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Discoloration and degradation of azo dyes by nanoscale iron particles

Shun Yi Chen
Lehigh University

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Discoloration and Degradation of Azo Dyes by Nanoscale Iron Particles

January 2005
Discoloration and Degradation of Azo Dyes by Nanoscale Iron Particles

by

Shun-Yi Chen

A Thesis
Presented to the Graduate and Research Committee
_of Lehigh University
in Candidacy for the Degree of
Master of Science
in
Civil and Environmental Engineering

Lehigh University

January, 2005
This thesis is accepted and approved in partial fulfillment of the requirements for

the Master of Science

December 14th 2004
Date

Thesis Advisor

Chairperson of Department
Acknowledgements

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"Never worry about anything, but in every situation let your petitions be made known to God in prayers and requests, with thanksgiving. Then God's peace, which goes far beyond anything we can imagine, will guard your hearts and minds in Christ Jesus."
--- Philippians 4:6-7
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Abstract

The reduction of azo dyes by nanoscale zero-valent iron particles (Fe\textsuperscript{0}) at specific pH values of 3, 7, and 9 was investigated in anaerobic batch systems. A higher reaction rate is shown at a lower pH value. In comparison to microscale iron particles, this study showed removal rates of Orange II, Chrysoidine, and Tropaeolin O are 8.0, 8.7, 57.0 times higher, respectively. All of the three azo dyes tested corresponded to pseudo-first-order reaction. In the degradation mechanisms of Chrysoidine in nanoscale Fe\textsuperscript{0}- Systems, it consists of a two-step reaction with the first step reversible. The following relationship for removal efficiency was devised on the kinetics of azo dyes:

\[ k_{\text{Chrysoidine}} (1.6510) > k_{\text{Orange II}} (0.240) > k_{\text{Tropaeolin O}} (0.185) \]
1. Introduction

Every year, there are more than $7 \times 10^5$ tons in quantities of azo dyes used in textile and dyestuff industries (Zollinger et al.). Approximately, during the manufacturing and processing operations, there are 12% of synthetic textile dye used losing to waste streams and 20% of these losses will enter the environment by effluents from water treatment plants (Tan et al.). Furthermore, due to the design of stable, strong color, and high organic content, azo dyes are difficult to degrade and result in the threat of environmental pollution. Under the above trend of environmental pollutions, the concern of azo dye contaminations arises from its association with the efficient and inexpensive treatment, the decolorization or degradation of azo dyes.

In terms of decolorization of azo dyes by multi-technologies, studies had been carried out in several major fields, including physical (Vankelecom), electrochemical (Nobutake Suzuki et al.) (Hosono et al.) (Bagyo, Arai and Miyata) (Daneshvar, Ashassi-Sorkhabi and Tizpar), chemical (F. Zhang et al.) (F. F. Zhang et al.), biological processes (Percy et al.) (Perey et al.), and other applied processes, such as Fenton reagent oxidation (Feng et al., "Degradation of Azo-Dye Orange II by a Photoassisted Fenton Reaction Using a Novel Composite of Iron Oxide and Silicate Nanoparticles as a Catalyst") (He et al.) (Feng, Hu and Yue) (Feng et al., "Discoloration and Mineralization
of Reactive Red He-3b by Heterogeneous Photo-Fenton Reaction") (Barbusinski and Majewski) (Parra et al.) and Ultrasonic approach (Ince et al.) (Vinodgopal et al.), as illustrated by Table 1. Recently, in order to approach a significant degradation in practical application, some research uses multi-step processes for a better treatment (Xiong and Karlsson). Among these technologies, reducing degradation of azo dyes with zero-valent iron particles provides not only an economic and convenient model system, but also a biodegradable product, aromatic amine, which is readily and easily degraded by micro-organisms (Appelton) (Tan et al.). Of particular interest of this study is to improve the traditional zero-valent iron technology by synthesis nanoscale particles and to discuss the possible effect of the overall degradation. Through the overall degradation, as a redox reaction, nanoscale zero-valent iron, Fe$^0$, plays a powerful reducing agent and an electron donor. With the oxidation of azo dyes, Fe$^0$ is transformed into dissolved divalent form, concomitantly. The typical reductive reaction is shown as following in Eq. (1)-(2):

