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Photochemical degradation of 2,4-D and atrazine in well-defined media

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Photochemical Degradation of 2,4-D and Atrazine in Well-defined Media

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May 24, 2001
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Submitted in partial fulfillment of the Requirements for Honors in Chemistry

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Abstract

Atrazine and 2,4-D are common herbicides used for crop, lawn, and rangeland management. Photochemical degradation has been proposed as one safe and efficient remediation strategy for both 2,4-D and Atrazine. In the presence of iron(III) and hydrogen peroxide these herbicides decay by both thermal and light induced oxidation. Past studies have focused primarily on sun light as an energy source. This work provides a mechanistic description of herbicide degradation incorporating intermediate degradation products produced in the dark and under well-defined light conditions.
1. Introduction

1.1 Background Information on Herbicides

Herbicide application has become the status quo for agriculturalists around the world. It enhances production, saves money, and reduces labor hours. Millions of pounds of herbicides are applied annually worldwide. Herbicides must be water-soluble so that they can easily be applied to crops, and resistant to natural degradation processes so that their effective life on crops is maximized. Although herbicides are designed to kill unwanted weeds, they are not entirely selective in what species they attack. Both Atrazine and 2,4-D are plant-growth regulators that stimulate nucleic acid and protein synthesis and change enzyme activity, respiration, and cell division. These herbicides are absorbed by plant leaves, roots, and stems. They move throughout the plant and accumulate in growing tips (1). Once absorbed, the plant undergoes rapid cellular activity leading to death. Because of herbicides' non-selectivity, they pose potential threats to other living organisms in proximity to application sites. Water migration, soil migration, and aerial dispersion are the methods through which non-target plant and animal species are affected.

Potential compromises to water, human health, and wildlife health have created the need for rapid, safe, and effective methods of waste herbicide disposal. Herbicide disposal is of greatest concern where wastes are found in high concentrations. Thus, there is the need for remediation strategies for organic wastes produced by herbicide tank and machine rinsates, commercial spills, and small amounts of unused product. Increasingly stringent restrictions on herbicide land disposal combined with the need to increase safety at existing waste sites augments the demand for effective remediation technology (14).
1.1 Background on 2,4-D

![Chemical structure of 2,4-dichlorophenoxyacetic acid (2,4-D)](image)

Figure 1. Chemical structure of 2,4-dichlorophenoxyacetic acid (2,4-D)

The herbicide 2,4-dichlorophenoxyacetic acid (Figure 1) is a member of the phenoxy family of herbicides. It has been used for over 50 years, and to this day it remains the third most commonly used herbicide in the United States and Canada and the most commonly used herbicide in the world (2). It was the first successfully developed selective herbicide, which means that it kills weeds in an agricultural crop without harming the crop itself. Thus, 2,4-D is used to control broadleaf weeds, grasses and other monocots, woody plants, aquatic weeds, and non-flowering plants by confounding plant-growth regulation (1). Its forestry, right-of-way, and rangeland uses include noxious and poisonous weed control, range improvement, right-of-way maintenance, site preparation, aquatic weed control, lawn care, thinning, timber management, wildlife habitat improvement, range management, recreation management, fire-break management, and nursery stand improvement (2). Agriculturally, it is primarily used on wheat and small grains, sorghum, corn, rice, sugar cane, and low-till soybeans (1). Herbicides containing 2,4-D generally use the amine salt or an ester form of the compound.
An agriculture study (NAPIAP Report NO. 1-PA-96) found that, in the United States alone, if 2,4-D were no longer available, the cost to farmers and other users in terms of more expensive weed control practices would total $1,683 million annually (1). Thus, the economic benefits to growers are very clear; however, the potential for adverse environmental externalities due to application and disposal are not weighed into this calculation. Thus, in order to maximize the benefits that society at large receives from the use of 2,4-D, costs due to environmental hazards must be minimized. These hazards are broken down into toxicological and ecological effects.

Plants absorb 2,4-D through their roots and leaves within four to six hours after application. Once in the plant, 2,4-D mimics the effect of the auxins, which are plant growth regulating hormones, stimulating growth, rejuvenation of old cells, and over stimulates young cells leading to abnormal growth and death to some plants. The herbicide 2,4-D also affects plant metabolism and food transport. This compound specifically targets broadleaf plants because of their larger leaf area, which leads to sufficient absorption for plant death (7).

1.3 Toxicity of 2,4-D

Like most organochlorine pesticides, 2,4-D poses health risks to both humans and animals. This herbicide has moderate to low acute toxicity for humans and animal species according to recent studies under the EPA re-registration program for 2,4-D (3-6). Subchronic and chronic effects in humans are generally limited to high doses, and neurotoxicity is the predominant effect of exposure, with symptoms including stiffness of
limbs, incoordination, lethargy, anorexia, stupor, and coma (15-16). Direct dermal contact is the most common means of exposure to 2,4-D. For those working around 2,4-D application, eye and skin irritation is the greatest concern as dermal absorption is rapid. Skin and eye protection is imperative while working in the presence of aerial 2,4-D. Irritation to the gastrointestinal tract also can occur, and with chronic oral exposure, adverse effects on blood, liver, and kidneys occurs (15-16). Due to 2,4-D's high degree of water solubility, it is evenly transported throughout the body and does not accumulate in any particular tissue (7).

The US EPA has established the Reference Dose (RfD) for 2,4-D at 0.01 mg per kg body weight per day. The EPA further estimates that sustained consumption of this dose or less over a lifetime would not likely enhance one's occurrence of chronic, non-cancer effects (3). 2,4-D has a short biological half-life, which ranges from 10 to 36 hours. Without sustained exposure 2,4-D is cleared from the body in two to four days (7). Recent studies indicate minimal 2,4-D induced reproductive or developmental effects in humans, although animal studies have reported decreased fetal weights, increased fetal mortality, skeletal malformation, and other effects. In addition no concrete evidence for connection between 2,4-D exposure and human carcinogenicity has been found (1-4).

1.4 Environmental Fate of 2,4-D

The environmental fate of 2,4-D depends on the form of herbicide in consideration. Traces of 2,4-D in its amine form can be found in soil 120 days after application, but when applied on crops, most forms of 2,4-D can be detected for approximately two
weeks (6). Such a rapid soil half-life is due in large part to rapid degradation by soil microorganisms (23). The half-life in natural water is two to four weeks (1). 2,4-D dissolves rapidly in water. Despite its relatively short half-life in soil and aquatic environments, this rapid dissociation allows it to quickly move through water tables such that it has been detected in groundwater supplies in trace amounts throughout the United States and Canada (22) and in low concentrations in surface waters (24).

1.5 Background on Atrazine

Atrazine (Figure 2), a selective triazine herbicide, is used mainly to control broadleaf and grassy weeds in corn, sorghum, sugarcane, pineapple, Christmas trees, and in conifer reforestation plantings. It is also used as a nonselective herbicide on non-cropped industrial lands and on fallow lands (25).

![Figure 2. Chemical structure of 2-chloro-4-ethylamine-6-isopropylamino-S-triazine (Atrazine)](image)

A study submitted to the EPA by Ciba Crop indicates that, according to studies based on data from weed scientists and farm economists, the total minimum annual economic benefit of Atrazine and simazine approaches $1.66 billion, of which Atrazine is the more common triazine herbicide (26). As one of the most commonly used herbicides in the United States, Atrazine is considered one of the most effective and economically valuable
herbicides produced. Like 2,4-D, Atrazine's economic benefits do not come without the potential for adverse ecological and toxicological effects.

