Photocatalytic Degradation of Aqueous C.I. Reactive Violet 5 Using Bulk Zinc Oxide (ZnO) Slurry

Jeannie Lynn J. Cabansag*, Jesus C. Dumelod†, John Cyrus O. Alfaro‡, John D. Arsenal‡, Jolivette C. Sambot‡, Lorna T. Enerva‡, and Julius L. Leaño Jr.†

1Research and Development Division, Philippine Textile Research Institute, Department of Science and Technology, Bicutan, Taguig City
2Department of Natural Sciences, College of Science, Polytechnic University of the Philippines

The degradation of aqueous C.I. Reactive violet 5 dye under UV light with bulk zinc oxide (ZnO) slurry as the photocatalyst was studied. The effects of varying amounts of zinc oxide, dye concentration, exposure time, pH, temperature and lamp intensity on degradation were evaluated. UV irradiation was found to enhance dye degradation by about 90% immediately after 30 minutes of exposure time, for low dye concentration of 2 x 10⁻⁵ M. The rate of dye degradation increased as the amount of zinc oxide increased until optimum loading was achieved. At 3840 ppm ZnO concentration, 5 x 10⁻⁵ M (40 ppm) dye is degraded by 74% after 30 min of irradiation and was nearly 100% degraded after 90 min at pH 7 and temperature of 30°C. The degradation rate follows a first order kinetics with respect to dye concentration, with the rate constant decreasing as dye concentration increases at constant amount of zinc oxide. The rate of RV5 degradation is determined at 9.3 x 10⁻⁵ M/h using 3840 ppm ZnO under neutral pH, temperature of 30°C and 20W lamp intensity. Increased pH, temperature and lamp intensity further accelerate dye degradation by about 38.0%, 53.3%, and 43.2%, respectively. The use of zinc oxide provides a simple and efficient method for photocatalytic degradation of azo dyes in wastewater.

Key Words: degradation; photocatalysis; reactive violet 5; zinc oxide

INTRODUCTION

Dye pollutants from the textile industry contribute to considerable environmental contaminants. In dyeing process, about 1-15% of dye is discharged, accounting to a large volume of effluents which could lead to aesthetic pollution, eutrophication, and perturbations in marine and aquatic ecosystem (Li-Song 2010).

Several methods have been employed in the treatment of dye wastewater effluents. Among these are costly and tedious chemical processes, which do not readily apply to all dye classes. A more efficient approach and relatively cost-effective is biological treatment. However, not all dye classes are degraded through this process. Hence, the need to find alternative methods that are not only more efficient but also practical and would cover a larger class of dye effluents (Comparelli et al. 2005).

In the recent years, photochemical reactions have been studied to effect degradation of dyes. The mechanism of the reaction consists of activation of a semi-conductor (photocatalyst) material by absorption of ultraviolet, visible, or infrared radiation. The photocatalyst helps in overcoming large activation barriers in a short period of time and allows reactions that are inaccessible by thermal methods to occur. Among the most studied photocatalysts are TiO₂, ZnO, Fe₂O₃, CdS, and ZnS. Zinc oxide was
employed in this study due to its relatively lower cost than TiO₂. The two photocatalysts have almost the same characteristics, most notable of which are their band gaps at approximately 3.0 eV. Zinc oxide absorbs a larger fraction of the UV spectrum, offering a possible greater photocatalytic application as compared to other photocatalysts (Yassitepe et al. 2008).

CI Reactive Violet 5 (RV5) is an azo colorant classified as a reactive dye and is usually applied on cellulosic fibers. It contains a reactive group, either a haloheterocycle or an activated double bond, that, when applied to a fiber in an alkaline dye bath, forms a covalent bond with a hydroxyl group on the cellulosic fiber. RV5 can also be applied on wool and nylon under weakly acidic conditions (Chung and Chen 2009).

![Figure 1. CI Reactive Violet 5 (Chung and Chen 2009).](image)

The study focused on analyzing the degradation of aqueous C.I. Reactive Violet 5 dye under UV light with bulk zinc oxide (ZnO) slurry as the photocatalyst. The effects of varying amounts of zinc oxide, dye concentration, exposure time, pH, temperature and UV lamp intensity on degradation were also evaluated. The kinetics of dye degradation was also established.

MATERIALS AND METHODS

Materials
Bulk zinc oxide powder, 99.0% purity (JT Baker), was used as the photocatalyst to degrade C. I. Reactive Violet 5 (RV5) dye (Sigma Aldrich). All reagents were of analytical grade and were used without further purification.

