

Photocatalytic Mineralization of Chlorazol Black E (Direct Black 38) over Zeolite-Supported Titania-Based Catalysts

Desiree A Young¹, Abdul K Mohammed², Shawn K Blue³ and Kenneth L Roberts^{4,*}

¹Refineries Additives, Oil & Gas Division, Johnson Matthey Process Technologies Inc., Savannah, GA 31408, USA

²Department of Chemistry, North Carolina Central University, Durham, NC 27707, USA

³U.S. Food and Drug Administration, Center for Drug Evaluation and Research, Silver Spring, MD 20993, USA

⁴Department of Chemical Engineering, King Faisal University, Al Ahsa, Kingdom of Saudi Arabia

*Corresponding author: Kenneth L Roberts, Department of Chemical Engineering, King Faisal University, Al Hofuf, Al Ahsa, Kingdom of Saudi Arabia, 31982; Tel: +9660135895403; Fax: +9660135817068; E-mail: kroberts@kfu.edu.sa

Received Date: November 05, 2014 Accepted Date: December 08, 2014 Published Date: December 08, 2014

Citation: Desiree A Young, et al. (2014) Photocatalytic Mineralization of Chlorazol Black E (Direct Black 38) over Zeolite-Supported Titania-Based Catalysts. J Chem Proc Eng 1: 1-7

Abstract

The reactivity of a TiO₂ / zeolite-Y photocatalyst was investigated for the assisted photodegradation of Chlorazol Black E (Direct Black 38). This work is the first report of the utilization of a zeolite-Y supported TiO₂ catalyst for the photocatalytic demineralization and full kinetic characterization of Chlorazol Black E (Direct Black 38) dye. Reaction species formed after complete dye mineralization were identified using spectroscopic and conductivity measurements. Because complete mineralization requires prolonged irradiation, which in turn causes a barrier for the application of photocatalytic degradation in wastewater treatment, this investigation involved the “optimal” reaction conditions for TiO₂ photodegradation. To define these conditions, dye concentration, pH of dye solution, conductivity and temperature during photodegradation were utilized in this study.

Keywords: Photocatalysis; Dye degradation; Chlorazol E; Direct black 38; Titania; Zeolite Y; Zeolite Y supported titania

Background

Commercial dyes make up the palette that is used to color our world. Synthetic dyes have a strong resistance to fading while simultaneously providing an array of bright colors in the modern textile products. Guidelines and regulations for proper disposal and treatment have become stricter in order to protect the environment and human health. Because of this fact, dye manufacturers have become more interested in developing effective methods to remediate synthetic dyes. The toxicity of these synthetic dyes has led to increased research for improved treatment and disposal of textile dye effluents [1]. If wastewater effluents are not completely decolorized prior to discharge, the burden of treatment falls upon publicly owned water treatment facilities. Once in a publicly owned water treatment facility, wastewater effluent will end up in sludges. These sludges are dewatered and then deposited into landfills. Benzidine, a precursor in the synthesis of most azo dyes, is a known carcinogen. Although benzidine is no longer manufactured in the United States, benzidine-based azo dyes are still imported and used commercially. Be-

cause of the carcinogenic nature of these organic pollutants, they pose a specific threat to the environment if they are not disposed of and treated properly.

Presently, there are a variety of nondestructive methods for treating industrial wastewaters [2]. Filtration using granulated active carbon (GAC) or chemical coagulation has mainly been used to treat dye waste. Additionally, ultra filtration, air stripping, carbon adsorption, extraction, incineration, and oxidation via ozonation or hydrogen peroxide have been used for the azo dye remediation process. However feasible, these methods present several disadvantages, which include transference of the contaminant from a liquid phase to a solid phase that requires subsequent treatment. Owing to the stability of these dyes against biological degradation, biodegradation has not been deemed as advantageous for these compounds.

Alternative approaches are under investigation for the treatment of dye wastewaters. Nondegradative processes have been almost completely replaced by degradative processes. These degradative processes can be referred to as advanced oxidation processes (AOP). AOPs are associated with the aqueous phase production of the hydroxyl radicals that result in the destruction of the target pollutant. Photocatalytic

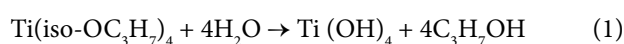
processes are included in this class of water purification technology. Reported advantages of these methods include being able to be carried out under low ambient temperatures, no expensive oxidant or catalyst requirements, UV activation and usually complete mineralization can be achieved [3-4].

In this work, a zeolite Y-supported TiO₂ catalyst was synthesized and characterized for the photocatalytic degradation of Chlorazol E (Direct Black 38) dye. Previous work has investigated the photocatalytic remediation of Direct Black 38 dye contained within tannery wastewater [5]. Work that is more recent has examined N-doped TiO₂ for the photocatalytic degradation of Direct Black 38 dye [6]. This will be the first investigation reported of a zeolite Y-supported TiO₂ photocatalyst for the demineralization of Chlorazol E (Direct Black 38) synthetic azo dye.