Plants absorb Atrazine primarily through the roots, although it also is absorbed through the foliage (24). After the plant absorbs the Atrazine, it is translocated upward and accumulates in the growing tips of the plant's new leaves. Tolerant plants metabolize the herbicide, while susceptible plants die through inhibited photosynthesis (12).

1.6 Toxicity of Atrazine

Atrazine is slightly to moderately toxic to humans and animals, practically nontoxic to birds, and slightly toxic to fish and other aquatic life (25, 9). It can be absorbed orally, dermally, and by inhalation. Symptoms of poisoning include abdominal pain, diarrhea and vomiting, eye irritation, irritation of mucous membranes, and skin reactions (8). Numerous acute and chronic toxicological studies have been conducted on rats and have found that at extremely high doses, rats show excitation followed by depression, slowed breathing, incoordination, muscle spasms, and hypothermia (8). After consuming a large oral dose, rats exhibit muscular weakness, hypoactivity, breathing difficulty, prostration, convulsions, and death (9). Dermally, Atrazine is a mild skin irritant—rashes associated with exposure have been reported. Upon chronic exposure, rats, mice, and rabbits, exhibited structural and chemical changes in the brain, heart, liver, lungs, kidney, ovaries, and endocrine organs (8, 9). As with 2,4-D, there is no conclusive evidence regarding Atrazine's carcinogenicity.
1.7 Environmental Fate of Atrazine

Despite Atrazine's moderate water solubility, it has a high potential for groundwater contamination due to its relatively long half life in aqueous environments (60 to 100 days) and because it does not strongly adsorb to soil particles (27). Atrazine is the second most common pesticide found in private and community wells. Trace amounts have been found in drinking water and groundwater samples in a number of states (9). Hydrolysis, followed by degradation by soil microorganisms, accounts for most of the natural breakdown of Atrazine. Hydrolysis is rapid in acidic or basic environments and slower at neutral pHs, although adding organic material increases the rate of hydrolysis. Atrazine can persist for longer than 1 year under dry or cold conditions (25). The 1990 National Survey of Pesticides in Drinking Water found Atrazine in nearly 1% of all of the wells tested (11).

1.8 Why this study and why this technique?

There is a need for a rapid, clean, and inexpensive pathway for the degradation of Atrazine and 2,4-D to reduce ecological and toxicological threats to the environment. Incineration, although effective in remediating local herbicide exposure, is costly for highly contaminated areas due to the large volume of water associated with the waste and because of high transport cost (13). Viable pesticide remediation methods must incorporate environmentally benign components that reduce harmful herbicide residues to non-toxic intermediates. Such a strategy also needs to accommodate small scale,
aqueous, and dilute wastes in soil and sludges to prevent further contamination of regional water and terrestrial environments. Complete mineralization to carbon dioxide is the desired end for herbicide remediation so as to prevent toxic intermediate degradation products.

Fenton photochemical reactions present such a remediation strategy by introducing hydroxyl radicals into the system, which react rapidly and non-selectively with organic compounds including 2,4-D and Atrazine. Several studies have investigated the use of Fenton photochemical systems to determine the degradation rate for both Atrazine and 2,4-D in aqueous environments (13-14, 18, and 20).

The proposed Fenton photochemical system (eq 1-3) combines Fe(III) with H₂O₂ and UV light to create hydroxyl radicals, which go on to mineralize 2,4-D and Atrazine. Fe(III) acts a catalyst for peroxide decomposition to O₂, H₂O, and 'OH. These reactions produce a low steady state concentration of Fe(II), which is an intermediate that reacts with H₂O₂ to generate 'OH.

\[
\begin{align*}
\text{Fe(III)} + \text{H}_2\text{O}_2 & \rightleftharpoons \text{Fe}^\text{3+} \cdot \text{O}_2 \text{H}^+ + \text{H}^+ \rightarrow \text{Fe}^\text{2+} + \text{O}_2 + \text{H}_2\text{O} & (1) \\
\text{Fe(III)} + \text{HO}_2^- & \rightarrow \text{Fe}^\text{2+} + \text{H}^+ + \text{O}_2 & (2) \\
\text{Fe}^\text{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^\text{3+} + \text{OH}^- + \text{OH} & (3)
\end{align*}
\]

With excess H₂O₂, the concentration of Fe²⁺ is small relative to the concentration of Fe³⁺ because reactions 1 and 2 are slower than reaction 3 (18). The oxidation power of Fenton chemistry is enhanced by irradiation with UV light by forming an additional hydroxyl radical (eq 4). Past studies have shown that complete mineralization of 2,4-D (eq 5) using the proposed system can be achieved in less than two hours (14). The general form of the photochemically enhanced reactions is as follows:
The net result of reactions 1–4 is the production of two \( \cdot \text{OH} \). One \( \cdot \text{OH} \) comes from reaction 4, the other from reaction 3. Iron described using roman numerals will thus forth represent all solution phase species of a given oxidation state whereas specific iron species will be represented in their ionic forms. Not all Fe(III) species are photoreactive (18). Iron speciation controls the photoreactivity. FeOH\(^{2+}\) and Fe(OH)_2\(^{+}\) are both photoreactive Fe(III) species involved in light induced \( \cdot \text{OH} \) generation (14). However, as will be described below, FeOH\(^{2+}\) is believed to be the dominant \( \cdot \text{OH} \) generating species in acidic conditions (14). Thus, \([\text{Fe(H}_2\text{O)}_2\text{OH]}^{2+}\), the fully hydrated FeOH\(^{2+}\) species, is the Fe(III) species that we focus on in developing and describing the Fenton photochemical system. In our system, we try to maximize \( \cdot \text{OH} \) production. As Fe(III) speciation controls the relative abundance of \([\text{Fe(H}_2\text{O)}_2\text{OH]}^{2+}\) in solution, understanding Fe(III) speciation is essential to establishing an ideal pH.

The Fe(III) hexa(aqua)cation readily undergoes hydrolysis reactions to form the following Fe(III) species in their fully hydrated forms: \([\text{Fe(H}_2\text{O)}_6]^{3+}\), \([\text{Fe(H}_2\text{O)}_5\text{OH]}^{2+}\), \([\text{Fe(H}_2\text{O)}_4\text{(OH)}_2]^{+}\), and \([\text{Fe(H}_2\text{O)}_3\text{(OH)}_3]\). These species will be hitherto represented in their simplified (unhydrated) forms. Fe(III) hydrolysis reactions are shown below (eq 6–8) and values for equilibrium constants for these Fe(III) reactions are tabulated in Table 1.

\[
\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^{2+} + \text{H}^+ \quad \text{(6)}
\]

\[
\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2^{+} + 2\text{H}^+ \quad \text{(7)}
\]
Table 1: Fe(III) equilibrium coefficients for the Fenton System