\[
\begin{align*}
\text{Fe}^0_{(s)} + 2\text{H}^+ & \rightarrow \text{Fe}^{2+}_{(aq)} + \text{H}_2 \quad (1) \\
\text{Fe}^0_{(s)} + 2\text{H}_2\text{O} & \rightarrow \text{Fe}^{2+}_{(aq)} + \text{H}_2 + 2\text{OH}^- \quad (2)
\end{align*}
\]
<table>
<thead>
<tr>
<th>Types</th>
<th>Process</th>
<th>References</th>
</tr>
</thead>
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<tr>
<td>Physical</td>
<td>Polymeric membranes</td>
<td>(Vankelecom)</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Redox</td>
<td>(Nobutake Suzuki et al.) (Hosono et al.) (Bagyo, Arai and Miyata)</td>
</tr>
<tr>
<td>Chemical</td>
<td>Coagulation/precipitation</td>
<td>(Daneshvar, Ashassi-Sorkhabi and Tizpar)</td>
</tr>
<tr>
<td></td>
<td>Chlorination/ozonation</td>
<td>(F. F. Zhang et al.)</td>
</tr>
<tr>
<td></td>
<td>Wet Air Oxidation</td>
<td>(Arslan-Alaton and Ferry)</td>
</tr>
<tr>
<td></td>
<td>Fenton Reagent Oxidation</td>
<td>(Fernandez, Dhananjeyan et al.) (Feng et al) (He et al.) (Fernandez, Nadtochenko et al.)</td>
</tr>
<tr>
<td></td>
<td>ZVI</td>
<td>(Liao, Kang and Hsu; T. Bigg and S.J. Judd; Perey et al.)</td>
</tr>
<tr>
<td>Others</td>
<td>Anaerobic/anoxic</td>
<td>(Coughlin, Kinkle and Bishop; Yuranova, Garamszegi et al.; Ma et al.)</td>
</tr>
<tr>
<td></td>
<td>(Agrawal et al.; Nurmi, Bandstra and Tratnyek)</td>
<td></td>
</tr>
<tr>
<td>Biological</td>
<td>Anaerobic/anoxic</td>
<td>(Supaka et al.; Manu and Chaudhari)</td>
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<tr>
<td>Photocatalytic</td>
<td>UV/H₂O₂; TiO₂</td>
<td>(Konstantinou and Albanis; Arslan-Alaton; Yuranova, Enea et al.)</td>
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<td>Related Review Report</td>
<td></td>
<td>(Slokar and Le Marechal; Arslan-Alaton; Hao, Kim and Chiang; Balko and Tratnyek)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Canonica and Tratnyek; Neamtu et al.; Weber)</td>
</tr>
</tbody>
</table>

*related table of this type can be found in Ref. (Hao, Kim and Chiang)*

Table 1. Decolorization of azo dyes by multi-technologies*
To advance the understanding of the decolorization of azo dyes and its applications of reduction by zero-valent iron, Fe$^0$, the investigation of three azo dyes, Orange II, Chrysoidin, and Tropaeolin O, reacted with nanoscale and microscale zero-valent iron particles in batch systems had been carried out in this study.

Nanoscale processes for environmental applications are highly anticipated (C.-B. Wang and W.-X. Zhang) (Venkatakrishnan et al.), and many believe that such technology holds future investment opportunities. Working at the molecular level, atom by atom, will increase the total surfaces in nanoscale particles and permit higher rate of various reactions (Feng et al., "Degradation of Azo-Dye Orange II by a Photoassisted Fenton Reaction Using a Novel Composite of Iron Oxide and Silicate Nanoparticles as a Catalyst") (C. B. Wang and W. X. Zhang). Based on this promising technology for environmental remediation, the objective of this research is to evaluate the comparison between using nanoscale and microscale zero-valent iron particles.
2. Experimental

2.1 Chemicals

Nanoscale iron particles By adding 1:1 volume ratio of NaBH$_4$ (0.25 M) into FeCl$_3$ (0.045 M) solution, nanoscale iron particles were synthesized at the temperature (25±1°C). At the mixing rate of 36.5 mL/min, the suspension was mixed completely in 20 minutes. Generally, the nanoscale particles have a diameter of 100-200 nm and a surface area of 33.5 m$^2$/g (C. B. Wang and W. X. Zhang). Based on the following Eq. (3), the ferric iron was reduced by borohydride:

$$4\text{FeCl}_3 + 3\text{NaBH}_4 + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^0 + 3\text{NaH}_2\text{BO}_3 + 12\text{H}^+ + 12\text{Cl}^- + 6\text{H}_2$$  (3)

Microscale iron particles (> 98 %) By purchasing from Fisher Co., US, the microscale iron particles were pretreated with 10mL HCl and flushed more than three times with distilled water in order to remove the residual HCl and Fe$^{2+}$. The microscale iron particles have a rough diameter of 10 μm and a surface area of 0.8955 cm$^2$/g (Cao et al.).