Materials and Methods

Chlorazol Black E (Direct Black 38) in Figure 1, used commercially in printing, and dyeing leathers, at an approximate 50% dye content, was obtained from Sigma-Aldrich Chemical Company. Titania (IV) oxide, anatase powder (99.8%), Titanium (IV) isopropoxide (99.99%), and Molecular Sieve Na-Y zeolite were also all obtained from Sigma-Aldrich Chemical Company. The materials were used without additional purification.

The procedure used in the synthesis of the zeolite supported TiO₂ has been reported previously for the photocatalytic degradation performance of photocatalyst TiO₂ supported on 13-X, Na-Y, 4A zeolites with different loading content was evaluated using the photocatalytic oxidation of dyes Direct Fast Scarlet 4BS and Acid Red 3B in aqueous medium [7]. The titania hydrolysis reaction of this procedure is given in the following equation:



The TiO₂ sol was synthesized by a method called acid-catalyzed sol-gel formation. The reactant composition started with 7.4mL of titanium (IV) isopropoxide (TTIP) and 20mL of HNO₃. The TTIP was added drop wise to the solution of HNO₃ acid with continuous stirring. The solution was stirred for an hour and a transparent TiO₂ sol was formed. The pH of the titania colloidal solution was adjusted to 2.5 with the addition of 1M NaOH to avoid a reaction between the acid and the zeolite. This reaction could cause the zeolite to become unstable and decompose.

About 5g of the Na-Y molecular sieve zeolite was mixed with about 30mL of distilled water for about half an hour. Next,

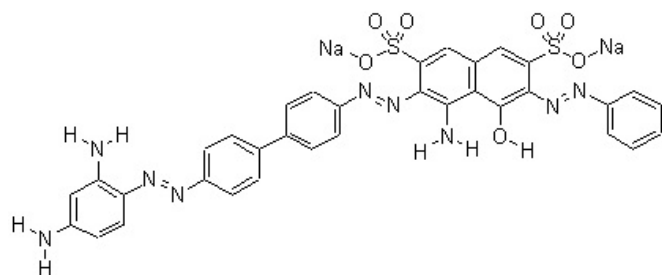


Figure 1: Chlorazol E (Direct Black 38) Dye Molecular Structure

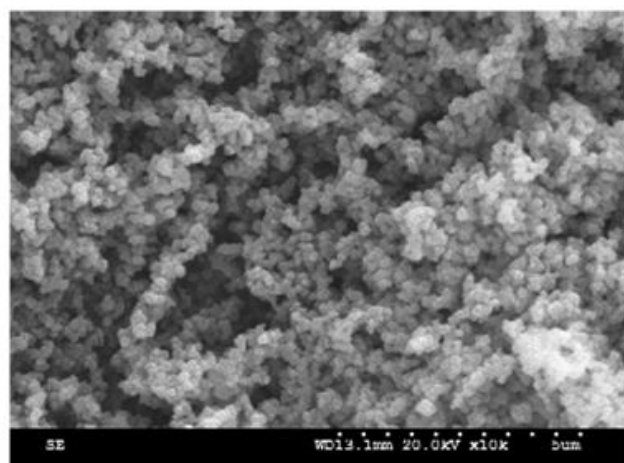
about 5 mL of the TiO₂ sol was added to the zeolite mixture followed by stirring for about an hour. The pH of supernatant of the solution was adjusted to approximate value of 6. The mixture was subsequently dried in a pressurized vacuum oven for thirty minutes and then calcinated at 300°C for approximately 2-3 hours. The product was later cooled under desiccation, ground into powder and stored under desiccation away from direct light. Three zeolite-Y supported TiO₂ samples were used in aqueous mixtures of the azo dye and the measurements were repeated with each sample to confirm reproducibility of the kinetic data.

Results and Discussion

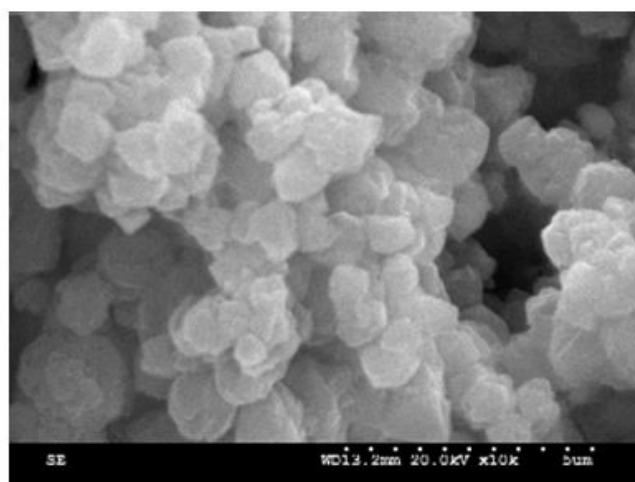
XRD data of the TiO₂ supported on zeolite-Y was obtained using a Bruker D8 ADVANCE Series-2 X-ray diffractometer (Bruker AXS) equipped with a CuK α radiation source ($\lambda = 1.54\text{\AA}$). The characteristic diffraction pattern for anatase TiO₂ was observed with a reflection pattern at $dA = 3.57$ ($2\theta = 24.9^\circ$). The XRD reflection pattern for the (101) crystal plane of anatase TiO₂ has been reported to be $dA = 3.52$ ($2\theta = 25.3^\circ$) [7-8]. The Scherrer Equation was utilized to estimate mean titania nanoparticle sizes supported on zeolite-Y from the x-ray diffraction data:

