

Laboratory #3: Process Kinetics

Objective: The purpose of this lab is to develop a kinetic rate equation (a mathematical model) for the destruction of Naproxen with aqueous chlorine, then use the rate equation to help assess relative costs of a water and wastewater treatment process which will, in turn, inform process design.

Introduction:

Naproxen is a very commonly used NSAID (non-steroidal anti-inflammatory drug). It is sold under the brand name, “Aleve” among many others, a drug widely used for relieving the symptoms of arthritis, muscle pain, joint pain, etc. It is also a major active ingredient in other drugs such as “Sudafed sinus & pain”. Its chemical structure features two “Fused” benzene rings with a methoxy group (R-O-CH₃) on one and a propionic acid (CH₃-RCH-COOH) on the other (Fig 1). The acid group has a pK_a of 4.2.

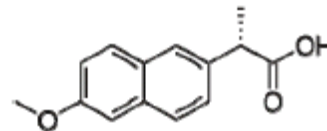


Figure 1. Chemical structure of Naproxen.

Chlorine is used as a disinfectant in drinking water and wastewater treatment processes. In addition to its efficacy in inactivating pathogenic organisms, it can react with many types of organic and inorganic contaminants in water. Chlorine carries other benefits too, such as being relatively fast-acting and cheap.

1. Measurement of Residual Naproxen by Spectrophotometry

Genesys 10s Ultraviolet-Visible (UV-Vis) Spectrophotometer is used to monitoring the concentration of Naproxen over the course of the reactions.

Basic theory: Molecular absorption spectroscopy is based on the measurement of the transmittance or the absorbance of solutions contained in transparent cells having a path length of l cm. Ordinarily, the concentration of an absorbing analyte is linearly related to the absorbance as given by Beer’s Law (Skoog et al., 2007):

$$A = -\log(T) = \log\frac{I_0}{I} = \epsilon lc \quad (1)$$

where A is the absorbance (dimensionless); T is the transmittance (dimensionless); I_0 is radiant power incident on the sample (Watts); I is radiant power transmitted by sample (Watts); ϵ is molar absorptivity ($M^{-1}cm^{-1}$); l is length over which attenuation occurs (usually 1 cm, which is what we’ll be using); c is concentration in specified units (usually in M) (Fig 2).

Principle of spectrophotometer: A spectrometer works by splitting light made of many wavelengths into individual rays that can be detected. This allows the spectrometer to be able to find the absorbance of the specific wavelength and determine what molecules are in the solution. Light of a particular wavelength passes through the solution inside the cuvette and the amount of light transmitted is measured by a light meter. A recorder can display measurements (Fig 3).

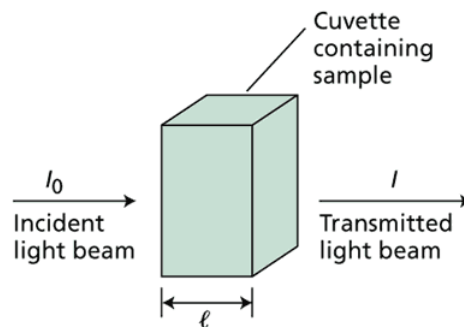


Figure 2. Definition of absorbance (Taiz et al., 2015)

Because other compounds in a solution (or the solvent itself) may absorb the same wavelengths as the compound being analyzed, we compare the absorbance of our test solution to a **reference blank**. Ideally, the reference blank should contain everything found in the

sample solution except the substance you are trying to analyze or measure. In this lab, you will measure the absorbance of Naproxen dissolved in water. The reference blank in this case would be water alone.

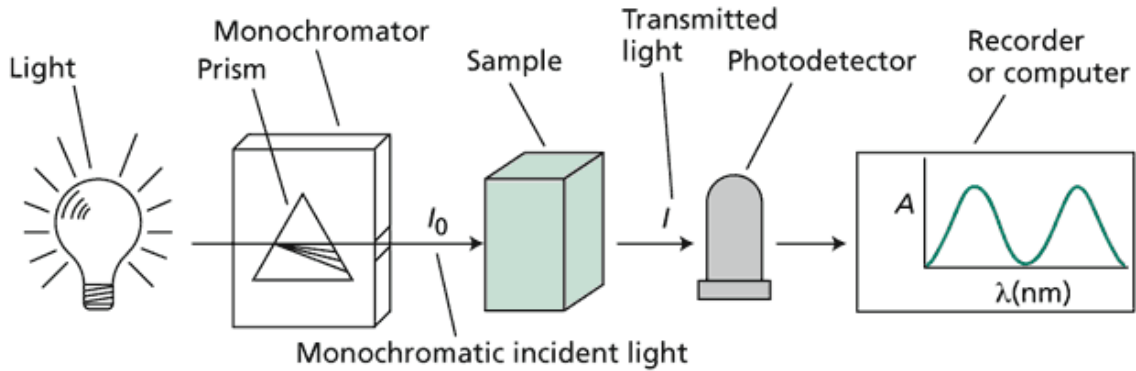


Figure 4. Schematic diagram of a spectrophotometer (Taiz et al., 2015).

