

A Brief Note on the Temperature-Dependent Photocatalytic Degradation of Congo Red Using Zinc Oxide

Jacob White*, Whitney Smith

Chemistry Department, University of Rio Grande, Rio Grande, USA

*Corresponding author: jwhite@rio.edu

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Abstract Congo red, a conjugated diazo dye which is a derivative of benzidine and naphthionic acid, has experienced commercial success because of its ability to dye cotton easily. The unregulated disposal of textile dyes, such as Congo red, has created a challenge for environmental chemists to determine effective, inexpensive treatment processes for remediating contaminated water. Studies involving semiconductors such as titanium dioxide (TiO₂) and zinc oxide (ZnO) have investigated their affects on wastewaters after being irradiated. However, few reports have described the influence temperature has on such systems. The objective of this study was to briefly characterize, via UV-Visible spectroscopic techniques, the temperature-dependency of the photocatalytic degradation of Congo red using zinc oxide and an inexpensive radiation source. The results indicate that the rate of degradation is catalytically dependent, photo-induced, and potentially temperature dependent with the greatest rate of degradation observed in trials conducted at low (~5°C) temperature. The results may also suggest the prevalence of aggregate dye formation at elevated (~40°C) temperature, although photocatalytic degradation is likely to occur concurrently.

Keywords: Congo red, textile dye, water remediation, water treatment, photocatalysis

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1. Introduction

Congo red, a conjugated diazo dye, first experienced commercial success because of its ability to dye cotton easily. It is a derivative of benzidine and naphthionic acid and it has been used more recently as a histological stain for studies involving amyloid plaques. The unregulated disposal of textile dyes, such as Congo red, has created a challenge for environmental chemists to determine effective, inexpensive treatment processes for remediating contaminated water. Studies involving semiconductors such as titanium dioxide (TiO₂) and zinc oxide (ZnO) have investigated their affects on wastewaters after being irradiated [1-6]. Fine suspensions of such inexpensive semiconductors can be added to wastewaters and irradiated at wavelengths less than approximately 380 nm to cause electron excitation within the semiconductors from the valence band to the conduction band [4,5,6]. A series of subsequent electron transfer steps then ultimately leads to the degradation of the dye. Depending on the method of degradation, proposed mechanisms for the degradation have included the formation of various 'OH-adducts [7] and conserved conjugation [8]. Regardless of their mechanisms, any such treatment processes aim to convert non-biodegradable pollutants into biodegradable species through inexpensive remediation efforts. Studies

have demonstrated the ability of zinc oxide to remediate water contaminated with Congo red through this photocatalytic process, and that this process is both pH-dependent and concentration-dependent [3]. Because of these properties, such photocatalytic mechanisms have been deemed both effective and inexpensive. However, reports illustrating any temperature-dependent characteristics of the photocatalytic degradation are limited. If temperature dependence exists, efforts to control the temperature of contaminated water may render a remediation effort cost-prohibitive.

The objective of this study was to briefly characterize any temperature-dependency of the photocatalytic degradation of Congo red using zinc oxide via UV-visible spectroscopic techniques using a practical and inexpensive irradiation source. This may be the first such report detailing the influence of temperature on the photocatalytic degradation of Congo red using zinc oxide.

2. Materials and Methods

Three separate trials were conducted to characterize the process at below ambient temperature (~5°C), at ambient temperature (~25°C), and above ambient temperature (~40°C). A 1.0 L solution of 25 ppm Congo red (TCI America, USA) was prepared in distilled water for each trial and allowed to stabilize at a controlled temperature in

the absence of irradiation for two days prior to each experiment. For each trial, the solution was then divided in half, with zinc oxide (Fisher Scientific, USA) added to only half (i.e., 500 mL) of the portions to produce a final concentration of 550 ppm. The solutions were then mixed via vortex mixer. Both portions were then divided in half again, resulting in four separate 250 mL solutions that were placed in shallow glass bowls. Two of the 250 mL portions—one with catalyst and one without—were placed in a closed system and maintained in the absence of irradiation for the duration of the experiment. The remaining two portions—one with catalyst and one without—were placed in a separate closed system and irradiated using a previously reported inexpensive radiation source [9]. The two irradiated solutions were placed on a magnetic stirrer directly under the radiation source and stirred continuously in the closed system. The bowls were surrounded in continuously replenished ice water baths for the below ambient temperature trials, and on electric hot plates for above ambient temperature trials, for a total of 4 hours for each trial. A Vernier LabQuest pH probe and temperature probe were placed inside each solution and recorded throughout each experiment at a scan rate of 1 measurement/minute.