$$d_{hkl} = 0.9 \lambda / B \cos \Theta \quad (2)$$

where d_{hkl} is the estimated particle size, λ is the wavelength of the XRD source, B is the broadening of the diffraction line at full width at half maximum (FWHM), and Θ is the diffraction angle. Using Scherrer analysis from the diffraction data, an estimated TiO₂ nanoparticle size within the zeolite-Y matrix was determined to be 14.6 nm within experimental agreement with previous work [7-8]. Ramaswamy and coworkers reported results for anatase TiO₂ sol gel synthesized ultrasonically from titanium ethoxide in an ethanol/acetic acid solution [7]. The resulting titania sol gel, with a reported nanoparticle size range from 8 to 30nm at 573K from BET, XRD and TEM analysis, was dried for 24 hours in air at 373 K and subsequently calcinated for 3 hours in air at temperatures from 473 to 873K. Gao and coworkers also reported similar results for nanocrystalline anatase TiO₂ prepared by means of TiCl₄ hydrolysis mixed with a (NH₄)₂SO₄ solution and later treated with a 2.5M dilute NH₄OH At 70°C [8]. The resulting anatase titania materials, with a reported nanoparticle size range from 4.0 to 6.8nm from calcination temperatures from 383 to 673K, were dried in air at 110°C and calcined in air at temperatures from 383 to 973K for 2 hours. For 20 weight % TiO₂ supported on zeolite Y photocatalyst calcined at 573K, a titania nanoparticle size of 7.6nm was reported by Wang and coworkers [9]. As the calcination temperatures increased for the TiO₂ / zeolite-Y photocatalyst, the nanoparticle sizes increased by approximately a factor of five to 35.9nm at 973K. For ion-exchanged prepared TiO₂ photocatalysts within a zeolite-Y matrix, the crystallinity of zeolite-Y has been reported to not be adversely affected by the presence of TiO₂, even within the pores and cavities of the zeolite [10]. Zhu and coworkers reported that XRD reflection pattern of TiO₂/Na-Y catalyst is complicated by the x-ray diffractometric analysis of the supports in this case it would be the zeolite [11].



(a)

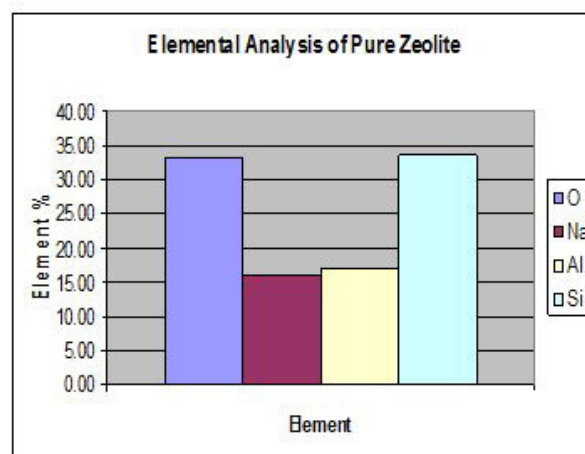


(b)

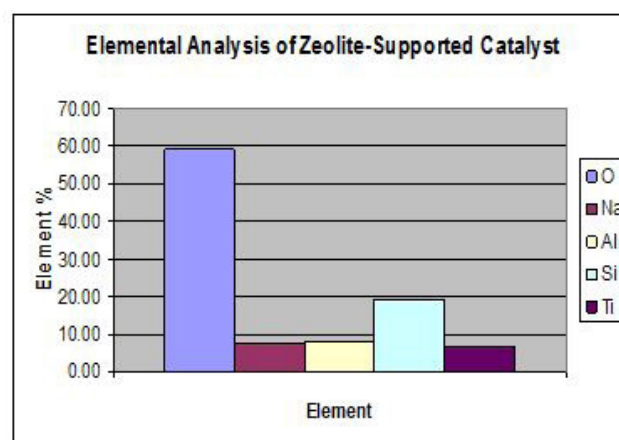
Figure 2: SEM images of (a) TiO_2 and (b) Zeolite Y-Supported TiO_2 . Elemental analysis was performed on zeolite-Y and the zeolite-Y supported TiO_2 . Figure 2(a) illustrates the element percentages for the pure Na-Y zeolite. Pure zeolite has the following composition: silicon (33.65%), aluminum (16.94%), sodium (16.12%) and oxygen (33.24%). Figure 2(b) illustrates the element percentages for the synthesized Zeolite-Y supported TiO_2 catalyst. It is shown that the percentages of Na, Al, and Si decrease. The synthesized catalyst was also shown to be composed of 59.30% oxygen and 6.69% titanium in addition to 7.34% Na, 7.76% Al, and 18.91% Si.