Components of Genesis 10s Spectrophotometer:

Genesis 10s Ultraviolet-Visible (UV-Vis) Spectrophotometer has a light source (Xenon lamp, 1), a monochromator (2) that selects for the desired wavelength, a cell compartment with changer (4), and a pair light detectors, one to monitor the lamp output (3) and one to measure the light transmitted through the sample (5) (Figure 4).

2. Measurement of Chlorine Residual by DPD Titration

The amount of chlorine added to a water is called the “chlorine dose”. The amount that persists or can be measured after addition is called the “chlorine residual”. After addition of aqueous chlorine to a water for treatment purposes, it is important to measure how much is left at any given time. This is because chlorine can become rapidly dissipated and its effectiveness is directly linked to its concentration and exposure time. In this kinetics experiment you will be adding a specific chlorine dose (0.200 or 0.500 mM), but the residual chlorine will be lower. At the end of each of the 5 tests, you will measure the final chlorine residual.

3. Costs of Treatment Processes

Qasim and colleagues (*Journal AWWA*, 84:8:56-62) estimated the total construction cost (CC in October 1978 US \$) for a chlorine contact tank as a function of its capacity (x) in m³ at:

$$CC_{1978} = 583.2x^{0.78} + 22,900 \quad (2)$$

This can be updated to the present by taking into account present construction costs as documented in the Engineering News Record’s Construction Cost Index (CCI):

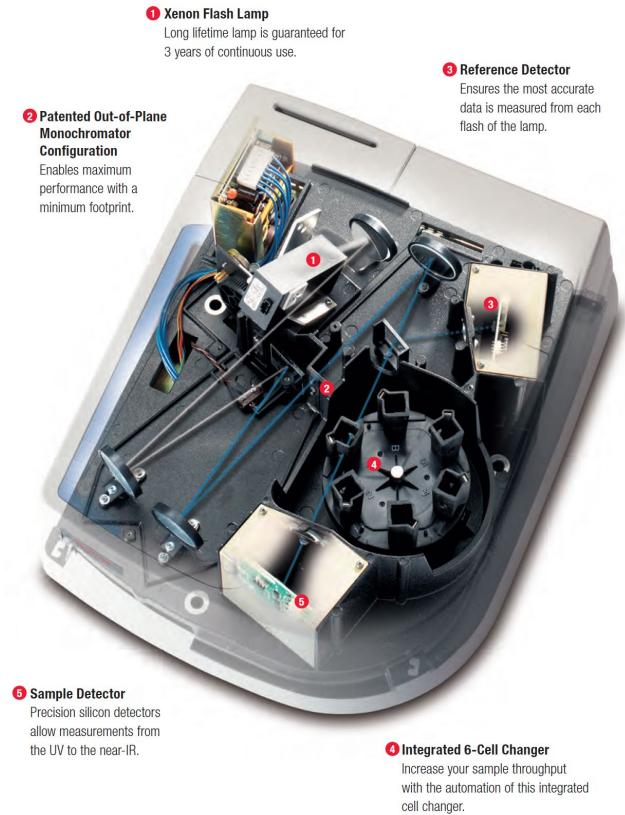


Figure 3. Components of Genesis 10s Ultraviolet-Visible (UV-Vis) Spectrophotometer

$$CC_{current} = CC_{1978} \times \frac{CCI_{current}}{CCI_{1978}} \quad (3)$$

The CCI₁₉₇₈ was 2776. The current CCI is about 10500 (see the Engineering News Record website at <http://enr.construction.com/economics/>). Note that Qasim and colleagues parsed out the CC into various categories, each of which was adjusted separately. For our purposes, we will use the general CCI to update the full cost. These authors also present the standard method for translating a capital cost to an equivalent annual cost (EAC) using the capital recovery factor (CRF):

$$CRF = \frac{i(1+i)^n}{[(1+i)^n - 1]} \quad (4)$$

Where i is the interest rate per payment period (usually a year) and n is the number of payment periods (usually the design period in years). Note that the CRF is sometimes presented in an alternative equation giving the same value:

$$CRF = \frac{i}{[(1+i)^n - 1]} + i \quad (5)$$

So that:

$$EAC = CRF \times CC \quad (6)$$

Current Chemical costs based on recent bids: the cost of Sodium Hypochlorite is \$0.5645/gallon for a 5% solution. This is equivalent to \$2.57 per kilogram of pure hypochlorite as Cl₂.

References

- Skoog, D. A., Holler, F. J., & Crouch, S. R. (2007). Instrumental analysis. *Cengage Learning, New Delhi*, 135-151.
- Taiz, L., Zeiger, E., Moller, M. I., Murphy, A. (2015). Plant physiology and development. *Sinauer Associates, Inc.*, 100-120.