<table>
<thead>
<tr>
<th>constant</th>
<th>value</th>
<th>equation</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_1$</td>
<td>$4.27 \times 10^{-3}$</td>
<td>6</td>
<td>19</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>$1.58 \times 10^{-6}$</td>
<td>7</td>
<td>19</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>$6.30 \times 10^{-16}$</td>
<td>8</td>
<td>19</td>
</tr>
<tr>
<td>$K_{sp}$</td>
<td>1600</td>
<td>-</td>
<td>27</td>
</tr>
<tr>
<td>$\beta_{ox1}$</td>
<td>$5.89 \times 10^{8}$</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>$\beta_{ox2}$</td>
<td>$3.30 \times 10^{6}$</td>
<td>24</td>
<td>22</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$19.44 \times 10^{4}$</td>
<td>25</td>
<td>22</td>
</tr>
<tr>
<td>$K_{a1}$</td>
<td>$5.6 \times 10^{-7}$</td>
<td>21</td>
<td>22</td>
</tr>
<tr>
<td>$K_{a2}$</td>
<td>$5.42 \times 10^{-5}$</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

Hydrolysis constants are generalized in equation 9:

$$
\beta_i = \frac{[Fe(OH)_i^{3-i+}]}{[Fe^{3+}][H^+]} \quad (9)
$$

The distribution of the Fe(III) species in water between the complexes in eq 6-8 is a function of pH. The distribution function ($\alpha$) for Fe$^{3+}$ is the ratio of free Fe$^{3+}$ to total Fe(III) where the total Fe(III) is the sum of the mass balance of each individual Fe(III) species (eq 10).

$$
\alpha_{Fe^{3+}} = \frac{Fe^{3+}}{Fe^{3+} + FeOH^{2+} + Fe(OH)_2^{2+} + Fe(OH)_3^0} \quad (10)
$$

By writing all iron species in terms of Fe$^{3+}$, we can recast equation 10 as equation 11 by using the cumulative hydrolysis constants ($\beta_i$) provided in Table 1.
\[
\alpha_{Fe^{3+}} = \frac{Fe^{3+}}{Fe^{3+} + \frac{Fe^{3+} \beta_1}{[H^+] + \frac{Fe^{3+} \beta_2}{[H^+]^2} + \frac{Fe^{3+} \beta_3}{[H^+]^3}}}
\]

(11)

Condensing terms results in the common distribution function (eq 12).

\[
\alpha_{Fe^{3+}} = \frac{1}{1 + \frac{\beta_1}{[H^+]} + \frac{\beta_2}{[H^+]^2} + \frac{\beta_3}{[H^+]^3}}
\]

(12)

The distribution functions for FeOH\textsuperscript{2+}, Fe(OH)\textsuperscript{2+}, and Fe(OH)\textsubscript{3} in terms of \( \alpha_{Fe^{3+}} \), are described below (eq 13-15).

\[
\alpha_{Fe(OH)^{2+}} = \frac{\alpha_{Fe^{3+}} \beta_1}{[H^+]} \]

(13)

\[
\alpha_{Fe(OH)_{2}^{+}} = \frac{\alpha_{Fe^{3+}} \beta_2}{[H^+]^2}
\]

(14)

\[
\alpha_{Fe(OH)_3} = \frac{\alpha_{Fe^{3+}} \beta_3}{[H^+]^3}
\]

(15)

Using the equilibrium coefficients from Table 1, the distribution functions for Fe\textsuperscript{3+}, Fe(OH)\textsuperscript{2+}, and Fe(OH)\textsubscript{2} can be plotted against pH (Figure 3).
Figure 3. Iron speciation as a function of pH. Calculations were performed for pure water at 25°C.
Iron(III) solubility also plays a role in hydroxyl radical production. If the photon absorbing species is not in solution, hydroxyl radical production will not be efficient.

Equations 16 and 17 show the solubility expression and equation for Fe$^{3+}$:

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3(g) + 3\text{H}^+ \quad (16)$$

$$K_s = \frac{\left[ \text{Fe}^{3+} \right]}{[H^+]^3} \quad (17)$$

Equation 14 can be rearranged to give equation 18 or 19 representing free Fe$^{3+}$ in solution and Fe(III):

$$[\text{Fe}^{3+}] = K_s[H^+]^3 \quad (18)$$

$$\text{Fe(III)} = \frac{K_s[H^+]^3}{\alpha_{\text{Fe}^{3+}}} \quad (19)$$

Free FeOH$^{2+}$ in solution is found by multiplying the distribution function for FeOH$^{2+}$ by the total iron in solution, $T_{\text{Fe}^{3+}}$, which is determined by solubility and mass balance, where all added iron would dissolve.

$$[\text{FeOH}^{2+}] = T_{\text{Fe}^{3+}} \ast \alpha_{\text{FeOH}^{2+}} = \frac{K_s[H^+]^3}{\alpha_{\text{Fe}^{3+}}} \alpha_{\text{FeOH}^{2+}} \quad \text{or} \quad K_s[H^+]^3 \beta_i \quad (20)$$

To maximize hydroxyl radical production, it is necessary to maximize FeOH$^{2+}$ in solution because hydroxyl radical is produced when the Fe-O bond is broken. Figure 4 shows a plot of FeOH$^{2+}$ solubility and speciation and Fe(OH)$_2^+$ solubility calculated for a pure water solution. These plots can be used to determine the pH at which the concentration of FeOH$^{2+}$ is maximized. For more precise calculations of iron solubility, activity calculations must be performed.
Figure 4. Plot of FeOH\(^{2+}\) speciation and solubility and Fe(OH)\(_2^+\) vs. pH. Plot shows low relative solubility of Fe(OH)\(_2^+\). FeOH\(^{2+}\) species is maximized relative to other Fe(III) species at a pH = 2.9 whereas its solubility is maximized at pH = 2.1.
As hydroxyl radical production depends on photon absorbance by FeOH\(^{2+}\), it is important to establish conditions that maximize FeOH\(^{2+}\) absorption. Considering both solubility and speciation, we used a pH \(\approx 2.4\) in our system.

The Fe\(^{3+}\) ion binds to ligands other than water, which introduces additional Fe(III) complexes to our system. The following discussion will consider oxalate as an example of such a ligand. Oxalate ion (C\(_2\)O\(_4^{2-}\)) enters our system as an intermediate degradation product, as will be discussed further in section 4. The oxalate ion can bind to the Fe\(^{3+}\) ion to form an additional chromophore, Fe-Ox\(^{-}\).