SEM images of the unsupported TiO_2 and the zeolite-Y supported TiO_2 are shown Figures 3(a) and 3(b). The titania material produced as shown in Figure 3(a) possessed a crystalline powder. In Figure 3(b), the Zeolite-Y supported TiO_2 was observed to retain the overall physical structure of the Na-Y zeolite as has been reported in the literature [9-11].

To produce a 2.0×10^{-5} M solution of Chlorazole Black E, the volume of the volumetric flask, the molecular weight of the complex, and the desired molarity must all be known. The molecular weight of the dye is 781.7g/mol, and the mass required to dissolve in 1L of distilled water to obtain the desired molarity was gathered using this information. 0.0158g of the dye was measured and dissolved into one liter of distilled water to make a 2.0×10^{-5} M solution. This concentration was also equivalent to about 16ppm and could be used interchangeably.



(a)



(b)

Figure 3: Elemental Analysis of (a) Na-Y Zeolite and (b) Zeolite Y-Supported TiO_2

This concentration represented the dye concentration studied in this project. The characteristic dye concentrations in wastewater from the textile industry are in the range from 0.01g/L to 0.05g/L, or 10 to 50ppm. The base concentration of 2.0×10^{-5} was investigated. Dilutions from the stock solution were formulated to produce a calibration curve of different concentrations at a specified wavelength. The wavelength that was investigated for this dye was 533nm.

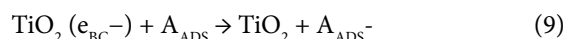
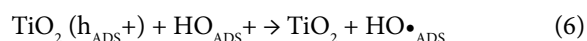
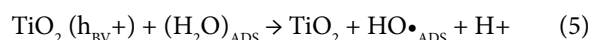
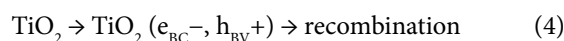
Using Beer's Law, the concentrations of each solution from a calibration curve of known concentrations could be determined. Beer's Law states that the absorbance of a sample is directly proportional to the concentration of the absorbing species.

$$A = \epsilon bc \quad (3)$$

Where A is absorbance and is dimensionless, c is the concentration and is measured in moles per liter, b is the path length and is usually measured in centimeters, and ϵ epsilon is the molar absorptivity and has the units $\text{M}^{-1}\text{cm}^{-1}$. The light absorbance at the wavelength of an estimated maximum absorbance, $\lambda_{\text{max}} = 533\text{nm}$ is proportional to the concentration of the color. This phenomenon suggests that the aqueous dye solution obey Beer's Law. The slope of the line was given as the estimated molar absorptivity (ϵ). Calibration curves were also prepared

for the purposes of calculating the concentrations of the solutions at pH 2, 6, and 11.

The general form of the proposed mechanism for the photodegradation of Direct Black 38 azo dye has been reportedly expressed using the equations below [12]:



where the following photocatalytic reaction species are defined as Conduction-Band Electrons (e_{BC}^-), Valence-Band Holes (h_{BV}^+), Hydroxyl Anion ($\text{HO}\cdot$), Hydronium Cation (H^+), Adsorbed Species (ADS), Electron Acceptor Species (A), and Donor Electron Species (D).

About 70 mg of catalyst was added to 100mL of 2×10^{-5} M dye solution under constant stirring until a well distributed mixture of the catalyst particles was observed in the reactor vessel. The reactor was a quartz 250mL Florence flask with a magnetic stirrer. Under constant mixing, the sample was subsequently irradiated using a LPS251SR Spectral Energy Hg lamp with a current setting of 1.0 ampere and 26 volts. Approximately 4mL samples were pipetted from the mixture at predetermined time intervals and later centrifuged for approximately 20 minutes. The supernatant was again separated and later centrifuged for approximately 20 minutes or more if needed. Finally the concentration of the dye was determined using UV-VIS Spectrophotometry. The absorbance of each sample was recorded as a way to monitor the concentration during the degradation. All three solutions, pH 2, pH 6, and pH 11 were analyzed in the same manner in order to determine the final dye concentration at varying pH levels. Each data point was repeated three times to confirm the reproducibility of the results.