Orange II (> 85 %), Chrysoidine (>90%), and Tropaeolin O (>65%) By obtaining from Acros Organics Co., US, the molecular structures and their prosperities are shown in Figure 2.1 and Table 2.1.
1. Orange II

2. Chrysoidine

3. Tropaeolin O

Figure 2.1 Structures of the three dyes used in this study
<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Synonym</th>
<th>C.I. No.</th>
<th>CAS No.</th>
<th>M.W.</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Orange II</td>
<td>Acid Orange 7</td>
<td>15510</td>
<td>633-96-5</td>
<td>350.3</td>
<td>486</td>
</tr>
<tr>
<td>2</td>
<td>Chrysoidine</td>
<td>Basic Orange 2</td>
<td>11270</td>
<td>532-82-1</td>
<td>248.7</td>
<td>459</td>
</tr>
<tr>
<td>3</td>
<td>Tropaeolin O</td>
<td>Acid Orange 6</td>
<td>14270</td>
<td>547-57-9</td>
<td>316.3</td>
<td>412</td>
</tr>
</tbody>
</table>

Table 2.1 Dyes and their properties
Buffer solutions By obtaining from Acros Organics Co., US, the buffer solutions are 3, 7, and 9, respectively. Their ingredients and pH ranges are illustrated in Table 2.2.
<table>
<thead>
<tr>
<th>Buffer Solution</th>
<th>Ingredient</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 3</td>
<td>Potassium Biphthalate Hydrochloric Acid Buffer</td>
<td>3 ± 0.02</td>
</tr>
<tr>
<td>pH = 7</td>
<td>Phosphate, Dipotassium Disodium phosphate Monopotassium phosphate</td>
<td>7 ± 0.02</td>
</tr>
<tr>
<td>pH = 9</td>
<td>Boric acid-potassium Chloride-sodium</td>
<td>9 ± 0.02</td>
</tr>
</tbody>
</table>

Table 2.2 Buffer solutions and their properties
2.2 Experimental device

The bath experimental apparatus is shown in Figure 2.2. In an anaerobic atmosphere (N₂), all the experiments were done at pH 3, 7, and 9 by adding buffer solutions, respectively. With the same mixing rate, 7 rpm, all dye reduction experiments were done at concentrations of 2500 mg/L in 200 mL vials sealed with Teflon-lined caps and shook for 2 hours on a Burrell Wrist-action shaker. To decolorize the samples, more of the construction grade iron was used: 0.1 g and 0.25 g of nanoscale iron particles and 0.2 g and 0.4 g of microscale iron particles from Fisher Co., US. During the reaction, the aqueous phase was sampled and filtered periodically and analyzed by UV-visible spectrometer (Model UV-8453, Agilent).

2.3 Analysis methods

To calculate the reduced concentration of all dyes regarded to Lambert-Beer’s Eq., a series of standard solutions were prepared from 1 ppm to 50 ppm, vs. a blank consisting of deionized water. Take Orange II for example, the absorbance spectrums of dyes are shown in Figure 2.3. The routine analysis of all dye decolorizations were recorded by measuring absorbance at the λ
\text{max} = 486 \text{ nm}. Samples were diluted 250 fold with deionized water. The results are in Figure 2.4.
Figure 2.2 The bath experimental apparatus
Figure 2.3 The absorbance spectrum of standard Orange II solution
Figure 2.4 2500 mg/L Orange II dye removal in batch reactor
3. Results and Discussion