Evaluation of photocatalytic activity
Irradiation was carried out inside a closed rectangular box with a two 10-Watt (W) UV lamp or black light having UV emission peak at 365 nm. A 1L reaction vessel immersed in a water bath with an inlet and outlet water pump system to maintain the desired temperature was used. The reaction vessel was stirred at a constant rate to ensure homogeneity of the reaction. Absorbance measurements were done using Shimadzu 160A UV – Vis spectrophotometer.

Photocatalytic degradation of Reactive Violet 5 was analysed by using an initial dye concentration of 5 x 10⁻⁵ M with 2560 ppm ZnO powder. The suspension in the vessel was stirred continuously and allowed to equilibrate in the dark for 30 min. After 30 min, the mixture was UV irradiated for 3 h with continuous stirring to maintain the homogeneity of the suspension. A 7 mL volume of sample was withdrawn from the mixture after every 30 min then centrifuged immediately for 10 min to separate ZnO particles. The absorbance of the sample supernatant was recorded and the corresponding concentration was determined from the calibration curve of standard concentrations from 1.0 – 10.0 x 10⁻⁵ M. Degree of dye photodegradation as a function of concentration was calculated using (1):

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\text{degree of degradation} = \frac{C_0 - C}{C_0}
\]

where \( C_0 \) is the initial dye concentration and \( C \) is the dye concentration at a specific time, \( t \).

Effect of dye concentration and ZnO loading
The effects of dye concentration and amount of ZnO used for photocatalytic degradation were determined using dye concentrations in the range of 2.0 – 8.0 x 10⁻⁵ M and ZnO loading of 640 – 5020 ppm at neutral pH.

Effect of pH, temperature and lamp intensity
The effect of pH on photocatalytic degradation of RV5 was evaluated using a pH range of 3-10. The pH of the solution was adjusted using 0.1 M sodium hydroxide and 0.1 M sulfuric acid solutions (Daneshvar et al. 2004). Temperature of the mixture was varied at 30°C and 70°C while UV lamp intensity of irradiation used were 10 W and 20 W.

RESULTS AND DISCUSSION
Dye decolorization occurred upon addition of ZnO and UV exposure of the dye solution, in which a color change, from violet to colorless is observed. This decolorization is further investigated by the UV-Vis absorption profile, Figure 3, in which a disappearance of peak at about 560 nm is shown, indicating the degradation of the chromophoric group of the dye. (Chen 2006 and Mozia et al. 2005). It can be seen in Figure 2 that photodegradation effectively takes place in the presence of both UV light and ZnO. Similar trials were performed allowing reaction to occur in the absence of ZnO, and negligible increase in degree of photodegradation was observed. The same was observed when the UV lamp was switched off.
Spectrophotometric changes
A time-dependent UV-Vis spectrum of RV5 during UV irradiation is shown in Figure 3. The spectrum is characterized by two peaks – at 560 nm in the visible region and at 320 nm in the UV region. The peak at the visible region with a maximum at 560 nm corresponds to the azo (N=N) functional group. The decrease of absorption peak at 560 nm and almost complete disappearance of peak after 2 hours, indicated degradation of the azo group. The presence of peak at lower absorbance implies that a certain percentage of the azo group which is also associated with the amount of dye present in the solution was degraded. The nitrogen to nitrogen double bond of the azo dye is the most active site for oxidative attack by hydroxyl radicals or positive holes – holes that act as positive charge. This site is also the most susceptible for reduction by electrons generated upon photoexcitation of ZnO. The degradation of the azo chromophore thus explains the observed decolorization of the dye solution. A decrease in absorption at 320 nm which is characteristic of aromatic rings further indicated that the aromatic rings of the RV5 structure were also partially degraded in the process (Mozia et al. 2005).

Effect of ZnO concentration
The effect of ZnO concentration on the photodegradation of RV5 is shown in Figure 4. The rate of dye degradation increased as the amount of zinc oxide increased until optimum loading was achieved.

At 3840 ppm ZnO concentration, RV5 dye having initial concentration of $5 \times 10^{-5}$ M, is degraded by 74% after 30 min of irradiation and was nearly 100% degraded after 90 min at pH 7 and temperature of 30°C. The increase in degradation efficiency could be accounted to the increase in surface area for the photocatalytic degradation of dye when the amount of ZnO is increased. Further increase in the amount of catalyst, beyond 3840 ppm, did not result to increased efficiency due to decrease in light penetration and increased light scattering (Chung and Chen 2009).

