Reductive degradation of azo dyes in aqueous solution by zero-valent iron

T. BIGG & S. J. JUDD
School of Water Sciences, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK
e-mail: s.j.judd@cranfield.ac.uk

Abstract Kinetics of zero-valent iron remediation of two azo dyes in aqueous solution were investigated. Both show pseudo first-order reaction kinetics. Typical apparent reaction rate constants \( k \) are 0.70 min\(^{-1}\) at 33.3 revolutions per second. \( k \) decreases with both increased pH and initial dissolved oxygen content increased over 5 mg l\(^{-1}\), but increases with both increasing iron concentration and mixing speed. The increase with iron concentration is linear at \( 3 \times 10^{-3} \) mg l\(^{-1}\) correlation. \( k \) increases linearly with the inverse square root of mixing speed—corresponding directly with increasing \( k \) with decreasing thickness of adhering boundary layer. Half-lives correlate well with values reported in the literature. The mass transfer limitation and surface dependency of these heterogeneous reactions is demonstrated.

Key words azo linkages; kinetics; mass transfer; passivation; zero-valent iron

NOTATION

\[
\begin{align*}
A & : \text{surface area (m}^2) \\
c_{DO} & : \text{initial dissolved oxygen concentration (mg l}^{-1}) \\
d_{imp} & : \text{diameter of impellor (m)} \\
d_{p} & : \text{diameter of reacting particle (m)} \\
f & : \text{mixing speed frequency (Hz or rpm)} \\
k & : \text{overall first order reaction rate constant (min}^{-1}) \\
K & : \text{mass transfer coefficient (m s}^{-1}) \\
k_{\text{chemical}} & : \text{non-mass-transfer limited (chemical) rate constant (min}^{-1}) \\
k_{MT} & : \text{mass transfer rate constant (min}^{-1}) \\
Re & : \text{Reynolds number} \\
Sc & : \text{Schmit number} \\
V & : \text{tank volume (m}^3) \\
\mu & : \text{dynamic viscosity (kg m}^{-1} \text{s}^{-1}) \\
\rho & : \text{mass density of the liquid (kg m}^{-3})
\end{align*}
\]

INTRODUCTION

Conventional methods for treating dye wastes are biological, physical and chemical. Specific examples include treatment by micro-organisms, adsorption onto activated carbon, and ozonation, but each of these methods has known shortcomings.

Zero-valent iron (Fe\(^{0}\)) is an effective reducing agent. It is easy to obtain and inexpensive, especially as scrap. Studies on reductive degradation of organic compounds have attracted increasing interest over the past decade (Bigg & Judd,
2000), and the practical application of Fe$^0$ to groundwater treatment has reached full scale (Appleton, 1996). When treated by Fe$^0$, azo dyes can be decolourized (Cao et al., 1999) and made more biodegradable (Tan et al., 1999) by destruction of the N=N chromophore (Fig. 1). The overall degradation reaction is a redox type, in which the reduction of the azo dye takes place concomitantly with the oxidation of Fe$^0$ to ferrous ion, and generates amino products.

![Chemical structure of Acid Orange II and Sulfanilic Acid](image)

**Fig. 1** Degradation mechanism of Acid Orange II in Fe$^0$-H$_2$O system.

**MATERIALS AND METHOD**

The kinetics of the reductive degradation of Acid Orange II (AOII) and Acid Blue 113 (AB113) were studied. Degradation was performed in a series of controlled experiments based on a fluidized bed system containing 5.4 l of aqueous dye solution under anoxic and pH controlled conditions (Fig. 2). System conditions are summarized in Table 1.

Decolourization was followed spectrophotometrically (Jenway 6505 UV-Vis Spectrophotometer) during the course of the reaction. pH, ORP and dissolved oxygen content (DO) were monitored with time (Jenway 3340 ion meter and Jenway 9300 dissolved oxygen meter). The effects of mixing speed, iron concentration and initial DO on the kinetics were specifically investigated, to assess the relative contributions of chemical and mass transfer process limitation.

![Schematic diagram of the fluidized bed system](image)