The pH of the dye solution was adjusted from 2 to 11. The initial pH of the solution was approximately 6.8. The acidic pH (pH 2) was achieved by adding 1M HNO_3 . The basic pH (pH 11) was adjusted by adding 1M NaOH drop wise. The pH of the solution was monitored with the help of a pH-30 Corning pH meter. The dye degradation of the solution was monitored at different temperatures ranging from 33 to 66°C degrees. Samples were taken at 30-60 minute time intervals to determine the dye concentration at a specific time. The absorbances of the samples were compared with a calibration curve of known concentrations from which the concentrations of the dye solutions were determined. The effect of the starting dye concentration on the degradation of the dye was also investigated. At a constant temperature, the different dye concentrations were degraded to see how the concentration affects the rate of degradation and this procedure was also repeated three times to confirm the reproducibility of the results.

The chemical oxygen demand (COD) was used to measure the oxygen equivalent of the organic matter content of a sample

that is susceptible to oxidation by a strong chemical oxidant. Standard Methods 5220D Closed Reflux was used to analyze the COD of the dye at the varying pHs. Mercury free reagent vials were obtained from CHEMetrics environmental testing supply company. About 2.5mL of the treated sample was taken and added to ampoules that were pre-mixed by CHEMetrics with a solution of Potassium Dichromate digestion solution. It was then digested for three hours at a temperature of 115°C. After the samples cooled, the absorbance reading was measured at 660nm using Spectronic 20 spectrophotometer the overall procedure was repeated overall three times to confirm the reproducibility of the results. The absorbance readings were compared with a concentration table provided by CHEMetrics.

The conductivity (k) is a measure of the ability of an aqueous solution to carry an electric current. This conductive ability depends on the presence of ions; their total concentration, mobility and valence. The conductance measurement was also temperature dependent. The conductance reading was taken at room temperature (25°C). Inorganic compound solutions are relatively good conductors and molecules of organic compounds are generally poor current conductors. The conductivity was taken directly using YSI 3100 conductivity instrument and this procedure was also repeated three times overall to confirm reproducibility. The conductivity was used to identify the ion species resulting from dye mineralization.

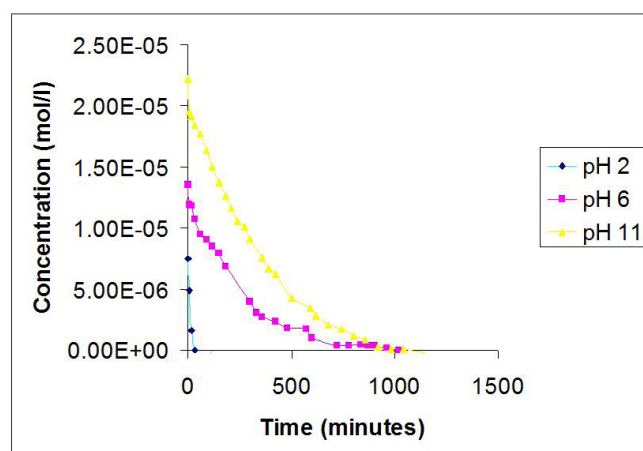


Figure 4: Chlorazol E Dye Degradation Profiles at pH 2, 6, and 11.

At varying pH levels, the degradation of a 2.05×10^{-5} M solution of Direct Black 38 over supported TiO_2 was examined as shown below in Figure 4. The degradation of the dye solution was observed to be pH dependent. In an acidic environment, the dye appeared to quickly adsorb onto the surface of the catalyst and the decomposition of the dye was very fast. Grzechulska and Morawski reported that dyes that have a sulfonic group have a negative charge [12]. This group also reported that the efficiency of the photocatalytic process was dependent upon the pH of the reaction solution. Grzechulska and Morawski observed that acidic solution favors adsorption of the dye onto the surface of the photocatalyst. The lowering the pH of the dye solution increases the positive charge of the TiO_2 and therefore promotes the adsorption of the dye to the surface of TiO_2 and therefore degradation is accelerated [4]. Figure 4 illustrates that as the pH increases the degradation in-

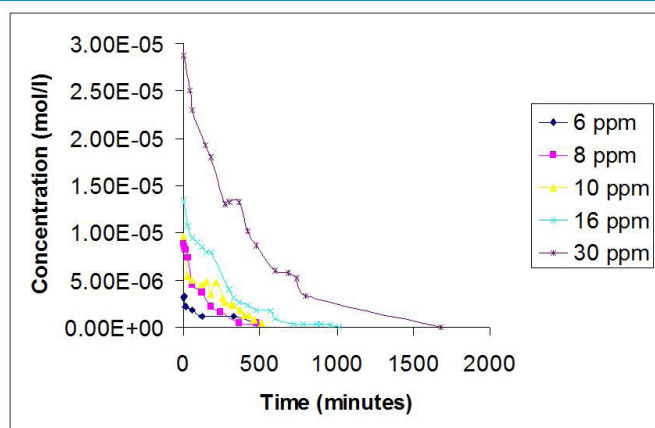


Figure 5: Chlorazol E Dye Degradation Profiles at Concentrations from 6 to 30ppm.

creases. With the addition of NaOH, the dye transformed from a deep purple color to a very intense dark blue color.