Within each temperature trial, a micropipette was used to withdraw 2 mL aliquots from each of the four solutions at 30 minute intervals. The solutions were centrifuged twice to remove suspended semiconductor particles, and then transferred to spectrophotometric cuvettes. A Shimadzu UV-VIS 2550 spectrophotometer was used to measure the absorbance of the solutions at 498 nm, with a decrease in absorbance being correlated with the degradation of the chromophoric structure of Congo red in the vicinity of the azo-linkage [3]. To control for differences in matrix compositions, a blank of distilled water was used in comparison with each uncatalyzed solution, and a blank containing the same concentration of zinc oxide in distilled water was used as a blank in comparison with each catalyzed solution. As a precautionary measure, an infrared thermometer was also used to record the temperature of the solution in the cuvette as it was placed into the spectrophotometer to ensure its temperature had not deviated from the controlled temperature of its irradiation chamber. Four trials were conducted at each of the three controlled temperatures—irradiated trials with and without catalyst, and non-irradiated trials with and without catalyst. The experimental design allowed for determining if the system was catalytically controlled and photo-induced, in addition to being influenced by temperature.

3. Results and Discussion

A baseline kinetics spectrum of the absorbance ($\lambda = 498$ nm) of Congo red in distilled water was first measured immediately after it was prepared. This spectrum demonstrated an increasing absorbance over time, leveling off only after approximately 38 hours. The solutions were therefore initially maintained at a controlled temperature in the absence of irradiation for two days prior to each experiment to allow stabilization of the solutions. For each experiment within each trial, the initial absorbance measurement was used to normalize the results by

dividing subsequent absorbance measurements by its initial value. This allowed for more clearly presenting the data with respect to how the absorbance values changed over time relative to the initial absorbance measurement.

The systems maintained relatively constant temperatures throughout each set of trials. For ambient temperature trials, the average temperature \pm SD throughout the experiments was $24.7^{\circ}\text{C} \pm 0.82^{\circ}\text{C}$. For low temperature trials, the average temperature \pm SD throughout the experiments was $4.67^{\circ}\text{C} \pm 0.40^{\circ}\text{C}$. For elevated temperature trials, the average temperature \pm SD was $38.62^{\circ}\text{C} \pm 1.04^{\circ}\text{C}$.

The results confirmed the photocatalytic properties of the degradation process. Figure 1 shows the normalized absorbance measurements for ambient temperature trials. As shown, the degradation of Congo red by zinc oxide appeared to be both catalytically dependent and photo-induced. When trials were conducted without catalyst or in the absence of radiation, little to no decrease in absorbance was observed. Only in trials simultaneously using both catalyst and irradiation were notable reductions in absorbance observed.

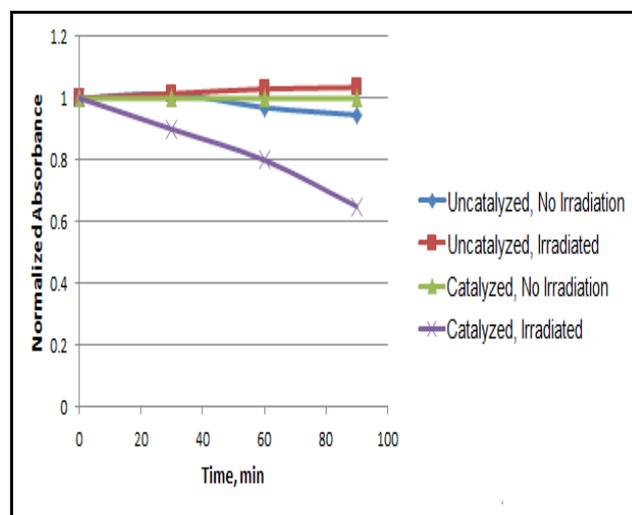


Figure 1. Normalized absorbance measurements for ambient temperature trials. The degradation of Congo red with zinc oxide appeared to be both catalytically dependent and photo-induced