**Fig. 2** Schematic diagram of the fluidized bed system. A sampling point; D dissolved oxygen probe; I impeller; M overhead mixer; N N$_2$ purge; O ORP probe; P pH probe; W water bath; V reactor vessel.
Table 1 Base system conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor type</td>
<td>5.4 l anoxic fluidized bed with 57 mm diameter impeller</td>
</tr>
<tr>
<td>pH</td>
<td>5.8 ± 0.5</td>
</tr>
<tr>
<td>Dissolved oxygen (mg l⁻¹)</td>
<td>0</td>
</tr>
<tr>
<td>Fe⁰ type and source</td>
<td>40–53 μm 90% Fe⁰ powder (P&amp;R Lab. Supplies, St Helens, UK)</td>
</tr>
<tr>
<td>Method of Fe⁰ treatment</td>
<td>Degreasing with methylated spirits then ethanol for 1 min each</td>
</tr>
<tr>
<td>Temperature in reactor (°C)</td>
<td>17.7 ± 1.3</td>
</tr>
<tr>
<td>Mixing speed range (Hz)</td>
<td>13.3 to 33.3 ± 0.1</td>
</tr>
<tr>
<td>Fe⁰ concentration range (mg l⁻¹)</td>
<td>231.5 to 23150</td>
</tr>
<tr>
<td>Fe⁰ specific surface area (m² g⁻¹)</td>
<td>0.5 to 1.0</td>
</tr>
<tr>
<td>Diffusion coefficient, D (m² s⁻¹)</td>
<td>3.035 × 10⁻¹⁰ (AB113) 4.537 × 10⁻¹⁰ (AOII)</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Greater than 90% reduction in absorbance were achieved in a few minutes. Five to ten replicates of each run demonstrated that reproducibility for the rate constant values was generally within ±15%. A lag period was noted, lasting up to ~1.5 min and preceded apparent first order decay (Fig. 3).

The reductive degradation of both dyes obeys pseudo-first order reaction kinetics from the end of the lag phase onwards:

\[ \ln \frac{c}{c_0} = -kt \]

where \( k \) is apparent reaction rate constant, \( c_0 \) and \( c \) are the respective dye concentration values initially and at time \( t \). Degradation rates increase both with increasing mixing rates and iron concentration (Table 2) suggesting mass transfer limitation.

According to simple mass transfer theory:

\[ \text{mass transfer rate} = KA(c - c^e) \]

where, \( A \) is total area available for mass transfer, \( c^e \) is concentration at the iron surface and \( K \) is mass transfer coefficient. It follows that, for total mass transfer limitation where

Fig. 3 First-order decay plots at 23150 mg l⁻¹ Fe⁰ reacted with 7 mg l⁻¹ dye at 800 and 2000 rpm, 18°C and 0 mg l⁻¹ DO. The gradients give the rate constant, \( k \) (min⁻¹).
Table 2 Reaction rates at different mixing speeds and iron concentrations for two azo dyes.

<table>
<thead>
<tr>
<th>Study</th>
<th>Dye</th>
<th>Mixing speed (rpm)</th>
<th>Iron conc. (mg l⁻¹)</th>
<th>(k) (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Acid Blue 113</td>
<td>800</td>
<td>23 148</td>
<td>0.215</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Blue 113</td>
<td>1200</td>
<td>23 148</td>
<td>0.26</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Blue 113</td>
<td>1600</td>
<td>23 148</td>
<td>0.44</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Blue 113</td>
<td>1800</td>
<td>23 148</td>
<td>0.55</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Blue 113</td>
<td>2000</td>
<td>23 148</td>
<td>0.6935</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Blue 113</td>
<td>2000</td>
<td>231.5</td>
<td>0.033</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Blue 113</td>
<td>2000</td>
<td>11 600</td>
<td>0.29</td>
</tr>
<tr>
<td>Nam &amp; Tratnyek (2000)</td>
<td>Acid Blue 113</td>
<td>100</td>
<td>143 000</td>
<td>0.064</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Orange II</td>
<td>800</td>
<td>23 148</td>
<td>0.14</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Orange II</td>
<td>1200</td>
<td>23 148</td>
<td>0.253</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Orange II</td>
<td>1600</td>
<td>23 148</td>
<td>0.30</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Orange II</td>
<td>2000</td>
<td>23 148</td>
<td>0.735</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Orange II</td>
<td>2000</td>
<td>11 600</td>
<td>0.43</td>
</tr>
<tr>
<td>This study</td>
<td>Acid Orange II</td>
<td>2000</td>
<td>7 870</td>
<td>0.35</td>
</tr>
<tr>
<td>Nam &amp; Tratnyek (2000)</td>
<td>Acid Orange II</td>
<td>100</td>
<td>143 000</td>
<td>0.161</td>
</tr>
<tr>
<td>Nam &amp; Tratnyek (2000)</td>
<td>Acid Orange II</td>
<td>120</td>
<td>143 000</td>
<td>0.245</td>
</tr>
<tr>
<td>Nam &amp; Tratnyek (2000)</td>
<td>Acid Orange II</td>
<td>130</td>
<td>143 000</td>
<td>0.306</td>
</tr>
<tr>
<td>Nam &amp; Tratnyek (2000)</td>
<td>Acid Orange II</td>
<td>140</td>
<td>143 000</td>
<td>0.380</td>
</tr>
</tbody>
</table>

the chemical reaction instantaneously reduces \(c^*\) to 0, equation (2) becomes, on integration:

\[
\ln \frac{c}{c_0} = -\frac{KA}{V} t
\]

