CORNING

Advanced-Flow™ Reactors

Controlling a Reaction: Light Intensity & Temperature

Application Note #7

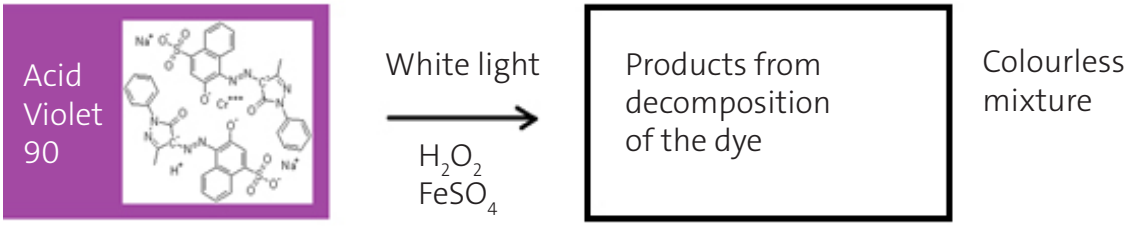
Issued: MAY 2019

Aim: This experiment is designed to show the effects of photochemistry. It is specifically designed to show these effects didactically in a "safe environment" with only the use of visible light and a limited amount of hazardous chemicals. Variations of the process parameters will directly impact the outlet color, showing their effect.

Setup: Corning® Lab Photo Reactor with one module, 2 chillers (one for LED panel, one for the Lab Photo Reactor)

Model reaction: Photo-Fenton reaction

Adapted from: Int. J. Chem. Sci., 2013, 11(2), 855-864



Analytics: Human eye

Safety:

Make sure you have read the MSDS of the chemicals and the safety notes in the Lab Reactor Manual. Keep the reactor protective shield closed to avoid spreading light, and use protective eyewear.

Feed preparation:

- Feed 1: 60.0 mg (0.02 mmol) of Iron Sulfate Heptahydrate (CAS 7782-63-0) is dissolved in 150 ml water. 0.2 ml of Hydrogen Peroxide (30% solution, CAS 7722-84-1) and 0.1 mL Sulfuric Acid Solution (30% solution, CAS 7664-93-9) are sequentially added to the solution. It is recommended to keep the solution protected from light.
- Feed 2: 580 mg (0.6 mmol) Acid Violet 90 (CAS 6408-29-3) is dissolved in 150 ml water. Keep the solution protected from light.

Information about the stoichiometry:

Based on Literature, iron salts react with Acid Violet and they are regenerated (up to six times) in active species by the acidic hydrogen peroxide conditions. Therefore, one molecule containing iron can react with up to six molecules of Acid Violet 90. Variations of ratio will impact the reaction rate.

Flow experiment:

The solutions are pumped with adequate flow rates (e.g. 1 ml/min for Feed 1, 2ml/min for Feed 2) through the module at 30°C. The LED panel is switched on at 70% of 4000K. The flow rates, light intensity and temperature (up to 70°C) can be varied.

Hint: Before checking color of solution, wait until any varied parameter is stable, then additionally wait for three times the residence time (e.g., 50 seconds x 3 = 150 seconds at a total flow rate of 3ml/min. Refer to Application Note #1 for Residence Time Calculations).

Cleaning:

Replace both feed solutions with water/ethanol and pump @ 1 ml/min for at least 20 min. Repeat with ethanol or isopropanol.

Results:

Depending on the flow rates, temperature and light intensity, the outlet solution will have colors of different shades of red. Below is a table of the corresponding results:

Solution	Acid Violet 90 Stock Solution	Diluted Acid Violet 90 Solution	Sample 1	Sample 2	Sample 3	Sample 4
Temperature	20°C	20°C	25°C	25°C	40°C	50°C
Light intensity	None	None	None	70%	70%	70%
Residence Time	None	60 seconds	50 seconds	75 seconds	90 seconds	90 seconds
Aspect of the solution						

Conclusion:

Yields and conversions are controlled via three parameters: light intensity, temperature, and residence time. A combination of these parameters can be explored in order to check the impact of each modification. The residence time is controlled via the flow rates of the pump. Changing the wavelength is also an interesting parameter. **Remember to always wear adequate eye protection.

Note: The reaction is accelerated by light, not catalyzed by it. It still occurs without light.

Tips & Tricks

This reaction is a good demonstration reaction to showcase flow photochemistry.

- At 80°C, light is not required as the rate of degradation is fast enough.
- At room temperature, light intensity is not enough to fully complete the reaction.
- An optimal combination of all parameters, including flow rate can be found quickly.

How to optimize the flux of light within the sample using Beer Lambert Law

- In order to ensure a better photoreaction, the absorption of the light through the sample is checked
- To do so, a UV visible spectrometer can be used to analyze a cuvette containing a solution sample. The cuvette should have the same path length as the reactor channel height in which the reaction occurs.
- Analysis of the solution contained within the cuvette indicates how much light is absorbed by the solution at the working concentration.
- The target is 1% transmission (i.e. 99% of light is absorbed).

Beer Lambert Law

$$\text{Absorbance} = \varepsilon \mathcal{T} c = \log \frac{I_0}{I} \qquad \text{Transmittance} = \frac{I}{I_0} = 10^{-A}$$

ε: Molecular absorption
$\mathcal{T}$: light path length
c: concentration of solution
I_0 : radiant flux received by the sample
I: radiant flux transmitted by the sample
A: Absorbance