Visible light-driven photocatalytic degradation and mineralization of neutral red dye in a slurry photoreactor

Brijesh Pare, Pardeep Singh & S B Jonnalagadda

Laboratory of Photocatalysis, Department of Chemistry, Govt. Madhav Science College (af. Vikram University), Ujjain 456 010, India

University of Kwazu-natal, Westville, Durban, South Africa

Email: brijeshpare2009@hotmail.com/pardeepchem@gmail.com

Received 23 February 2010; revised 2 August 2010

Hydroxyl radicals (OH·) induced photocatalytic degradation of neutral red was investigated in a batch slurry reactor, in the presence of visible light illuminated ZnO. The effects of process parameters such as catalyst loading, initial substrate concentration, Fenton reagent, temperature, solar light and oxidant, and anion concentration were investigated. In the presence of visible light, ZnO/Fenton process was found to be most efficient for the decolorization of dye. Both artificial visible radiation and solar light degraded dye efficiently in the presence of ZnO. The destruction of chromophoric part and aromatic skeleton of dye were ascertained by the disappearance of absorption bands in UV/Vis spectra of dye with respect to irradiation time. Complete COD reduction was observed in 8 h of irradiation time. CO₂ and NO₃⁻ ions were identified as final mineralization products.

Keywords: Photocatalysis, Vis/ZnO process, Neutral red, Decolourization, Aromatic ring destruction, Mineralization

About 15% of the total world production of dyes is lost during the dyeing process and is are leased in the textiles effluents. Dye wastewater has been traditionally treated by physical or chemical treatments such as flocculation, electroflotation, membrane filtration, ion exchange, electro kinetic coagulation, irradiation, precipitation etc. Nevertheless, they are non destructive, since they just transfer organic compounds from water to another phase, thus causing secondary pollution. Recently, semiconductor photocatalysis has emerged as an alternative to conventional methods involving generation of hydroxyl radical that oxidizes a broad range of organic pollutants quickly and non-selectively. Upon illumination of semiconductor particles with light energy greater than the band gap energy (ħν > E_g = 3.2 eV), electron-hole pairs are (e_CB/h_VB) are generated (Fig. 1). The photogenerated holes that are able to migrate to the hydroxylated surface can create the highly reactive radical OH· (standard redox potential 2.8 V). The role of reductive pathways in heterogeneous photocatalysis is very little as compared to oxidation. In second way, dye molecules act as a sensitizer by the absorption of visible light, and the transfer of photogenerated electrons from the dye molecule to semiconductor has been reported to be very effective.

Neutral red (NR), a phenazine class of dye has been used for staining cell cultures. It is used as intracellular pH indicator. The aim of present study is to investigate mineralization of neutral red dye in the presence of ZnO under visible irradiation (Vis/ZnO process. Decolorization of neutral red was also analyzed under photo-Fenton and Vis/ZnO/H₂O₂/Fe²⁺ system. The destruction of aromatic ring and mineralization of dye was confirmed by the estimation of COD, CO₂, NO₃⁻ ion and UV-Vis spectral analysis.

![Fig. 1—Mechanism of hydroxyl radical production. DP= Degradation product](image-url)
Experimental Procedure

Materials and Method

Neutral red (mol. wt. = 288.18 mg mol\(^{-1}\)) dye was purchased from Sigma-Aldrich Company (India) and was used as received. All chemicals used were of AR grade. The photocatalyst, ZnO used in the study was obtained from Merck, about 99% pure. FeCl\(_3\), FeSO\(_4\), NaCl and Na\(_2\)CO\(_3\) were of analytical grade and used without further purification. All the solutions were prepared by dissolving the calculated amount of appropriate chemicals in double distilled water.

The photocatalytic and photolytic experiments were carried out in a slurry type batch reactor having pyrex vessel of dimension of 7.5 × 6 cm (height × diameter) (Fig. 2). The pyrex vessel was surrounded by thermostatic water circulation arrangement to keep temperate in the range of 30±0.3°C. The irradiation was carried out using 500 W halogen lamp surrounded with aluminium reflectors in order to avoid loss of irradiation. During the photocatalytic experiment, after stirring for 10 min, the slurry composed of dye solution and catalyst was placed in dark in the order to establish equilibrium between adsorption and desorption. Now slurry containing dye and semiconductor catalyst was placed inside the reactor and stirred magnetically for agitation with simultaneous exposure to visible light. At specific time intervals, aliquot (3 mL) was withdrawn and centrifuged for 2 min at rate of 3500 rpm to remove the ZnO particles in order to assess the extent of decolorization photometrically. The intensity of visible radiation was measured by a digital lux-meter (Lutron LX -101). The pH was constantly monitored and not adjusted unless otherwise stated. The detection was realized at 520 nm. The chemical oxygen demand (COD) was measured by the closed reflux method. The unreacted oxidant was determined by titrating with ferrous ammonium sulphate using ferroin indicator\(^6\). The amount of CO\(_2\) was estimated by using NaOH as titrant with phenolphthlein as indicator\(^7\). NO\(_3\) ions were detected by UV spectroscopic screening method\(^8\). The performance efficiency was calculated by Eq. (1)

\[
X_{\text{COD or CO}_2} = \frac{C}{C_0}
\]  

where X is performance efficiency; \(C_0\) is initial COD of dye solution before irradiation; C is COD of dye solution after the process.