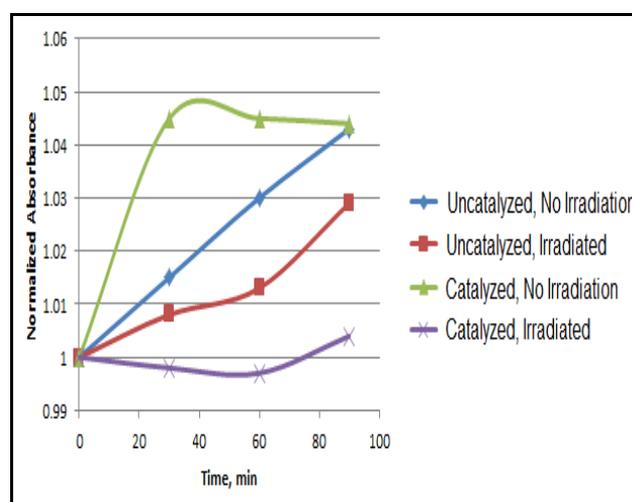


Figure 2. Normalized absorbance measurements for elevated temperature trials. Aggregate dye formation likely resulted in increasing absorbance at an elevated temperature, yet appeared to degrade via photocatalysis

Interestingly, the efficiency of the degradation was observed to be greatest in low temperature trials. By comparison, the process at low temperature reduced the absorbance of the solution by more than twice the amount observed at ambient temperature over the analysis time. Furthermore, the absorbance was observed to increase at high temperature ($\sim 40^{\circ}\text{C}$) for all trials (Figure 2). Congo red dye-semiconductor adsorption equilibrium has been previously shown to require considerably long time periods [8], and these results may be explained by the prevalence of an aggregation phenomenon observed in dye formations [3,11,12]. Although the absorbance was found to increase at high temperatures, it was found to increase the least amount with the presence of the catalyst and irradiation. As such, photocatalytic degradation of the dye was likely concurrent with aggregate formation at the elevated temperature.

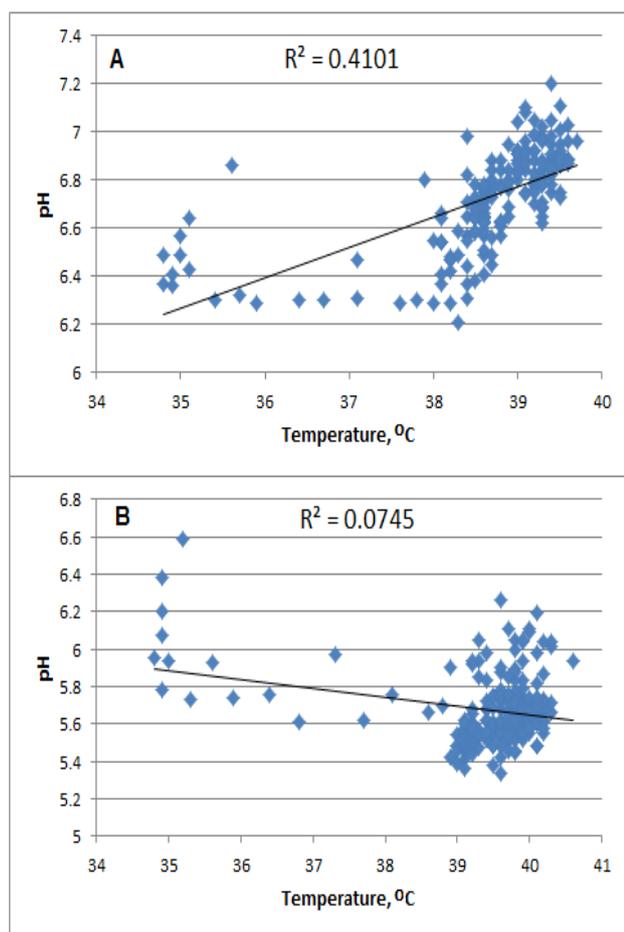


Figure 3. A correlation appeared to exist between pH and temperature for the photocatalytic degradation of Congo red using zinc oxide at an elevated temperature. Figure A shows the correlation observed in the presence of catalyst and irradiation. Figure B shows the lack of correlation observed in the presence of catalyst with no irradiation

Furthermore, the relationship between temperature and pH was also explored. As shown in Figure 3, a correlation appeared to exist between pH and temperature for the photocatalytic degradation of Congo red using zinc oxide at the elevated experimental temperature. A suspected correlation was only observed for photocatalysis at high temperature trials ($\sim 40^{\circ}\text{C}$), with all other trials at ambient and low temperatures yielding linear regression coefficients $R^2 < 0.15$. Figure 3A shows the correlation observed at elevated temperature in the presence of

catalyst and irradiation, while Figure 3B shows the lack of correlation observed at elevated temperature in the presence of catalyst with no irradiation. Based on the positive correlation observed, these results suggest the prevalence of a degradation mechanism which includes the formation of various $\cdot\text{OH}$ -adducts [7] at elevated temperatures.