3.1. Reaction mechanism and kinetics

The use of microscale zero-valent iron, Fe\(^0\), in the decolorization of mono-azo dyes had been mainly discussed (Nam and Tratnyek). By breaking the azo bond, which is the reason for having visible color and forming aromatic amine, the absorbance spectrum of Orange II solution, \(\lambda_{\text{max}} = 486\) nm, becomes lower (Cao et al.). The degradation mechanism for Orange II in Fe\(^0\)-H\(_2\)O system is shown in Figure 3.1.
Figure 3.1 Degradation mechanisms for Orange II in Fe\(^0\)-H\(_2\)O system
Cao et al. (1999) had shown that the reaction scheme for Orange II in Fe\textsuperscript{0} - H\textsubscript{2}O system consists of a two-step reaction with the first step reversible (Cao et al.). In this study, degradation mechanisms of Chrysoidine showed the same reaction scheme as Orange II, illustrated in Figure 3.2.
Figure 3.2 Degradation mechanisms of Chrysoidine in nanoscale Fe$^0$-H$_2$O systems
It is apparent from the Figure 3.3 and Figure 3.4. that transformation of Chrysoidine at 2,500 mg/ L by 0.1 g nanoscale iron involves a special structure, unstable transitional compound which decomposes rapidly into the end product. In Figure 3.4(a), absorbance decreases along with increasing time meaning reverse reaction cause the product increase, and the absorbance increasing at $\lambda = 451$ nm, because the transitional compound returned into Chrysoidine.
Figure 3.3 The product concentration of degradation of 2500mg/L Chrysoidine by 0.1g nanoscale Fe concentration at reaction time 13 min and 80 min and rescanned after 120 min delay.
Figure 3.4 UV-visible Absorption Spectrum of the degradation of Chrysoidine at reaction time=13min. (a) C=542 mg/L (b) 152 mg/L are the spectrum scanned immediately after the solution was taken out of the reaction bottle. (a) C=689 mg/L (b) 191 mg/L is the rescanned spectrum of the same solution after 120 minutes’ delay.)
The kinetics of Chrysoidine reduced by either microscale or nanoscale Fe\(^0\) was illustrated in Figure 3.5. The results indicate that the reductive degradations of azo dyes by adding either microscale or nanoscale iron particles obey the pseudo-first-order reaction kinetic models, as Eq. (4)-(5).

\[
\ln \frac{C}{C_0} = -k \cdot M_{Fe} \cdot t 
\]

\[
\ln \frac{C}{C_0} = -k_{obs} \cdot t 
\]

where \(k\) is the apparent reaction rate constant, \(C\) is the concentration of analysis at time \(t\), \(C_0\) is the initial concentration, \(k_{obs}\) is the pseudo-first-order disappearance rate constant, and \(M_{Fe}\) is the weight of iron particles. Assuming the initial iron concentration didn’t change during the whole reaction; therefore, \(k \cdot M_{Fe} = k_{obs}\).
Figure 3.5 Pseudo-first-order reaction rate constants of Chrysoidine at the concentration of 2500mg/L for different construction grade iron powders
3.2. Effect of iron particles

The effect of iron particles was investigated with azo dyes used in this study, and is shown in Figure 3.6 to Figure 3.8. Compared to microscale iron particles, the surface area of nanoscale iron particles increases from $8.955 \times 10^{-5}$ $m^2/g$ to 33.5 $m^2/g$. Due to the degradation reaction of organic compounds using zero-valent iron, $Fe^0$, occurring on the surface of metal iron (Weber), as well as azo dyes (Zollinger et al.), enlarging the surface area of the reactants creates a major benefit for shortening the reaction time of decolorization. Surface-area-normalized rate constants ($K_{SA}$) are calculated to be 10-100 times higher than those of commercially available iron particles (C. B. Wang and W. X. Zhang). In this study, for Orange II, Chrysoidine, and Tropaeolin O, removal rates are 8.0, 8.7, 57.0 times higher when comparing nanoscale iron particles to microscale, respectively.
Figure 3.6 The effect of iron particles on Orange II
Figure 3.7 The effect of iron particles on Chrysoidine
Figure 3.8 The effect of iron particles on Tropaeolin O
3.3. Effect of pH

It has been discussed that the effect of pH is a significant parameter for wastewater treatment by using zero-valent iron (T. Bigg and S. J. Judd). Some research projects have altered the pH of wastewater under an acidic environment with acid (Khudenko) (Young et al.) because the formation of iron oxides at pH ≥ 7 would reduce the reactive surface area tremendously. In order to increase the reaction rate for wastewater treatment, experiments were carried out at a lower pH range (4 - 9) and identical temperatures (20°C) (Ozdemir and Tufekci) as to inhibit deposition of ferric oxides when enhancing cathodic depolarization and hydrogenolysis.