Results and Discussion

Kinetics of photodecolorization of neutral red (NR)

Figure 3 indicates photocatalytic decolorization of \(3.0 \times 10^{-5}\) mol dm\(^{-3}\) dye solution containing 300 mg ZnO as function of irradiation time. The blank experiments with either illuminating NR or with the suspension containing ZnO and NR in the dark showed that both illumination and the catalyst were necessary for the destruction of dye. The plot between \(\ln(C/C_0)\) versus time was found to be pseudo first order \((R^2= 0.97)\). With the initial dye concentration \(3.0 \times 10^{-5}\) mol dm\(^{-3}\) solution containing 300 mg ZnO/100 mL and light intensity 8400 lux, the rate constant found to be \(3.07 \times 10^{-4}\) s\(^{-1}\).
Effect of substrate and catalyst concentration

The influence of initial dye concentration on photocatalytic degradation is very important aspect of the study. The initial concentration of dye was varied from 0.5 × 10⁻⁴ mol dm⁻³ to 4.5 × 10⁻³ mol dm⁻³. The rate of photodegradation (9.07 × 10⁻⁵ s⁻¹) was maximal at 1.5 × 10⁻⁵ mol dm⁻³ of dye.

In order to avoid an unnecessary excess of catalyst and to ensure total absorption of light, the effect of catalyst loading was studied. With increase in catalyst loading form 100 mg/100 mL to 300 mg/100 mL, the reaction rate increased from 1.68 × 10⁻⁴ s⁻¹ to 2.95 × 10⁻⁴ s⁻¹. The total active surface area increases with increasing catalyst dosage. However, further increase in catalyst loading (300 mg/100 mL to 700 mg/100 mL) caused a reduction in rate of decolorization. At higher loading level, there is decrease in the visible light penetration due to increased scattering of light.

Effect of hydroxyl radical acceptors and electron accepters

An increment in concentration of Cl⁻ from 1 × 10⁻⁶ mol dm⁻³ to 13 × 10⁻⁶ mol dm⁻³ results in reduction of photodegradation rate from 3.17 × 10⁻⁴ s⁻¹ to 1.4 × 10⁻⁴ s⁻¹ while with same CO₃²⁻ ion concentration variation, the rate constant had a decrease in value from 3.17 × 10⁻⁴ s⁻¹ to 1.34 × 10⁻⁴ s⁻¹. The inhibition is undoubtedly due to their ability to act as hydroxyl radical (OH⁻) scavengers.

The rate of decolorization of NR was maximal at 7.0 × 10⁻⁶ mol dm⁻³ of H₂O₂. Further addition of H₂O₂ retards degradation efficiency of process⁹. The added hydrogen peroxide could inhibit the electron-hole recombination by accepting photogenerated electron from the conduction band of semiconductor and promotes charge separation and also it forms ‘OH radicals according to Eqs (2) and (3).

\[ e_{\text{cb}}^{-} + \text{H}_2\text{O}_2 \rightarrow \text{OH}^{-} + \text{OH}^{-} \]  \hspace{1cm} (2)

\[ \text{H}_2\text{O}_2 + h_{\text{vb}}^{+} \rightarrow 2\text{OH}^{-} \]  \hspace{1cm} (3)

By addition of excess H₂O₂, it acts as hydroxyl radical or hole scavenger to form the perhydroxyl radical (HO₂⁻), which is much weaker oxidant than hydroxyl radicals⁹.

K₂S₂O₈ can also trap the photogenerated conduction band electron to produce sulphate ion with (standard reduction potential = 2.6 V). Photocatalytic process was accelerated due to increased production of hydroxyl radicals. The decrease in rate of photodegradation above optimal concentration (9.0 × 10⁻⁶ mol dm⁻³), is due to the adsorption of sulphate ions on surface of ZnO formed during the reaction⁹.

Effect of pH

The photo degradation of neutral red dye was studied at different pH values (in the range 3-10). The rate of reaction was maximal at pH value 7.5. Further, increase in pH caused a reduction in the rate of decolorization. The pH of zero point charge for ZnO is about 9⁹. At pH 7-8, due to metal-bound OH⁻, negatively charged active sites on the surface of catalyst are preferentially covered by positively charged dye molecule. At lower value of pH ~ 4, positively charged active sites on the surface of catalyst, results in low concentration of positively charged of dye molecule on the surface of catalyst. At higher pH, surface concentration of dye molecules and hydroxyl radicals increases. But ZnO is amphoteric in nature. It gets dissolved at lower pH, forming Zn²⁺. At higher pH, it forms zincates such as [Zn(OH)₄]²⁻. All these factors are responsible for optimum value of photodegradation of neutral red at pH 7.5.

