitrate ions were released into solution after 12 h of irradiation time. Under optimum reaction conditions, 8-10 h of irradiation time is required for complete mineralization of VBB.

Photocatalytic degradation can be represented as

$$R = R_1 + R_2 \quad \ldots(4)$$

where $R$, $R_1$, and $R_2$ are net degradation, photocatalysis and photolysis rates respectively.

Under chosen experimental condition, photolysis had no effect on degradation process. Therefore, Eq. (4) reduces to

$$R = -\frac{d[VBB]}{dt} = R_1 \quad \ldots(5)$$

Simple power law model was examined to find rate of photocatalytic degradation as

$$R = k_1[VBB]^{n_1} \quad \ldots(6)$$

where $n_1$ and $k_1$ are appropriate order and rate constant of reaction.

In order to obtain appropriate parameters in Eq. (6), differential method of analysis based on data of dye concentration vs time was used to get

$$\log R = \log k_1 + n_1 \log [VBB] \quad \ldots(7)$$

Fit of Eq. (7) to the data was presented (Fig. 10). Order of reaction for photocatalysis (2.16) indicates intricacy of degradation process. Rate constant for degradation of VVB was found to be 9.9 x 10$^{-2}$ (mol dm$^{-3}$)$^{-1}$s$^{-1}$. Results are in agreement with reported studies. Under chosen experimental conditions, net rate of degradation of VBB (mol dm$^{-3}$ s$^{-1}$) can be written as

$$R = 9.9 \times 10^{-2} [\text{VBB}]^{2.16} \quad \ldots(8)$$

Conclusions

Photo assisted mineralization of VVB is possible in aqueous suspension of ZnO using a slurry batch reactor. Carbonate and chloride ions have detrimental effect on rate of reaction. Catalyst loading and pH have affected efficiency of degradation. Most suitable conditions were found to be: catalyst conc., 350 mg/l; and pH, 7.4. Synergetic action of H$_2$O$_2$, K$_2$S$_2$O$_8$ and FeCl$_3$ was observed. H$_2$O$_2$/Fe$^{3+}$/ZnO/Vis process was found to be most efficient for dye decolourisation. Under optimum reaction conditions, for complete mineralization of VBB (9.0 x 10$^{-3}$ mol dm$^{-3}$), 8 h of irradiation time is required. Decolourisation and mineralization are not simultaneous but tend to approach each other as time of irradiation is increased.

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