Kinetics of Dye Oxidation by Fenton’s Reaction

Introduction

One of the important parameters associated with the success of an environmental treatment or remediation operation is the kinetics of the process (e.g., how fast a compound will degrade). This parameter is taken into consideration after a thermodynamic analysis reveals that the process can technically work.

Chemical oxidation using a variety of oxidants (e.g., chlorine, ozone, and hydrogen peroxide) is used to transform recalcitrant compounds into less toxic or more easily biodegradable products. One such chemical oxidation approach involves the addition of H$_2$O$_2$ and ferrous ion in solution, traditionally called Fenton’s reaction (Rajeshwar and Ibanez, 1997). Although numerous reactions occur upon the addition of Fenton’s reagents, the most desirable reaction involves the formation of •OH radicals,

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + •OH
\]  

(1)

•OH is a strong oxidizing agent and it decomposes variety of organic compounds.

This experiment involves evaluating the kinetics of oxidation of a dye using Fenton’s reaction. Groundwater and industrial wastewater can be polluted by organic dyes that come from the textile, paper, food, and other chemical industries. The procedure outlined can be applied to various other types of chemical contaminants that can be detected using UV-VIS spectrophotometry.

Safety Requirements

EYE PROTECTION must be worn when working in the lab.

Procedure

NOTE: Students are to work in groups of 5 for this lab.

1. Using a 100-ml graduated cylinder, transfer 80 ml of tap water in a 100-ml beaker.

2. Add two drops of dye to the beaker.

3. Place the stirrer bar in the beaker and place the beaker on the stirrer plate.

4. Mix the solution to obtain a uniform color of dye.
5. Immerse the fiber optic dip probe into the solution. The probe is extremely sensitive and prone to cracking, so take care in immersing the probe.

6. Set the UV-VIS spectrophotometer to gather absorbance readings at 0.1 second intervals for 2 minutes at a wavelength of 627.3 nm. (Note that prior to this, the instructor has subtracted the background absorbance obtained using tap water). Set the spectrophotometer to save the data as an ASCII (*.cvs) file.

7. Start gathering absorbance readings.

8. Add 2 ml of 3% H₂O₂ solution after about 0.1 minute.

9. Add 2 ml of a 50 g/L ferrous ammonium sulfate solution after about 0.5 minute.

10. Transfer the data to a diskette.

11. Perform the test in duplicate.

Data Analysis and Calculations

In Excel, plot the absorbance as a function of time as shown in Figure 1.

![Figure 1. Typical absorbance versus time plot.](image)

For this particular test, the addition of H₂O₂ after about 0.1 minute did not decrease the absorbance of the dye solution, indicating minimal oxidation occurring with H₂O₂. After addition of Fe²⁺, rapid oxidation is detected as shown by the decrease in the absorbance of the dye.
To obtain the kinetic parameters for an \( n \)-th-order irreversible reaction,

1. Calculate the initial concentration by taking the average absorbance readings before \( Fe^{2+} \) addition.

2. Equation (2) describes an \( n \)-th-order irreversible reaction.

\[
\frac{dA}{dt} = -kA^n
\]  

(2)

where \( A \) is the absorbance; \( t \) is time; \( k \) is the reaction coefficient, and \( n \) is the reaction order. Equation (2) can be integrated to obtain (Schmidt, 1998),

\[
A(t) = A_o \left[ 1 + (n-1)kA_o^{n-1}/t \right]^{1/n}
\]  

(3)

where \( A_o \) is the initial concentration. Note that equation (3) is not valid for \( n=1 \).

3. Using an Excel spreadsheet, input the absorbance data \( A(t) \) in column 1. In column 2, input the time normalized to the time of \( Fe^{2+} \) addition (i.e., \( t - t_{Fe} \)). The first data in column 2 should be zero. For both columns, use the data between the time of \( Fe^{2+} \) addition and the lowest point.

4. Specify two cells in Excel to contain initial guesses for \( k \) and \( n \). Using these initial guesses, calculate the predicted \( A^*(t) \) using equation (3).

5. Calculate the square of the differences in the predictions and data in one column, i.e., \( (A(t) - A^*(t))^2 \).

6. In one cell of Excel, calculate the total sum of the square of the differences of the errors.

7. Using the Tool/Solver function in the toolbar of Excel, minimize the error by changing \( k \) and \( n \). Obtain the values for \( k \) and \( n \). Note that you may have to assign different initial values to obtain final values for \( k \) and \( n \). You should not obtain any \#NUM! in your cells.

8. A copy of the Excel spreadsheet used for a sample test is posted on the web site.

9. Take the average of the \( k \) and \( n \) values obtained for the duplicate test.

**Scenario for Memo**

A client has an industrial wastewater that contains significant amounts of blue dye in the effluent (the one you tested in the lab). Convince your client that you can treat his wastewater. Based on the kinetic parameters and the average initial absorbance of the dye obtained by your group, determine the required volume of a CSTR and a PFR to remove 99% of the absorbance from the effluent assuming a flowrate of 10 million gallons per day (10 mgd).
References


Data Sheet

Please bring a diskette for your group.