The effect of the dye concentration on the degradation was also examined and the results are provided in Figure 5. Dye concentrations ranging from 50mg/l to 10mg/l were tested as is characteristic of dye effluents found in the environment [12]. Figure 5 indicates that as the concentration of the dye increases the time for degradation increases as well. Similar observations have been reported for the decomposition of Acid Black 1 [12]. These reported observations have been attributed to the formation of several layers of adsorbed dye onto the catalyst surface, which is higher at higher dye concentrations. With the extra accumulation of the dye adsorbed on the surface of the catalyst and the reaction of the dye molecules with photogenerated hydroxyl radicals is expected to be inhibited [5]. Increasing dye concentration was observed to promote the adsorption of light by the dye molecules. This result can be explained as a result of the increases sensitivity of the dye molecules instead of the photocatalyst, which inhibit photons from reaching the photocatalyst surface.

The effect of temperature on the degradation of azo dyes was also examined for the Direct Black 38 system and was not observed to affect dye degradation [12]. The kinetic data in Figure 6 indicates this result. Some investigations have observed decreases in photocatalytic degradation of organics with increasing temperature due to increases the recombination of charge carriers and also the desorption process of adsorbed reactant species in accordance with the Arrhenius equation [13].

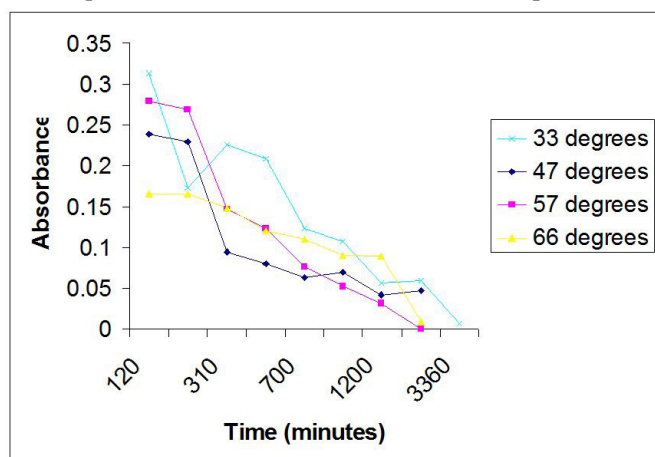


Figure 6: Chlorazol E Dye Degradation Profiles from 30 to 70°C.

pH	Before Treatment	After Treatment
2	16 mg/l	20 mg/l
6	18.5 mg/l	10 mg/l
11	13.8mg/l	10.8 mg/l

Table 1: COD Measurements for Dye Solutions at pH 2,6, and 11 Before and After Chlorazol E Degradation.

Chemical oxygen demand was used to measure the oxygen equivalent of the organic content in a sample that is susceptible to oxidation by a strong oxidant under acidic conditions. COD is a test that is widely used to measure the pollution associated with both biodegradable and non-biodegradable organic matter present in wastewaters. Table 1 illustrates the COD concentration of the dye solution at different pH levels. There was an observed decline in concentration for pH 6 and 11. For the acidic pH, there was a slight increase in the COD concentration. The COD concentration was measured from samples taken before and after photocatalytic degradation treatment as shown in Table 2. The decrease in COD concentration is much slower than the decolorization. Kiriakidou and coworkers also observed the same result in the photocatalytic degradation of Acid Orange 7 [14]. The group suggested this might be due to the formation of smaller intermediates. In order to achieve complete breakdown of these smaller organic compounds, longer irradiation time is required. Kiriakidou's group also noted in the photocatalytic degradation of Acid Orange 7 the intermediates formed are biodegradable and biological methods can be used in combination with photocatalytic processes to completely mineralize the dye [14]. This may be the case with the dye that was investigated in this study. Chun and coworkers also observed the same result in the photocatalytic degradation of azo dyes and textile wool wastewater [15]. They reported that after 30 minutes of treatment, there was complete decolorization of the wastewater but only a 44.78% reduction in the COD concentration. Chun's group added that the decolorization of a dye or wastewater enhances the biodegradability and therefore could be further treated biologically. This would actually improve or decrease the photocatalytic treatment time and would be more practical for an actual wastewater treatment plant.

The conductance of the degraded dye solution was measured to help verify mineralization of the dye solution. In theory, as the dye degrades, it will break down into ions. As the dye solution decomposes, the concentration of ions should increase as well. Because ions carry an electrical charge, these species can be detected by measuring the conductance of the dye solutions before and after treatment.