Speciation calculations are more complex when oxalate enters the system. Equations 21-25 show the additional iron speciation upon oxalate addition. Equations 21 and 22 are deprotonation reactions, and equations 23-25 are Fe\(^{3+}\) and oxalate ion reactions.

\[
\begin{align*}
H_2Ox & \leftrightarrow H^+ + HOx^- \\
HOx^- & \leftrightarrow H^+ + Ox^{2-} \\
Fe^{3+} + Ox^{2-} & \leftrightarrow FeOx^+ \\
FeOx^+ + Ox^{2-} & \leftrightarrow (FeOx)_2^- \\
Fe^{3+} + 2Ox^{2-} & \leftrightarrow (FeOx)_2^-
\end{align*}
\]

The distribution of total Fe(III) does not change when considering oxalate in our system because oxalate is of much lower concentration. The distribution function of oxalate does depend on pH and the presence of Fe(III). The distribution function for oxalate is described below (eq 26) where \(K_{a1}\) and \(K_{a2}\) are defined in Table 1.
\[ \alpha_{\text{Ox}^{2+}} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \quad (26) \]

Multiplying \( \beta_1 \) by equation 26 gives \( \beta^* \), which is the pH dependent conditional stability constant for FeOx\(^+\) formation. Multiplying \( \beta^* \) by the total Fe(III) concentration, as shown in equation 27 below, gives us insight into the relative concentration of FeOx\(^+\).

\[ \alpha_{\text{Ox}^{2+}} \beta_1 T_{\text{Fe(III)}} = \beta^* T_{\text{Fe(II)}} = \frac{[\text{FeOx}^+]}{[\text{Ox}^{2+}]} = 7394 \quad (\text{pH 2.4, } T_{\text{Fe(III)}}=0.001) \quad (27) \]

In our system, the above ratio of FeOx\(^+\) to Ox\(^2+\) is far greater than one (7394\(>>\)1). This allowed us to make the simple approximation that all oxalate in solution is complexed by the Fe\(^{3+}\) ion. Therefore, the pH of the solution, the solubility of the Fe(III) species, and the presence of oxalate control Fe(III) speciation. These parameters are known and can be controlled experimentally.

Before photochemical Fe-O bond cleavage, FeOH\(^{2+}\) or FeOx\(^+\) must absorb a photon. Upon photon absorption, the molecule is promoted to an excited state. Once in the excited state, the molecule can decay by one of two pathways: release energy through thermal decay or produce hydroxyl radical by breaking the Fe-O bond. The relationship between these two processes known as the quantum yield and is defined as the rate of hydroxyl radical formation (\( k_p \)), divided by the thermal decay rate plus the rate of hydroxyl radical formation (\( k_p + k_d \)). The quantum yields for FeOH\(^{2+}\) and FeOx\(^+\) are described in equation 28 and 29.
\[ \Phi_{FeOH^{+}} = \frac{k_{p2}}{k_{p2} + k_{d2}} \] (28)

\[ \Phi_{FeO^+} = \frac{k_{p3}}{k_{p3} + k_{d3}} \] (29)

Figure 5 illustrates the excitation and decay possibilities for the major photoreactive Fe(III) species.
Figure 5. Schematic diagram of Fenton photo-reactions including oxalate with thermal decay and OH· formation rate labels. Those species marked with an * represent Fe(III) species in an excited state. The equilibrium between unexcited species is controlled by iron speciation.
A calculation of the fraction of FeOH$^{2+}$ absorbing light in solution is necessary for the calculation of the photochemical hydroxyl radical production rate. Absorbance (A) is dependent on concentration (c), the cell path length (b), and the extinction coefficient ($\varepsilon$). These variables are related through the Beer-Lambert law shown as equation 30.

$$A = \varepsilon bc \quad (30)$$

However, with an optically dense solution, absorbance does not depend on the path length or concentration, because all photons are absorbed by the solution. From this, we know that total photons absorbed equals total photon flux. To compare the absorbances of the different Fe(III) species, and to calculate the fraction of FeOH$^{2+}$ absorbing photons, the relative absorbances of the species must be compared. To calculate the relative absorbance of the absorbing species the partitioning of photons to specific chromophores must be calculated. The partitioning of photons is calculated in the same way that a distribution function is calculated. It reflects the distribution of photons to absorbing species as a ratio of relative absorbances in terms of concentration weighted by molar absorptivities. Equation 31 shows the fraction of FeOH$^{2+}$ absorbing photons where $f$ represents fraction.

$$fA_{FeOH^{2+}} = \frac{A_{FeOH^{2+}}}{A_{Fe}} = \frac{\varepsilon_{FeOH^{2+}} \alpha_{FeOH^{2+}} [T_{Fe}]}{\varepsilon_{FeOH^{2+}} \alpha_{FeOH^{2+}} [T_{Fe}] + \varepsilon_{Fe^{2+}} \alpha_{Fe^{2+}} [T_{Fe}] + [T_{Os}] \varepsilon_{Fe^{0}}} \quad (31)$$
The hydroxyl radical production depends on the cleavage of the Fe-O bond in FeOH\textsuperscript{2+}, which can be expressed as the quantum yield. The quantum yield is wavelength dependent because the wavelength determines the energy of the photon, which determines the energy of the excited state of a species. To maximize hydroxyl radical production quantum yield must be maximized, which means that the wavelength must also be considered. Previous work in the King lab concluded that the quantum yield for FeOH\textsuperscript{2+} photochemistry is significant at wavelengths shorter than 330nm.

Therefore, it is clear that FeOH\textsuperscript{2+} speciation, absorption and the corresponding quantum yield need to be maximized in order to maximize hydroxyl radical production per photon. Using a pH of 2.4 maximizes speciation and solubility. However, percent absorbance of FeOH\textsuperscript{2+} and quantum yield are both wavelength dependent, thus, this study focuses on the wavelength dependence of 2,4-D and Atrazine degradation rates.
2 Experimental

2.1 Experimental Conditions

For 2,4-D experiments, 2,4-Dichlorophenoxyacetic acid (Sigma) was dissolved in Milli-Q purified water to give a concentration of 100 μM. For Atrazine experiments, Atrazine (Supelco Lot: LA85579) was dissolved in Milli-Q purified water to give a concentration of 25 μM. Solutions were sonicated for at least 2 hours to ensure full dissolution. Solutions were then added to a 1000 mL Pyrex reaction vessel equipped with two quartz windows that transmit 93% of UV light. The reaction vessel was thermally maintained at 25.0 ± 0.5 °C. A magnetic stir bar was added to the vessel and the solution was continuously stirred and allowed to thermally stabilize for at least 60 minutes. Iron(III) perchlorate (GFS Chemicals, Inc. Lot: L503982) was dissolved to give a concentration of 0.001 M and hydrogen peroxide (Fisher Scientific Lot: 970978) was diluted to 0.0025 M; both concentrations were confirmed by UV-vis spectroscopy.

The experimental apparatus consisted of an Oriel Instruments 1000 Watt high power Xenon short-arc lamp (model: 6269) powered by an Oriel Instruments 220 V power supply (model: 68820). The lamp was coupled to a Spectral Energy high throughput monochromator (model: GM252) for emission of high-intensity, monochromatic UV light. Light flux passing through the reaction vessel was measured using an International Light IL 700 Research radiometer. A diagram of the experimental apparatus is depicted in Figure 6.
Figure 6: Diagram of Experimental Apparatus

The radiometer output, in units of amps, was subsequently converted to power (P) in Watts per cm$^2$ using the work function for the detector, which is wavelength dependent. The radiant energy of the light beam for a given wavelength was then calculated using equation 32 where $h$ is Planck's constant, and $c$ is the speed of light.

$$E = \frac{hc}{\lambda} \quad (J/\text{photon})$$

The photon flux was then calculated in units of Einsteins, which are moles of photons, using equation 33 where $A$ is the area of the light beam, $T$ is the transmission of one vessel window, $N$ is Avogadro's number, and $P$ is the radiant power in J/(sec*cm$^2$).

$$\text{Flux} \left( \frac{\text{Einsteins}}{\text{sec}} \right) = \frac{P}{EN} \cdot AT$$

(32)

(33)
Under red light, to begin the dark phase reaction, iron(III) perchlorate and hydrogen peroxide stocks were simultaneously added to the reaction vessel giving a final concentration of 1.0 mM Fe(III) species and 2.5 mM H₂O₂, at which point dark decay of the herbicide began. After approximately thirty minutes of dark phase reaction time, the vessel was illuminated at one of the wavelengths of interest (260, 300, 300, 360 nm).