Vis/ZnO/Fenton hybrid system

In Fe²⁺/Vis system, an increment in rate constant from 1.5 × 10⁻⁴ s⁻¹ to 5.2 × 10⁻⁴ s⁻¹ was observed with increase in [H₂O₂: Fe²⁺] from [1:3] to [11:1]. This is due to increased production of hydroxyl radicals due to reactions according to Eqs (4)-(6).

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \xrightarrow{hv} \text{Fe}^{3+} + \text{OH}^{-} + \text{OH}^{-} \]  \hspace{1cm} (4)

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe} + \text{OOH}^{2+} + \text{H}^{+} \]  \hspace{1cm} (5)
Fe(OOH)_{2+} \xrightarrow{h\nu} HO_{2^-} + Fe^{2+} \quad \ldots(6)

The rate of decolorization increased rapidly from $3.07 \times 10^{-4}$ s$^{-1}$ to $6.02 \times 10^{-4}$ s$^{-1}$ on addition of [H$_2$O$_2$: Fe$^{2+}$] in molar ratio [3:1]. The rate constant attained optimal value of $9.86 \times 10^{-4}$ s$^{-1}$ by use of molar ratio [1: 1.4] of [H$_2$O$_2$: FeSO$_4$]. Dye absorbs visible irradiation and gets excited into high energy state. These excited dye molecules reduce the ferric ion complex to ferrous ion complex followed by the transfer to ferric ion$^{10,11}$. The photoactivation of surface adsorbed [Fe$^{2+}$(OH)] in the presence of Vis/H$_2$O$_2$ results in the enhancement of production rate of OH$^\cdot$. This activated [Fe$^{2+}$(OH)] specie is also responsible for the promotion of electrons to the conduction band of ZnO. Hence, production of OH$^\cdot$ and HO$_2^-$ has been accelerated. Above optimal value, reduction in rate of decolorization was attributed to lower rate of formation of OH$^\cdot$ radicals due to ability of peroxide molecules to act as hydroxyl radical scavenger. This study reveals that Fenton reagent in the presence of ZnO and visible irradiation degrades NR dye efficiently.

**Effect of solar light and temperature**

Aqueous solution of NR and ZnO was exposed to sunlight (Fig. 4). It was found that the degradation of selected dye proceeds much more rapidly in the presence of solar light. Blank experiments were carried out under sunlight in absence of ZnO where no observable loss of dye was observed.

The influence of temperature was studied in the range 30-55°C. The rate constant was found to increase (2.9 $\times$ 10$^{-4}$ s$^{-1}$ to 4.2 $\times$ 10$^{-4}$ s$^{-1}$) with increment in temperature from 30-45°C. However, further increase in temperature reduced the rate of reaction. Increased temperature tends to reduce electron-hole recombination. However, an increment in temperature decreases the solubility of oxygen in water$^9$. Both above mentioned conflicting factors have been equipoised at 45°C. Significant amount of solution was evaporated at higher temperature.

**Aromatic ring destruction and mineralization of neutral red dye**

In a precedent study, Fig. 5 shows a time-dependent UV-Vis absorption spectrum of NR (6.0 $\times$ 10$^{-5}$ mol dm$^{-3}$) during irradiation by visible light in the presence of ZnO. The complete disappearance of band at 523 nm and 269 nm indicates the complete destruction of chromophore group and phenazine ring of selected organic dye. No additional, UV/Vis signals were detected in the analysed wavelength range after 8 h of illumination, meaning that no radiation absorbing intermediates at this wavelength range, were detected.

COD values have been related to the total concentration of organics in the solution. After 8 h of irradiation, 90% COD-removal was achieved (Fig. 6).
The formation of CO$_2$ and NO$_3^-$ increased significantly catalytic with irradiation time. Here, simple power law model was examined to find rate of the photocatalytic degradation$^{12}$. The order of reaction for both photocatalysis (3.14) and photolysis (2.98) more than one indicates complex nature of overall mechanism. Under chosen experimental conditions, the net rate of degradation of neutral red was found to be $12 \times 10^{-2}\text{[NR]}^{3.14} + 11 \times 10^{-6}\text{[NR]}^{2.98} \text{mol dm}^{-3} \text{s}^{-1}$.

**Conclusions**

This study shows that visible light-induced AOP is an efficient process for decolorization and mineralization of neutral red dye. Rate constant had a maximal value at optimum concentration of dye, catalyst, H$_2$O$_2$ and K$_2$S$_2$O$_8$. Cl$^-$ and CO$_3^{2-}$ ion had detrimental effect on the photodegradation of selected dye. Fenton reagent on combination with ZnO/Vis system was found to increase the rate of colour abatement significantly. Temperature had very little effect on decolorization of selected dye.

From UV-Vis spectral analysis, COD, CO$_2$, and NO$_3^-$ ion estimation, it is evident that neutral red degrades completely in 10 h of illumination. In Vis/ZnO process, artificial irradiation could be replaced by solar light for the photodegradation of neutral red dye. Kinetic studies indicate complex nature of photodegradation process. Visible light assisted method could be an effective method for degradation of neutral red dye on pilot scale application. Photoassisted catalytic degradation promises to be a versatile, economic, environmentally benign and efficient method of wastewater treatment if all parameter are properly optimized.

**References**