The evolution of sulfate, nitrate, and ammonium ions were chosen to facilitate in verifying complete degradation. The release of sulfate ions can be accounted for by an initial attack by a photo-induced OH radical [16]. The stoichiometric equation

pH	Before Degradation	After Degradation
2	52.36mS/cm	3309mS/cm
6	16.31mS/cm	288mS/cm
11	4427mS/cm	170mS/cm

Table 2: Conductivity Measurement of Dye Solutions at pH 2, 6, 11; Before and After Chlorazol E Degradation

of the complete oxidation of Congo Red was reported by Lachheb and coworkers [16]. The following equation was given:



Congo Red is a diazo dye and also exhibits similarities in molecular structure with Direct Black 38. Congo Red dye possesses two sulfur atoms in its molecular structure. Lachheb and coworkers reported that the sulfur containing dyes did not release the expected stoichiometric quantities of sulfate. Based on this observation, Lachheb's group suggested that the results observed may have been influenced by partially adsorbed sulfate ions at the surface of titania. Vautier et al. also observed this effect in an earlier study [17]. For the purpose of this research, only a qualitative analysis of sulfate ions was attempted. 1M solution of BaSO₄ was added drop wise to solutions after treatment. Due to the insolubility of sulfate in the BaSO₄ solution, a white precipitate should be observed. However, this was not observed. In control experiments of solutions with high sulfate ion concentration, a precipitate was observed. Based on these observations, the sulfate ion concentration was assumed to be beyond the lower limits of detection as a product of the mineralization reaction.

A linear correlation was determined by graphing the log of the dye concentration as a function of time. These kinetic analysis results are shown in Figure 7. The photodegradation of Direct Black 38 dye followed first order kinetics. First order kinetics have also been observed in previous studies of photocatalytic degradation of dyes as well from previous reports [16–18]. Table 3 shows the reaction rate constant values determined for the photodegradation kinetics of Chlorazol E at various initial dye concentrations and initial solution pH.

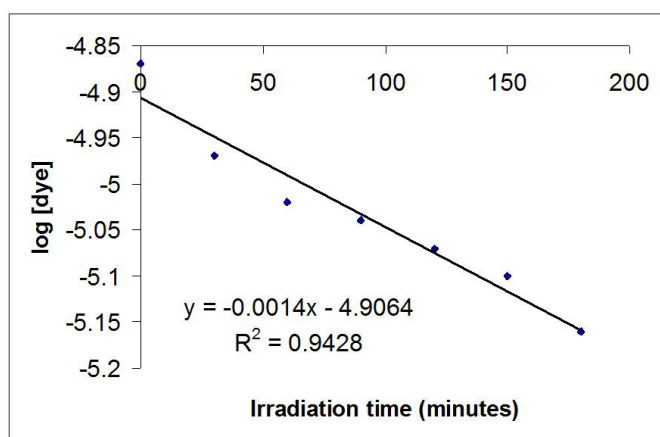


Figure 7: Semi log Plot of Chlorazol E Dye Concentration (ppm) with Time (minutes).

Initial concentration	k (min ⁻¹)	R ²
10 ppm	0.0023	0.8572
16 ppm	0.0018	0.9789
30 ppm	0.001	0.9592
Initial pH	k (min ⁻¹)	r ²
pH 6	0.0014	0.9428
pH 11	0.0013	0.9947

Table 3: Kinetics of Chlorazol E Photodegradation at Different Concentrations and pH.

Conclusions

The photocatalytic degradation of Direct Black 38 (Chlorazol Black E) azo dye over zeolite Y-supported TiO₂ was achieved. This is the first reported photodegradation of Chlorazol Black E dye using a TiO₂/zeolite Y catalyst. The pH of the dye solutions plays a very significant role in the zeolite Y-supported TiO₂-assisted photocatalytic degradation of organic pollutant. In the degradation of Direct Black 38, an acidic solution enhances the decolorization of the dye solution. As indicated by the results, complete decolorization is observed after about 30 minutes of irradiation. This rapid decolorization could be due to the surface properties of the TiO₂ and the zeolite. There are strong electrostatic attractions between the TiO₂/alumina and the anionic dye species. Titania and alumina are both amphoteric. There are strong electrostatic attractions between the TiO₂/alumina and anionic dye causing strong adsorption to the catalyst surface at pH levels below the point of zero charge <6.8 for TiO₂ and 9.1 for alumina. This in turn results in a rapid decolorization. The same can be assumed to occur with the interaction between the dye and the TiO₂/zeolite Y that was used in this study. One component of the zeolite is alumina. Decolorization occurs more slowly at pH levels near or above the point of zero charge for the photocatalyst system. After about 20 hours at pH 11 and about 17 hours for the initial pH of the dye solution which around 6.8, complete decolorization occurred. This could be due the negative charges that are acquired on the surface of the photocatalyst. Electrostatic repulsion and decolorization will occur at a slower rate than in an acidic environment due to the negative charges.

The photocatalytic degradation of the dye is affected by the concentration of the initial dye solution. This could be due to the capacity of high concentrations to be sensitized instead of the catalyst. Layers form on the surface of the photocatalyst at high dye concentrations; as a result, the adequate photons necessary for excitation cannot reach the photocatalyst surface. The temperature of the dye solution did not have a significant effect on the degradation of the dye.