To monitor herbicide degradation 200 μM aliquots were taken approximately every ten minutes and preserved with 300 μM methanol (Acros). Trifluoroacetic acid (Sigma) was added giving a final water to methanol to trifluoroacetic acid ratio of 40:60:0.08. The samples were contained in 0.7 mL sealed 7 x 40 mm conical amber glass vials for HPLC analysis. The methanol addition quenched further hydroxyl radical reactivity, prevented continued photoreactions, and prepared the samples for immediate HPLC analysis.

2.2 HPLC

High Performance Liquid Chromatography (HPLC) was used to analyze the preserved aliquots. Solvents were degassed using a Thermo Separation Products Membrane Degasser and pumped into the column using an LDC Analytical constametric 4100 solvent delivery system with a Gilson 401C Diluter. Sample volumes of 300 μL were injected onto a 53 mm Alltech C₁₈ Rocket Column by a Gilson 231 XL automated sampling injector using a 40:60:0.08 water to methanol to trifluoroacetic acid isocratic
mobile phase. Samples were detected at 225 nm by a UV/vis LDC Analytical SpectroMonitor 3200 variable wavelength detector.

The HPLC system was connected to a Gilson Keypad with Gilson 720 software and a Gilson SN4000 computer interface, which connected the entire system to a PC using Thermo Separation Products PC1000 software for OS2.

Our column needed to be replaced half-way through the experiments, which resulted in disparate peak areas between the old and new columns. Atrazine came off of the column at retention times around 2.5 minutes on the old column and 3.3 minutes on the new column. 2,4-D came off the column at 1.4 minutes on the old column and 3.7 minutes on the new column. Acquisitions were run for 8.5 minutes to allow all products to fully elute.

Standards for both Atrazine and 2,4-D were run before each respective herbicide experiment. Atrazine standards were made at concentrations of 25 μM, 12.5 μM, and 6.26 μM. 2,4-D standards were run at 100 μM, 50 μM, and 25 μM concentrations. Triplicate runs for each standard were taken to produce calibration curves for each herbicide standard. Figure 7 shows an example of a Atrazine standard curve, and Figure 8 shows an example of a 2,4-D standard curve.
Figure 7. Sample Atrazine standard curve correlating peak area to concentration in μM. Standards were run at 25, 12.5, and 6.25 μM.
Figure 8. Sample 2,4-D standard curve correlating peak area to concentration in μM. Standards were run at 100, 50, and 25 μM.
After generating standard curves, it is also necessary to calculate the limits of detection for each herbicide in the system. Equation 34 describes the Limit of Detection (L.O.D.) in μM, where $\sigma_{\text{min}}$ is the standard deviation of the lowest standard concentration and $m$ is the slope of the standard curve.

$$L.O.D. = \frac{3\sigma_{\text{min}}}{m}$$

The limit of detection for 2,4-D was 1.11 μM and 0.5 μM for Atrazine. These detection limits allow us to accurately determine degradation rates.
3. Results

3.1 Dark Phase Degradation Results for 2,4-D and Atrazine

Before beginning light phase reaction experiments, it was necessary to establish dark phase degradation curves. Preliminary dark phase degradation runs were executed in 200 mL black Teflon bottles over extended periods of time (greater than 12 hours). These experiments were performed in order to establish dark phase degradation rates against which we could compare dark phase degradation rates from our experimental apparatus. Because of Atrazine's low solubility, its initial concentration was much lower than for 2,4-D, which is highly water soluble. Atrazine concentrations fell below the L.O.D. after 6 hours of dark phase degradation, and 2,4-D was undetectable after 1.2 hours of dark phase degradation. Figure 9 shows the extended dark phase degradation run for Atrazine and Figure 10 shows the extended dark phase degradation run for 2,4-D.
Figure 9. Atrazine extended dark phase degradation curve with initial Atrazine concentration of 14 μM.
Figure 10. 2,4-D extended dark phase degradation curve ran with a starting concentration of 68μM.
3.2 Photochemical degradation curves

Each photochemical run was preceded by a 30 minute dark phase reaction period to establish dark phase degradation. After 30 minutes, the vessel was irradiated at the experimental wavelength (260, 300, 330, 360 nm). Figures 11-14 below show photochemical degradation curves for 2,4-D, and Figures 16-29 show photochemical degradation curves for Atrazine. Once the solution was irradiated, 2,4-D took between .35 and .6 hours to reach an undetectable concentration, and Atrazine took from 1 hour to greater than 2 hours.

In addition, to gain a simplistic, qualitative understanding of the degradation curves for both 2,4-D and Atrazine, plots of the percentage of herbicide remaining in solution were compared for each experimental wavelength (Figures 15 and 20).
Figure 11. 2,4-D degradation with a 30 minute dark period followed by illumination at 260 nm.
Figure 12. 2,4-D degradation with a 30 minute dark period followed by illumination at 300 nm.
Figure 13. 2,4-D degradation with a 30 minute dark period followed by illumination at 330 nm.
Figure 14. 2,4-D degradation with a 30 minute dark period followed by illumination at 360 nm.
Figure 15. 2,4-D degradation curves at all studied wavelengths (260-360nm) plotted in terms of %herbicide remaining in solution vs. time.
Figure 15. 2,4-D degradation curves at all studied wavelengths (260-360nm) plotted in terms of %herbicide remaining in solution vs. time.
Figure 16. Atrazine degradation with a 30 minute dark period followed by illumination at 260 nm.
Figure 17. Atrazine degradation with a 30 minute dark period followed by illumination at 300 nm.
Figure 18. Atrazine degradation with a 28 minute dark period followed by illumination at 330 nm.
Figure 19. Atrazine degradation with a 30 minute dark period followed by illumination at 360 nm.
Figure 20. Summary of Atrazine degradation at all experimental wavelengths plotted as % Atrazine remaining in the experimental solution vs. time.
Figure 20. Summary of Atrazine degradation at all experimental wavelengths plotted as % Atrazine remaining in the experimental solution vs. time.
From Figures 11-20, it appears that, in our system, maximum 2,4-D and Atrazine degradation occurs at 300 nm. This finding agrees with previous studies conducted in the King lab (29). However, this is a simplistic analysis and does not account for wavelength dependent variations, quantum yield of FeOH$^{2+}$, or variation in the mechanism of herbicide degradation. Degradation of both herbicides is inherently non-linear in both light and dark degradation. To understand the processes behind the Fenton photochemical degradation of 2,4-D and Atrazine, kinetic models had to be constructed.

4. Discussion

4.1 Kinetic modeling

Dark phase degradation rates were significantly different for Atrazine and 2,4-D. Due to solubility differences between the two compounds, the initial concentrations were also different, 15µM for Atrazine and 65 µM for 2,4-D. A simple first or second order kinetic model is inappropriate for description of dark and light phase degradation. The production of free radical oxidants is inherently nonlinear as oxidants can react with numerous species.