4. Conclusions

In summary, the results of this study indicate that the rate of degradation of Congo red by zinc oxide is catalytically dependent, photo-induced, and potentially temperature dependent with the greatest rate of degradation observed in trials conducted at low ($\sim 5^{\circ}\text{C}$) temperature. The results also suggest the prevalence of aggregate dye formation at elevated ($\sim 40^{\circ}\text{C}$) temperature, although photocatalytic degradation is likely to occur concurrent with aggregate formation. These results suggest that if photocatalytic degradation of contaminated waters already at lower temperatures may show greater efficiency. Likewise, contaminated waters already at elevated temperatures may not as readily degrade using this remediation strategy. Although first cooling the water may show positive results, this step will also increase the overall cost of the remediation. For treatment efforts in cooler climates, this approach may prove more cost effective.

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Statement of Competing Interests

The authors have no competing interests.

References

- [1] Wang, C. Wang, X., Xu, B. Enhanced Photocatalytic Performance of Nanosized Coupled ZnO/SnO₂ Photocatalysts for Methyl Orange Degradation. *Journal of Photochemistry and Photobiology*. [Online] 2004, Volume 168, Issue 1-2, p47-52.
- [2] Akyol, A. Bayramoglu, M. The Degradation of an Azo Dye in a Batch Slurry Photocatalytic Reactor. *Chemical Engineering and Processing*. [Online] 2008, Volume 47, Issue 12, p2150-2156.
- [3] Movahedi, M., Mahjoub, A.R., Janitabar-Darzi, S. Photodegradation of Congo red in Aqueous Solution on ZnO as an Alternative Catalyst to TiO₂. *Journal of the Iranian Chemical Society*. [Online] 2009, Volume 6, Issue 3, p570-577.
- [4] Ollis, D. Photocatalytic Purification and Remediation of Contaminated Air and Water. *Comptes Rendus de l'Academie des Sciences Series IIC Chemistry*. [Online] 2000, Volume 3, Issue 6, p405-411.
- [5] Chakrabarti, S., Dutta, B. Photocatalytic Degradation of Model Textile Dyes in Wastewater Using ZnO as Semiconductor Catalyst. *Journal of Hazardous Materials*. [Online] 2004, Volume 112, Issue 3, p269-278.
- [6] Valenzuela, M.A., Bosch, P., Jimenez-Becerril, J., Quiroz, O., Paez, A.I. Preparation, Characterization and Photocatalytic Activity of ZnO, Fe₂O₃ and ZnFe₂O₄. *Journal of Photochemistry and Photobiology*. [Online] 2002, Volume 148, Issue 1-3, p177.

- [7] Ma, H., Wang, M., Yang, R., Wang, W., Zhao, J. Shen, Z., Yao, S. Radiation Degradation of Congo Red in Aqueous Solution. *Chemosphere*. 2007, Volume 68, p1098-1104.
- [8] Wojnarovits, L., Palfi, T., Takacs, E., Emmi, S.S., Reactivity Differences of Hydroxyl Radicals and Hydrated Electrons in Destructing Azo Dyes. *Radiat. Phys. Chem.* 2005, Volume 74, 239-246.
- [9] Bumpus, J.A. Remediation of Water Contaminated with an Azo Dye: An Undergraduate Laboratory Experiment. *Journal of Chemical Education*. [Online] 1999, Volume 76, Issue 12, p1680.
- [10] Wahi, R.K., Yu, W.W., Liu, Y., Mejia, M.L., Falkner, J.C., Nolte, W., Colvin, V.L. Photodegradation of Congo Red Catalyzed by Nanosized TiO₂. *Journal of Molecular Catalysis A: Chemical*. 2005, Volume 242, p48-56.
- [11] Habibi, M.H., Hassanzadeh, A., Zeini-Isfahani, A. Effect of Dye Aggregation and Azohydroneautomerism on the Photocatalytic Degradation of Solophenyl Red 3BL Azo Dye Using Aqueous TiO₂ Suspension. *Dyes and Pigments*. 2006, Volume 69, p111-117.
- [12] Hihara, T., Okada, Y., Morita, Z. Photo-Oxidation and -Reduction of Vat Dyes on Water-Swollen Cellulose and Their Lightfastness on Dry Cellulose. *Dyes and Pigments*. 2002, Volume 53, p153-177.