COD measurements were used to analyze the degree of degradation of the dye. The results show that complete mineralization of the dye is occurs more slowly than the decolorization of the dye. This effect is observed due to the formation of intermediates. Conductivity measurements confirmed the presence of these ions in solution. Further research is required to identify these product ion species. Finally, the kinetics of the photocatalytic degradation were observed to follow first order rate kinetics.

Acknowledgements

The authors would like to thank the National Science Foundation Science and Technology Center for Environmentally Responsibly Solvents and Processes (CHE-9876674), the National Institutes of Health-BRIDGE Program, National Science Foundation Science and Technology Center for Advanced Materials and Smart Structures at North Carolina A&T, the Departments of Chemistry and Chemical Engineering at NC A&T, and the College of Engineering and Department of Chemical Engineering at King Faisal University for their support.

References

- 1) Sun J, Qiao L, Sun S, Wang G (2008) Photocatalytic degradation of Orange G on nitrogen-doped TiO₂ catalysts under visible light and sunlight irradiation. *J Hazard Mater* 155: 312-319.
- 2) Khin MM, Nair AS, Babu VJ, Murugan R, Seeram Ramakrishna S (2012) A review on nanomaterials for environmental remediation. *Energy Environ Sci* 5: 8075-8109.
- 3) Pelaez M, Nolan NT, Pillai SC, Seery MK, Falaras P, et al. (2012) A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl Catal B* 125: 331-349.
- 4) Akpan UG, Hameed BH (2009) Parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts: A review. *J Hazard Mater* 170: 520-529.
- 5) Sauer TP, Casaril L, Oberziner AL, José HJ, Moreira Rde F (2006) Advanced oxidation processes applied to tannery wastewater containing Direct Black 38--elimination and degradation kinetics. *J Hazard Mater* 135: 274-279.
- 6) Collazzo GC, Foletto EL, Jahn SL, Villetti MA (2012) Degradation of Direct Black 38 dye under visible light and sunlight irradiation by N-doped anatase TiO₂ as photocatalyst. *J Environ Manage* 98: 107-111.
- 7) Awati PS, Awate SV, Shah PP, Ramaswamy V (2003) Photocatalytic decomposition of methylene blue using nanocrystalline anatase titania prepared by ultrasonic technique. *Catal Commun* 4: 393-400.
- 8) Zhang Q, Gao L, Guo J (2000) Effects of calcination on the photocatalytic properties of nanosized TiO₂ powders prepared by TiCl₄ hydrolysis. *Appl Catal B* 26: 207-215.
- 9) Wang C-C, Lee C-K, Lyu M-D, Juang, L-C (2008) Photocatalytic degradation of C.I. Basic Violet 10 using TiO₂ catalysts supported by Y zeolite: An investigation of the effects of operational parameters. *Dyes Pigm* 76: 817-824.
- 10) Anandan S, Yoon M (2003) Photocatalytic activities of the nanosized TiO₂-supported Y-zeolites. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 4: 5-18.
- 11) Zhu C, Wang L, Kong L, Yang X, Wang L, et al. (2000) Photocatalytic degradation of AZO dyes by supported TiO₂ + UV in aqueous solution. *Chemosphere* 41: 303-309.
- 12) Grzechulska J, Morawski A (2002) Photocatalytic decomposition of Azo Black 1 in Water over Modified Titanium Dioxide. *Appl Catal B* 36: 45-51.
- 13) Rauf MA, Ashraf SS (2009) Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution. *Chem Eng J* 151: 10-18.
- 14) Kiriakidou F, Kondarides DI, Verykio XE (1999) The effect of operational parameters and TiO₂-doping on the photocatalytic degradation of Azo Dyes. *Catal Today* 54: 1-7.
- 15) Chun H, Yizhong W, Hongxio T (2001) Preparation and characterization of surface bond-conjugated tio₂-sio₂ and photocatalysis for azo dyes. *Appl Catal B* 30: 277-285.
- 16) Lacheb H, Puzenta E, Houas A, Ksibi M, Elaloui E, et al. (2002) Photocatalytic degradation of various types of dyes (alizarin s. crocein orange g, methyl red, /congo red, methylene /blue) in water by uv-irradiated titania. *Appl Catal B* 39: 75-90.
- 17) Vautier M, Guillard C, Herrmann JM (2002) Photocatalytic degradation of dyes in water: case study of indigo and of indigo carmine. *J Catal* 201: 45-59.
- 18) Tang W, An H (1995) Photocatalytic degradation kinetics and mechanism of acid blue 40 by tio₂/uv in aqueous solution. *Chemosphere* 31: 4171-4183.

Submit your manuscript to a JScholar journal and benefit from:

- ¶ Convenient online submission
- ¶ Rigorous peer review
- ¶ Immediate publication on acceptance
- ¶ Open access: articles freely available online
- ¶ High visibility within the field
- ¶ Better discount for your subsequent articles

Submit your manuscript at
<http://www.jscholaronline.org/submit-manuscript.php>