To gain further insight into the dark phase degradation mechanisms, we developed kinetic models using the non-linear modeling software Stella 5.1.1. Figure 21 is a schematic diagram summarizing the major dark phase reactions in the model. Major reactions, equilibrium constants, and rate constants (M$^{-1}$s$^{-1}$) are summarized below (eq 35-44) and are represented in Figure 21.
\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ & k_1 = 0.02 \ (13) \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- & k_2 = 53 \ (22) \\
\text{HO}_2^- + \text{Fe}^{3+} & \rightarrow \text{O}_2 + \text{Fe}^{2+} + \text{H}^+ & k_3 = 1 \times 10^6 \ (22) \\
\text{HO}_2^- + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 + \text{H}^+ & k_4 = 1.2 \times 10^5 \ (22) \\
\text{HO}_2^- + \text{HO}_2^- & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 & k_5 = 8.3 \times 10^5 \ (22) \\
\text{Atrazine} + \text{OH}^- & \rightarrow \text{degradation products} & k_6 = 3 \times 10^9 \ (22) \\
\text{2,4-D} + \text{OH}^- & \rightarrow \text{degradation products} & k_7 = 3 \times 10^6 \ (41) \\
\text{Fe}^{3+} + \text{C}_2\text{O}_4^{2-} & \leftrightarrow \text{Fe} (\text{C}_2\text{O}_4)^+ & K_1 = 3.31 \times 10^6 \ (22) \\
\text{Fe}^{3+} + \text{H}_2\text{O} & \rightarrow \text{FeOH}^{2+} & K_2 = 4.57 \times 10^{-3} \ (22) \\
\text{HO}_2^- & \leftrightarrow \text{O}_2^- + \text{H}^+ & K_{\text{superox}} = 1.58 \times 10^{-5} \ (44)
\end{align*}
\]
Figure 21. Schematic diagram representing major reactions in kinetic model where the intersection of two lines represents two reactants coming together and arrow heads point to products. The upper left corner of the diagram represents Fe(III) speciation. The center of the diagram represents superoxide equilibration. The upper right corner represents Fe(II) production and decay. The bottom center represents herbicide decay.
Complete, continuous analytical solutions to equations 35-44 were possible using Stella modeling software; however, these solutions were only possible for simulated reactions of less than 15 minutes. To model the data for longer reaction times, a number of steady state approximations were made.

Superoxide is an intermediate product in the Fenton hydroxyl radical production pathway. It is a highly reactive species whose residence time is extremely short in our system (eq 37-39). As can be seen in reactions 35-41, the reactions in our system have vastly different rate constants. Looking at all of the reactions for superoxide production and consumption, it is possible to make a reasonable steady state estimate for superoxide. Because superoxide sources equal superoxide sinks, equation 45 follows from equations 35, 37, and 38.

\[
[Fe^{3+}] \times [H_2O_2] \times k_1 = [HO_2^-] \times [Fe^{3+}] \times k_3 + [HO_2^-]^2 \times k_4
\]  

(45)

With \([Fe^{3+}] = 0.001\), \([H_2O_2] = 0.0025\), \(k_1 = 0.02\), \(k_3 = 1 \times 10^6\), and \(k_4 = 1 \times 10^6\), equation 45 simplifies to equation 46:

\[
0.001 \times 0.0025 \times 0.02 = [HO_2^-] \times 0.001 \times 10^6 + [HO_2^-]^2 \times 1 \times 10^6
\]  

(46)

The hydroperoxyl radical, the protonated superoxide species \(HO_2^+\), is highly reactive and usually does not exist above nanomolar concentration. Thus, hydroperoxyl radical has a concentration of much less than 0.001 M, and the \([HO_2^-]^2 \times 10^6\) term becomes insignificant. Equation 46 then simplifies to equation 47.
\[ [\text{HO}_2^-] = 0.0025 \times 0.02 / 1 \times 10^6 = 5 \times 10^{-11} \text{ M/sec @ steady state} \] (47)

An additional superoxide sink comes from the combination of superoxide with Fe\(^{2+}\) to give Fe\(^{3+}\) (equation 38). This reaction was considered in the models; however, it was insignificant for superoxide loss because the reaction in equation 37 outcompeted the reaction in equation 38 by more than two orders of magnitude. This was due to the much higher concentration of Fe\(^{3+}\).

The dark phase Fenton photochemical reactions (equations 35-37) result in a net production of Fe(II). Because Fe(III) is at a high concentration relative to Fe(II), it was assumed to be constant throughout all reactions. Once a steady-state superoxide approximation is established, all of the necessary values exist to make dark phase Fe(II) flux approximations. Sources of Fe(II) are represented in equation 48, as follows:

\[ [\text{Fe(II)}] \times [\text{H}_2\text{O}_2] \times 0.02 + [\text{Fe(III)}] \times [\text{HO}_2^-] \times 1 \times 10^6 = 0.001(0.0025 \times 0.02 + 5 \times 10^{11} \times 10^6) = 1 \times 10^{-7} \] (48)

Using the dark phase flux approximations the kinetic model simulated continuous Fe(II) oxidation and herbicide concentrations. There are two competing reactions for Fe(II) loss, equations 36 and 38. Through equation 36, Fe(II) reacts to form hydroxyl radical, whereas equation 38 takes Fe(II) back to Fe(III) without generating a hydroxyl radical. These two reactions are in competition in the kinetic models creating steady state dark phase hydroxyl radical flux.
Herbicide molecules are broken down upon reaction with hydroxyl radical. However, all hydroxyl radicals in solution do not necessarily react with herbicide molecules. An additional hydroxyl radical sink comes from the reaction of hydroxyl radical with hydrogen peroxide (eq 49) (22).

\[
\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad k_{\text{OH}} = 2.7 \times 10^7 \quad (49)
\]

Competition between hydrogen peroxide and the herbicide for hydroxyl radicals was described in the kinetic model by a term called the herbicide fraction. Equation 50 describes the Atrazine fraction and equation 51 describes the general herbicide decay.

\[
f_{\text{Atrazine}} = \frac{[\text{Atrazine}] \cdot k_5}{[\text{Atrazine}] \cdot k_5 + [\text{H}_2\text{O}_2] \cdot k_{\text{OH}}} \quad (50)
\]

\[
\frac{d\text{Herbicide}}{dt} = \text{steadystate(OH}^-\text{)} \cdot f_{\text{Herbicide}} \quad (51)
\]

In our extended dark phase herbicide runs (Figures 9-10) 2,4-D degrades in approximately 1.2 hours whereas Atrazine takes about 7 hours. It was expected that this disparity was due to differences in initial herbicide concentration. Different herbicide concentrations will react with hydroxyl radical at different efficiencies as described in equation 50. Initial fitting of modeled dark phase degradation curves with experimental degradation curves indicated that the modeled dark phase degradation rate was too rapid for Atrazine. Upon reexamining the sources and sinks of our dark Fe(II) production rate, it was recognized that the \( k_1 \) rate constant is not well-established at varying pH levels. This rate constant also plays a major role in the dark phase production of Fe(II). We
found that, upon adjusting the k₁ value to 0.002, the modeled Atrazine dark phase degradation curve fit the extended Atrazine dark phase experimental run much better than when k₁ was equal to 0.02. The kinetic model fit (k₁ = 0.002) for the dark phase Atrazine degradation experimental results is shown in Figure 22 below. Changing the k₁ value by an entire order of magnitude (from 0.02 to 0.002) resulted in a more accurate curve fit for the Atrazine. However, the modeled dark phase degradation for 2,4-D was significantly slower than the extended 2,4-D dark phase experimental result. The dark phase 2,4-D decay was accurately modeled at a k₁ equal to 0.005 (Figure 23).