Hence, according to equations (1) and (3):

\[
K = \frac{kV}{A} \quad (4)
\]

Rate constants were found to increase both with increasing mixing speeds (Table 2) and increasing iron concentration (from 0.35 min⁻¹ at 7870 mg l⁻¹ to 0.73 min⁻¹ at 23 148 mg l⁻¹ for Acid Orange II, according to Fig. 4). According to the recorded data:

\[
k\ (\text{min}^{-1}) = 3.0 \times 10^5 c \ (\text{mg l}^{-1}) + 0.14 \quad (R^2 = 0.999), \text{Acid Orange II, and}
\]

\[
k\ (\text{min}^{-1}) = 3.0 \times 10^5 c \ (\text{mg l}^{-1}) + 0.002 \quad (R^2 = 0.98), \text{Acid Blue 113.}
\]

\(k\) appears to follow an inverse square-root relationship with mixing speed (Fig. 5) as is evident in previously reported data by Nam & Tratnyek (2000). According to these data:

\[
k^-1\ (\text{min}) = 659.0 f^{\frac{1}{2}} \ (\text{rpm}) - 13.3 \quad (R^2 = 0.998), \text{Acid Orange II, this study, cf.}
\]

\[
k^-1\ (\text{min}) = 227.6 f^{\frac{1}{2}} \ (\text{rpm}) - 16.6 \quad (R^2 = 0.998), \text{Acid Orange II, Nam & Tratnyek}
\]

\[
k^-1\ (\text{min}) = 254.5 f^{\frac{1}{2}} \ (\text{rpm}) - 4.1 \quad (R^2 = 0.94), \text{Acid Blue 113, this study.}
\]

The large difference in the proportionality coefficient for the two studies may indicate the influence of the reactor system itself. Nam & Tratnyek (2000) employed a small reaction volume (0.007 l) and high iron concentration (140 000 mg l⁻¹), with a dye concentration of 105.1 mg l⁻¹ in an orbital shaker, making reported rpm values incomparable. The negative apparent intercept value appears similar for the two studies.

This relationship between \(k\) and stirrer speed \(f\) is indicative of mass transfer control. Since, from equation (4), \(k \propto K\). Moreover, rate constants are inversely additive, hence:
Reductive degradation of azo dyes in aqueous solution by zero-valent iron

Fig. 4 $k$ ($\text{min}^{-1}$), with iron concentration and inverse of $k$ with Sherwood number for both dyes. Each coordinate is a mean of duplicate runs. Arrows indicate axis to read.

Fig. 5 $k^{-1}$ vs inverse square root of rotational speed ($f^{-0.5}$).

\[
\frac{1}{k} = \frac{1}{k_{MT}} + \frac{1}{k_{\text{chemical}}} \tag{5}
\]

where $k_{MT}$ refers to the mass transfer-limited component and $k_{\text{chemical}}$ to the chemical reaction. The noted inverse-root relationship derives from mass-transfer control, since:

\[
k \propto K = \text{Sh}D/d \tag{6}
\]

\[
\text{Sh} (\text{Re}, \text{Sc}) \tag{7}
\]

where Sh is the Sherwood number, Re the Reynolds number, Sc the Schmidt number, $d$ the representative linear dimension of the system. Values for $D$ (Table 1) were taken from the literature (Nam & Tratnyek, 2000).

The most appropriate expression Sherwood number in terms of the Schmidt and Reynolds numbers in a fluidized bed is (Hayhurst, 2000):

\[
\text{Sh} = 0.69 \text{Re}^{0.5} \text{Sc}^{0.3} \tag{8}
\]
where the Schmidt is the ratio of kinematic viscosity to diffusion coefficient and the
Reynold's number, for a vigorously-stirred turbulent system is given by:
\[
Re = \frac{(d_{imp})^2 \rho f}{\mu}
\]
(9)

where \(d_{imp}\) is the impeller blade width and \(f\) takes SI units of revolutions per second. It
follows from equations (4), (8) and (9) that \(k_M f \propto f^{0.5}\), and hence, according to
equation (5), \(k^1 f^{0.5}\). However, the large negative intercept appears inconsistent: one
would expect a positive intercept representing the inverse chemical rate constant
attained at infinite mass transfer. Surprisingly, with the exception of Nam & Tratnyek
(2000), there appears to have been no recognition of the mass transfer limitation of this
system reported in the literature on similar metallic iron decolourization systems (Cao
et al., 1999).