Effect of dye concentration
For low dye concentrations UV irradiation was found to enhance dye degradation by about 90% immediately after 30 min of exposure time as shown in Figure 5. The decreasing rate of degradation as dye concentration increased was determined to follow a linear curve, as in Figures 6 and 7. The degradation rate follows a first order kinetics with respect to dye concentration, with the rate constant decreasing as dye concentration increases at constant amount of zinc oxide. This is based on the Langmuir-Hinshelwood kinetic treatment, which had been used for previous degradation studies and solid-liquid interactions. (Sauer et al 2002; Nageswara Rao et al. 2009; Mozia et al. 2005) The change in concentration as a function of time can be expressed as:

$$\frac{-dC}{dt} = kC_0$$  \hspace{1cm} (2)

Integrating (2) and taking the natural logarithm gives (3) and (4):

$$C = C_0e^{kt}$$  \hspace{1cm} (3)

$$\ln \frac{C}{C_0} = kt$$  \hspace{1cm} (4)
Figure 3. Time-dependent UV-Vis spectrum of Reactive Violet 5 during photocatalytic degradation with zinc oxide (RV5 = 5 x 10^{-5} M; ZnO = 2560 ppm; neutral pH).

Figure 4. Effect of ZnO loading on photocatalytic degradation (RV5 = 5 x 10^{-5} M; neutral pH).
**Figure 5.** Effect of dye concentration on photocatalytic degradation (ZnO = 3840 ppm; neutral pH).

**Figure 6.** Plot of \(\ln\left(\frac{C_0}{C}\right)\) vs time (varying dye concentration; ZnO = 3840 ppm; neutral pH).
From equation 4, a linear relationship is established between \( \ln C_0/C \) and time. A plot of \( \ln C_0/C \) versus time for each dye concentration gives a straight line with the slope corresponding to the first order rate constant values \( k \) (h\(^{-1}\)) (Figure 7) (Mozia et al. 2005 and Nageswara Rao et al. 2009).

The equation of the linear portion is obtained and the corresponding \( k \) values (slope of the linear curve) are plotted against reciprocal of initial dye concentration \( (1/C_0) \). The linear plot of \( k \) vs dye concentration, as in Figure 7, indicated a first order degree of degradation with respect to dye concentration. The rate of dye degradation is \( 9.3 \times 10^4 \) M/h as obtained from the slope of the line (Nageswara Rao et al. 2009).

Effect of pH
Photodegradation of RV5 was also affected by pH of the solution (Figure 8). At lower pH values, below pH 7, the rate of degradation decreased while it increased at higher pH. At pH of 10, rate of degradation increased by about 38.03%, whereas at pH 3, rate of degradation decreased by about 76.35%. Under acidic conditions, photocorrosion of ZnO took place. On the other hand, no photocorrosion occurred at higher pH, instead, more efficient formation of hydroxyl radical occurs. This is equated to increased rate of photodegradation (Chen 2006).

Effect of temperature and lamp intensity
Temperature and lamp intensity were found to enhance photodegradation, as seen on Figures 9 and 10. The rate of dye degradation is found to increase with increased temperature. At 1 h irradiation time, only about 60% of dye is degraded at 30°C as compared to 84% dye degradation at 70°C at the same time. The dependence of dye photodegradation was also observed in other similar studies and is supported by the Arrhenius theory, for which the reaction rate is dependent on temperature of the system (Mozia et al. 2005).

Variation in lamp intensity, from 20 W to 10 W, was also seen to effect the rate of degradation (Figure 10). The change in lamp intensity is associated with change in the intensity of UV radiation that facilitated photodegradation. Higher lamp intensity produced higher intensity of UV radiation that can excite more ZnO.

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**Figure 7.** Linear plot of \( k \) vs reciprocal of initial dye concentration \( (1/C_0) \).
Figure 8. Effect of pH on photodegradation (RV5 = 5 x 10^-5 M; ZnO = 3840 ppm).

Figure 9. Effect of temperature on photodegradation (RV5 = 5 x 10^-5 M; ZnO = 3840 ppm; neutral pH).
particles to generate more electron-hole pairs that degrade RV5. At low lamp intensity, photodegradation occurred at a slower rate, hence, full dye degradation proceeded at a longer irradiation time (Chung and Chen 2009).

CONCLUSION AND RECOMMENDATIONS

Photocatalytic degradation of Reactive Violet 5 (RV5) was efficiently done using 3840 ppm zinc oxide at neutral pH with UV light. Increased pH, temperature and lamp intensity further accelerate dye degradation. The degradation rate followed first order kinetics with respect to dye concentration, with the rate constant decreasing as dye concentration increases at constant amount of zinc oxide. The use of zinc oxide provided a simple and efficient method for photocatalytic degradation of azo dyes in wastewater. However, further studies are needed to be done identifying the degradation products and the corresponding toxicity before they can be adopted for upscale industrial textile wastewater treatments. The kinetics of the reaction with respect to ZnO loading should also be determined for complete evaluation of degradation rate and dependence on concentration of dye and photocatalyst.

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