Dark phase hydroxyl radical production should be the same for both Atrazine and 2,4-D, as hydroxyl radical production is independent of the herbicide in solution. Thus, we would expect both Atrazine and 2,4-D to fit equally well under the same dark phase model. When the 2,4-D model was run at an initial concentration of 15 μM, the starting concentration for Atrazine dark decay, it was found that the two herbicides did not degrade in the dark Fenton system at the same rate. Because the model does not accurately reproduce the data of both herbicides at a given k₁ value, either there was significant experimental error within the system or there was a fault in the model.
Figure 22. Kinetic model fitting for Atrazine dark phase degradation. The solid line represents the kinetic model's curve fit.
Figure 23. Kinetic model fitting ($k_1 = 0.005$) for 2,4-D extended dark phase degradation experiment.
Expanding our analysis of dark phase degradation to include all data sets, including the 30 minute dark period before each photochemical reaction, it was found that the extended dark phase 2,4-D degradation rate is much more rapid. Replicate 2,4-D dark phase experiments showed differences in degradation rates greater than uncertainty. The 30 minute dark reaction period measurements show inconsistencies, which we attributed to Fe(II) contamination in the initial solutions. Despite these inconsistencies, the pooled 30 minute dark reaction data for 2,4-D fit well (Figure 24) using $k_1$ equal to 0.002 (the same as for Atrazine).
Figure 24. Kinetic model fit for 2,4-D using $k_1$ values of 0.002 and 0.005. The graph shows a better fit for $k_1=0.002$ than 0.005. After 0.5 hours of dark phase decay, the UV lamp is turned on and the dark phase decay is no longer distinguishable light phase decay.
Figure 24. Kinetic model fit for 2,4-D using $k_1$ values of 0.002 and 0.005. The graph shows a better fit for $k_1=0.002$ than 0.005. After 0.5 hours of dark phase decay, the UV lamp is turned on and the dark phase decay is no longer distinguishable light phase decay.
4.2 Light phase kinetic modeling for Atrazine

The model also needs to consider the photochemical reactions. As FeOH\(^{2+}\) is the photoreactive species that produces hydroxyl radicals, determination of the fraction of FeOH\(^{+}\) (equation 20) in solution was necessary for the models. The fraction of Fe\(^{3+}\) in solution was set equal to one minus the fraction of FeOH\(^{2+}\) in solution in our models, as these are the dominant species (20). The absorbance for Fe\(^{3+}\) and FeOH\(^{2+}\) was calculated in the models by multiplying the fraction of each ion in solution by the total Fe(III) concentration and the molar absorptivity for each ion. Molar absorptivity for FeOH\(^{2+}\) and Fe\(^{3+}\) as a function of pH is plotted in Figure 25 below. The fraction of FeOH\(^{2+}\) absorbing photons is evaluated by dividing the absorbance of FeOH\(^{2+}\) by the absorbance of both species (see equation 31). The photochemical rate follows, as shown in equation 52 below, where I represents the photon flux, V represents the volume of the reaction vessel, and Φ represents quantum yield.

\[ f_{\text{FeOH}^{2+}} \times I \times \Phi / V = \text{photochemical } \cdot \text{OH and Fe(II) production rate} \quad (52) \]

Quantum yield values for FeOH\(^{2+}\) were taken from King (unpublished) and held constant at 0.2 regardless of wavelength.

Figures 26-29 show the kinetic model fit for the experimental photochemical Atrazine degradation at all studied wavelengths.
Figure 25. Plot of molar absorptivity vs. wavelength for Fe$^{3+}$ and FeOH$^{2+}$. Values are taken from Brown and Kester (reference 28).
Figure 26. Kinetic model fit \((k_1 = 0.002)\) for Atrazine experimental degradation run at 260 nm.
Figure 27. Kinetic model fit \((k_1 = 0.002)\) for Atrazine experimental degradation run at 300 nm.
Figure 28. Kinetic model fit ($k_1 = 0.002$) for Atrazine experimental degradation run at 330 nm.
Figure 29. Kinetic model fit \( (k_1 = 0.002) \) for Atrazine experimental degradation run at 360 nm.
Light phase kinetic models accurately fit Atrazine experimental data at wavelengths of 260 nm, 300 nm, 330 nm, and 360 nm. An important measure of the model’s prediction ability is the photochemical enhancement. This enhancement controls the angle between the curves representing the dark phase and light phase degradation rates on the above Figures. The kinetic model accurately accounts for not only the photochemical degradation rate, but also the photochemical enhancement.

4.3 Light phase kinetic modeling for 2,4-D

An additional Fe(III) complexing species comes into play during 2,4-D degradation. When 'OH reacts with 2,4-D oxalate is formed as an intermediate degradation product, as shown in Figure 30 below (17).

![Figure 30. Oxalate production resulting from 2,4-D degradation.](image)

Work by Sun and Pignatello (17) has suggested a mechanism (Figure 31) for the major degradation pathway for the complete mineralization of 2,4-D. This mechanism also includes a direct Fe(III)-2,4-D complex that is photoreactive. However, it does not fully account for oxalate formation, which is clearly observed in preliminary product distribution studies (29).
Figure 31. Pathway for 2,4-D mineralization (reference 17).
To further explore the formation of oxalate from 2,4-D degradation, a Facui calculation was run using Spartan molecular mechanics software. Using Hartree-Fock theory and the STO-3G basis set, orbital coefficients were determined for the minimized +1 and -1 structures of 2,4-D. Subtracting the +1 HOMO orbital coefficients from the -1 HOMO orbital coefficients elucidated the atoms on the structure of 2,4-D that show the greatest difference in electron density. This indicates the area in which a radical, such as the hydroxyl radical, would be mostly likely to attack. The Facui calculation showed the greatest change in electron density on both the carbon 1 atom and the oxygen 1 atom. This implies that the hydroxyl radical is prone to attack 2,4-D along the bond between the carbon 1 and the oxygen 1 that connects the major branch, the acetate group, to the phenyl ring producing a radical phenyl group and oxalate.

As described in section 1.8, oxalate quickly complexes with Fe$^{3+}$ to form FeOx$^+$, which has photoreactive properties such that it forms Fe$^{2+}$ and eventually hydroxyl radical when it is exposed to light. Balmer (20) published the mechanism for FeOx$^+$ degradation to hydroxyl radical (Figure 32). Once in the excited state, FeOx$^+$ cleaves at the Fe-O bond to form oxalate radical and Fe$^{2+}$. Oxalate radical then combines with molecular oxygen to form superoxide, which goes on to react and form hydroxyl radical.
Figure 32. Reaction mechanism for FeOx⁺(20).