If \(d\) is represented by \(d_{imp}\), comparison of the empirical and experimental
Sherwood numbers reveals that data for both dyes give near identical linear trend lines
(Fig. 6), but with a small over-prediction of absolute mass transfer value:
\[
Sh_{exp} = 0.751 Sh_{emp} - 3926 \quad (R^2 = 0.93)
\]

The most likely reason for the discrepancy is the assumption made about \(A\). It has
been assumed that the chemical reaction takes place across the entire surface area of
the powder. In fact a number of factors must be considered. Chemical reaction is
limited if a hydrophobic coating, such as grease, insulates the iron from the solution, or
if a corrosion product layer at the metal–water interface acts as a non-conductive
physical barrier to mass transport allowing electron transfer from metal to dissolved
dye through defects (Scherer et al., 1999). This protection is not electrical insulation,
since passive films have some electronic conductivity (Scully, 1990). The observations
of this study (Fig. 7) do not support the proposed role of the oxide layer as a semi-
conductor (Balko & Tratnyek, 1998). This may be due to the layer being produced
directly and forming on the metal surface, rather than indirectly as in the presence of
chloride ions (Shreir, 1976). Both factors will influence the overall reaction rate, and
can be qualitatively assessed by altering Fe° pretreatment and/or operating under

![Fig. 6 Relationship between experimental and empirical Sh for both dyes.](image)
Reductive degradation of azo dyes in aqueous solution by zero-valent iron conditions promoting oxidative passivation of its surface. Alcohol pretreatment of Fe⁰ prior to remediations increased reproducibility while moderately decreasing the mean $k$ from 0.35 min⁻¹ to 0.30 min⁻¹.

Oxidative passivation is influenced both by pH and initial DO ($c_{DO}$). According to the experimental data (Fig. 7), $k$ follows the relationships given in the figure for Acid Orange II at an iron concentration of 23 148 mg l⁻¹ and a mixing speed of 2000 rpm.

The reaction is strongly influenced by pH over the range investigated (1.4 - 9.6) and is sensitive to the DO level, with no discernible reaction taking place in saturated solutions and little apparent change in reaction rate between 0 and 5 mg l⁻¹. The first stage of iron passivation, a thin insoluble layer forming on the Fe⁰ surface (Shreir, 1976), appears to significantly effect reaction rate above 5 mg l⁻¹ DO. Below this level there is insufficient potential change sufficient excess of Fe⁰ for the overall reaction rate to be unaffected by the spent portion.

![Dissolved Oxygen (mg/l)](image)

**Fig. 7** Effect of $c_{DO}$ and pH on $k$ for AB113 (8 mg l⁻¹) and Fe⁰ powder (23 150 mg l⁻¹), HEPES buffered (833 mg l⁻¹) to pH 6, 2000 rpm, 20°C.

![Rate Constant, K (mg/l)](image)

**Fig. 8** Change in reaction rate with pH at different levels of dissolved oxygen.
Investigating the effect of pH at a range of $c_{DO}$ reveals that high values of $c_{DO}$ ($>10 \text{ mg l}^{-1}$) inhibit reaction at all pHs and that the effect is most marked at high pH. Figure 8 shows that to some extent the inhibitory effect of DO can be overcome by lowering the pH as $k$ at pH 3 with 20 mg l$^{-1}$ $c_{DO}$ is similar to $k$ at pH 6 with 10 mg l$^{-1}$ $c_{DO}$. At high DO values the inhibitory effect is such that there is little change in $k$ regardless of the change in pH. At high pH the effect is such that $k$ is little changed regardless of the change in DO.

CONCLUSIONS

Under the conditions described the azo dyes AOII and AB113 are 90% decolourized by Fe$^0$ in less than five minutes, according to first order kinetics, with a rate constant $k$ of ~0.7 min$^{-1}$. The rate-determining step is in the transfer of dye to the metal surface: the process is mass transfer limited. Increasing mixing speed or iron concentration increases $k$. For AOII, the inverse rate constant increases linearly with the inverse square root of mixing speed according to $k^{-1} (\text{min}) = 659.0 f^{-1/2} (\text{rpm}) - 13.3$ ($R^2 = 0.998$) and $k$ increases linearly with increasing iron concentration according to $k = 3 \times 10^{-5} (\text{mg l}^{-1}) + 0.21$ ($R^2 = 0.99$). At 26.7 Hz stirrer speed half-lives compare well to values reported by Cao et al. (1999). Comparison of the actual trend for inverse rate constant vs inverse root $f$ reveals substantial differences between data from this study and that of Nam & Tratnyek (2000). This has been attributed to differences in system design, including the agitation method, reaction volume and the dye:iron concentration ratio. The experimental Sherwood number is somewhat less than that derived empirically through an expression in terms of the system Reynolds and Schmidt numbers (Hayhurst, 2000). This has been attributed to surface passivation, which is highly sensitive to DO, with the reaction being effectively nullified at 20 mg l$^{-1}$.

Acknowledgements The authors gratefully acknowledge sponsorship from the EPSRC.

REFERENCES