To examine its effect, all the samples were adjusted to certain pH values (3, 7.01, and 9). Obviously, in each shown reaction rate, it's higher at pH < 7 and less at pH > 7. The results were shown by using nanoscale and microscale iron particles in Figure 3.9 to Figure 3.12. The best removals of Orange II and Tropaeolin O were observed at pH around 3.03 and 3.06, respectively, by using nanoscale iron particles 0.233 g. The comparison reduction kinetic constants of Orange II and Tropaeolin O by nanoscale and microscale iron particles at pH=3, 7, and 9 are shown in Table 3.1.
Figure 3.9 Reduction of 1000mg/L Orange II 200ml by 0.233g Nanoscale Fe$^0$ particles
Figure 3.10 Reduction of 1000mg/L Orange II 200ml by 2g Fe$^0$ particles
Figure 3.11 Reduction of 1000mg/L Tropaeolin O 200ml by 0.233g Nanoscale Fe^0\ particles

\[ \text{pH}=3.06 \]
\[ \text{pH}=7.13 \]
\[ \text{pH}=8.6 \]
Figure 3.12 Reduction of 1000mg/L Tropaeolin O 200ml by 2g Fe⁰ particles
<table>
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<tr>
<th>Dye</th>
<th>Dry weight of Nanoscale Fe</th>
<th>Weight of Iron Filling</th>
<th>pH</th>
<th>R-square</th>
<th>K(1/min)</th>
<th>$\frac{1}{gFe \cdot min}$</th>
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<tbody>
<tr>
<td>Orange II</td>
<td>0.1g</td>
<td></td>
<td>3.03</td>
<td>0.6826</td>
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<td>6.2750</td>
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<td>Orange II</td>
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<td>2g</td>
<td>8.6</td>
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<td>0.0035</td>
<td>0.0070</td>
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Table 3.1 The comparison reduction kinetic constants of Orange II and Tropaeolin O by nanoscale and microscale iron particles at pH=3, 7, and 9.
3.4. Removal efficiency of azo dyes

As shown in Figure 3.13, the degradation of azo dyes used in this study can be calculated by using nanoscale iron of the same dimension. The following relationship for removal efficiency was devised on the kinetics of azo dyes:

$$ k_{\text{Chrysoidine}} (1.6510) > k_{\text{Orange II}} (0.240) > k_{\text{Tropaeolin O}} (0.185) $$
Figure 3.13 The removal efficiency at the concentration of 2500mg/L by 0.1g nanoscale Fe⁰ particles in batch reactor
It's well known that the electronic attractive ability of O is stronger than N. Having two oxygen atoms on the benzene ring, Tropaeolin O has less removal efficiency compared to the two nitrogen atoms on the benzene ring of Chrysoidine. Based on the above explanation, the degradation of azo dyes used in this study can be clarified without any doubts.
4. Conclusion

As the results illustrate, all three of the azo dyes, Orange II, Chrysoidine, and Tropaeolin O, were rapidly decolorized within 90% by nanoscale iron particles, Fe$^0$, under the conditions described. The major reduction pathways of azo dyes in this study were proved as biodegradable reactions for further treatments. By reacting with either microscale or nanoscale iron particles, the reductive degradations obey the pseudo-first-order reaction kinetic models. Furthermore, the degradation mechanisms of Chrysoidine were shown as a two-step reaction with the first step reversible scheme. In the comparison between using nanoscale and microscale zero-valent iron particles, the effect of using nanoscale zero-valent iron particles creates a major benefit 8-57 times higher than that of commercially available microscale zero-valent iron particles. Finally, better removal of Orange II and Tropaeolin O was observed at a lower pH value.


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Vita

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Shun-Yi attended Tunghai University in Taichung, Taiwan from 1995 to 1999 where he earned his Bachelor of Science degree in Environmental Science in June 1999. During his undergraduate career in 1998, he interned on the research project, titled “The Effects of Physico-Chemical Property of Natural Organic Matter on the Formation of Disinfection Byproducts.” In 1999, he was awarded the Certificate of Athletic Excellence on the swimming team of Tunghai University.

After completing his B.S. from Tunghai University, Shun-Yi joined the Air Force for a required 2-year term of military service in Taiwan from 1999 to 2001. He was in charge of the security of Tainan Airport in Taiwan as a technical sergeant.

After his discharge from the Air Force, Shun-Yi started his career as an environmental inspection specialist for the Environmental Protection Agency of Kaohsiung City in 2001. He then became an environmental engineer for National Kaohsiung Institute of Marine Technology, Kaohsiung, Taiwan
from 2001 to 2003. After three years of working, he figured out the more professional responsibility that he receives, the more sense of inadequacy and stronger urge for him to pursue knowledge in the field of environmental analysis in both depth and breadth. Therefore, he came to the United States and began his further graduate study in Lehigh University, Bethlehem, Pennsylvania in July 2003. Working with Dr. Weixian Zhang, Shun-Yi finished his M.S. research in environmental nanotechnology in December 2004.