The kinetic model for 2,4-D is different from the Atrazine model in that it incorporates FeOx⁺ absorbance, quantum yield, and concentration as additional modeling components. The fraction of FeOx⁺ absorbing photons equals the absorbance of FeOx⁺ divided by the sum of the absorbances of FeOx⁺, Fe³⁺, and FeOH²⁺ (eq 53).

$$fA_{FeOx'} = \frac{A_{FeOx'}}{A_{Fe(OH)^+}} = \frac{\varepsilon_{FeOx'} \alpha_{FeOx'} [T_{Fe}]}{\varepsilon_{Fe(OH)^+} \alpha_{Fe(OH)^+} [T_{Fe(III)}] + \varepsilon_{Fe^3} \alpha_{Fe^3} [T_{Fe(III)}] + [T_{(O)}] \varepsilon_{FeOx'}}$$

(eq 53)

The fraction of FeOH²⁺ absorbing photons is represented by equation 31, which was described above. The overall photochemical rate changes in that the product of the fraction of FeOx⁺ absorbing photons and the quantum yield for FeOx⁺ are added to the numerator of equation 52 as shown below (54).
\[ 1^* (f_{FeOx} + \Phi_{FeOx^+} + f_{FeOH^2+} + \Phi_{FeOH^2^+})/V = \text{photochemical OH rate} \quad (54) \]

The 2,4-D solutions visibly change color from colorless before photolysis to light yellow following the photochemical experimental runs. This can be attributed to the formation of oxalate in solution (29). Figures 33-36 show the curves for the kinetic fitting of each photochemical experiment.
Figure 33. Kinetic model fit ($k_1 = 0.002$) for 2,4-D experimental degradation run at 260 nm.
Figure 34. Kinetic model fit ($k_1 = 0.002$) for 2,4-D experimental degradation run at 300 nm.
Figure 35. Kinetic model fit ($k_1 = 0.002$) for 2,4-D experimental degradation run at 330 nm.
Figure 36. Kinetic model fit (k1 = 0.002) for 2,4-D experimental degradation run at 360 nm. UV lamp on at 0.58 hours.
The light phase kinetic model for 2,4-D represents the shape, profile, and half life of the experimental data at wavelengths of 300 nm, 330 nm, and 360 nm. The model did not accurately fit degradation at 260 nm.

5. Conclusions

A detailed model accounting for speciation, dark and light phase Fenton chemistry, and intermediate degradation products was developed and compared to herbicide degradation experiments. A detailed mechanistic approach appears successful in predicting degradation rates; however, we have not fully tested the system. We have worked at optimum pH, but we have not tested the model over a varying pH range. The same is true for photon flux variations. The model also held quantum yield constant over all wavelengths. This assumption needs to be examined further.

Modeling was less accurate for 2,4-D than for Atrazine. The role of oxalate radical reactions and oxalate concentration was not independently explored. In our kinetic model, when 2,4-D reacts with hydroxyl radical, oxalate is formed. The oxalate then complexes with Fe^{3+} to form FeOx^{+}. Once in the excited state, the kinetic model made the approximation that all FeOx^{+} that decays and breaks the Fe-O bond immediately produces hydroxyl radical. However, this decay actually produces Fe(II) and superoxide, both of which go on to produce hydroxyl radical. It does not directly form hydroxyl radical.

In addition, photochemical experiments measured herbicide loss, not the full mineralization of the herbicides, which is the ultimate goal in using the Fenton
photochemical system for herbicide remediation. The focus on herbicide loss rather than complete mineralization required the simplified assumption that a single hydroxyl radical breaks an herbicide molecule to a form that does not react with hydroxyl radical. In reality, a single hydroxyl radical breaks a single bond. In the case of 2,4-D, this bond usually results in an oxalate species and a radical phenyl group.

The $k_1$ value used in the kinetic models appears to be inaccurate for our system. Values for $k_1$ equal to 0.002 seem to work better for the dark phase models than the literature value of 0.02.

While our modeling efforts were reasonably effective in predicting concentrations within our experimental system, they proved more useful in establishing a mechanistic understanding for pointing to future work.

6. Future Work:

The most significant problem encountered in this study involved dark phase herbicide degradation. The extended dark phase experiments for 2,4-D were not consistent with the 30 minute dark phase reactions prior to irradiation. Atrazine and 2,4-D dark phase degradation rates should be the same, as the production of hydroxyl radical is independent of the organic species that the hydroxyl radical goes on to degrade. Further comparative studies into 2,4-D and Atrazine dark phase degradation rates are necessary to clarify current questions surrounding dark phase kinetic modeling. Future work should emphasize clear and reproducible dark phase 2,4-D and Atrazine degradation curves before moving on to the photochemical reactions. In addition, an
evaluation of published $k_1$ values should be conducted to further consider its values at varying pH.

Analytical studies should be conducted not only at varying wavelengths, but also at varying pH and Fe(III) concentrations. Environmental soil and water conditions do not consistently have a pH of 2.4. Thus, further exploring the system's remediation performance at non-ideal pH levels is necessary. Adding oxalate to the solution, proven to complex with Fe(III) to give a species with a high quantum yield for hydroxyl radical production, would further elucidate the contribution of oxalate to the Fenton photochemical system.

Further studies could also be directed at the role of organic scavengers in the system. This would entail characterization of other possible sinks for the hydroxyl radical in the system, which would give information for more detailed modeling of all species in solution contributing to hydroxyl radical loss.

With the upcoming addition of an LC-MS at Colby, intermediate degradation products could be analyzed. This would grant insight into the flux of hydroxyl radical production necessary to fully mineralize a given concentration of Atrazine or 2,4-D.

Coupling photochemical studies with Flow Injection Analysis systems currently in design in the King lab to measure superoxide and Fe(II) concentrations below nanomolar concentrations could be used to test the steady-state superoxide approximations made in the kinetic models. Running a Fenton photochemical system in the absence of additional organic species (herbicides) using this type of FIA system would give insight into superoxide and Fe(II) concentrations. Combined with the use of LC-MS, we could monitor herbicide loss, superoxide and Fe(II) concentration, and
intermediate species production and decay. This would allow for a more complete picture for constructing kinetic models.

The ultimate goal of this research is to be able to understand the degradation of Atrazine and 2,4-D in the environment. This requires a detailed mechanistic description in order to generate an action spectrum, which is a plot of chemical reactivity as a function of wavelength incorporating in situ photon flux and all light and dark reactions. Establishing an action spectrum requires the combination of the solar spectrum with the Fenton photochemical system mechanisms and wavelength dependencies. This information could then be used to understand herbicide degradation in a pond or other water body. Wavelength, distribution, intensity, and degradation rates control surface degradation by hydroxyl radical as well as secondary photoreactive species. In addition, combining wavelength, distribution through the water column, intensity, and light attenuation would allow for a greater understanding of how an herbicide degrades through an entire water body.
References:


(3) Rowland, J., 2,4-Dichlorophenoxyacetic Acid: Review of a Chronic Toxicity/Carcinogenicity Study in Rats, a Carcinogenicity Study in Mice, and a Re-review of a Developmental Toxicity Study in Rats. EPA Memorandum. 1996.


(5) EPA, Health Effects Division, Carcinogenicity Peer Review Committee report on 2,4-D, January 29, 1997.