Lab Procedure

- Solutions
 - pH 6.4 phosphate buffer (10 mM total phosphate) 2L
 - pH 7.2 phosphate buffer (10 mM total phosphate) 5L
 - pH 8.0 phosphate buffer (10 mM total phosphate) 2L
 - Chlorine Stock solution (1000 mg/L) 500 mL
 - Naproxen Solution (11.5 mg/L) 5L
- Glassware
 - Amber bottles for each test (5 for each group)
 - Graduated cylinders for each group (10 mL, 100 mL)
 - Pipets and bulbs
 - Quartz spectrophotometer cell
- Equipment
 - pH Meters and electrodes (one for entire class)
 - UV-Vis Spectrophotometer (one for entire class)
 - Thermometers (one for each group)
 - Refrigerator (~4°C)

A. Measurement of Residual Naproxen by Spectrophotometry

1. This instrument must be turned on and warmed up well before use.
2. Set the wavelength using the panel controls.
 - a. For reasons related to its bond chemistry, the absorbance spectrum of Naproxen (Figure 5) has a maximum at 230 nm. We will use that wavelength to monitor the concentration of Naproxen.
3. It is then “calibrated”, or more accurately, “zero-ed” by placing a cuvette with distilled water into the cell changer and pressing the “B” button (stands for “Blank”).
4. Make sure you’ve selected the “Absorbance” readout. Then place your sample in a separate cuvette and press the button on the cell changer indicating the position of the sample. You will see a readout in absorbance units per centimeter (cm^{-1}). Also on the screen will be a reminder of the wavelength that this instrument is tuned to.

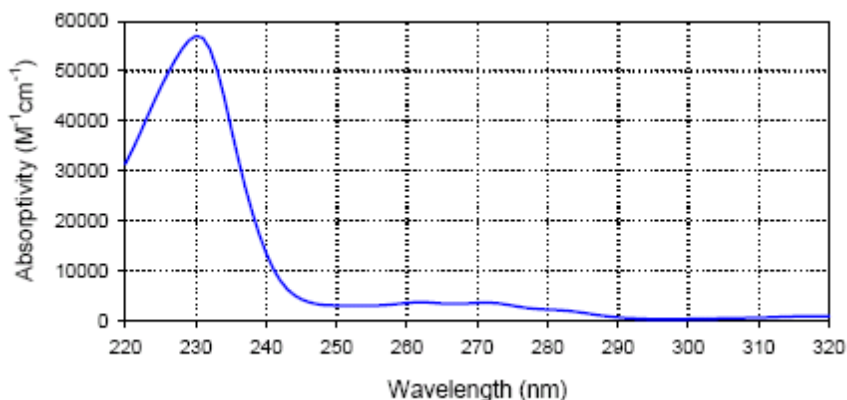


Figure 5. Spectra of Naproxen

B. Process Kinetics

Table 1. Summary of Test Conditions

Test #	Naproxen Conc. (mM)	NaOCl Dose (mM)	Chlorine Stock Addition	pH	Temperature	Recommended absorbance reading times (minute)	Groups
1	0.02	0.5	3.5mL	8.0	Room	0, 6, 13, 22, 32, 44, 60, 80, 120	A
2	0.02	0.5	3.5mL	7.2	Refrigerated	0, 6, 13, 22, 32, 44, 60, 80, 120	A
3	0.02	0.2	1.4mL	7.2	Room	0, 6, 13, 22, 32, 44, 60, 80, 120	B
4	0.02	0.5	3.5mL	7.2	Room	0, 1.5, 3, 5, 7, 10, 15, 20, 30	B
5	0.02	0.5	3.5mL	6.4	Room	0, 0.25, 0.75, 1.25, 2, 3, 5, 8	All

1. Combine 40mL of 0.050 mM Naproxen stock solution with 60mL of the buffer solutions. Prepare 100 mL of each of the 5 solutions in separate amber bottles.
 - a. for Test #2 use the refrigerated pH buffer and place solution back in the refrigerator; The others stay on the bench.
 - b. use the 100 mL graduated cylinders to measure these volumes.
2. Record the absorbance of each and check the temperature of each just prior to addition of chlorine;
3. One-by-one add the requisite volume of chlorine stock solution (column 4 of table 1.) to achieve the intended dose:
 - a. You may use the small graduated cylinder to measure out the chlorine stock solution.

- b. Swirl to mix.
 - c. ***The clock on each sample starts with the addition of chlorine as soon as chlorine is added and mixed.***
4. The elapsed time from the addition of chlorine to each measurement on the spectrophotometer should be recorded.
5. Transfer enough sample to a cuvette to fill it about 80% to the top and measure the absorbance.
 - a. You may use a Pasteur pipet to do the transfer.
6. Repeat absorbance measurements until all 8 have been recorded.
 - a. ***Don't be too concerned about getting a reading at the exact time in Table 1. However, it is important that you record the accurate reaction time at the moment you do make your measurement.***
7. Measure residual chlorine after the last sample is taken.
 - a. You must first dilute the sample by removing exactly 10 mL and diluting to 100 mL total volume with distilled water. This assures that the concentration you are measuring is < 4 mg/L as Cl₂ (0.056 mM).

Do steps 4-7 for all 5 tests

C. Measurement of Chlorine Residual by DPD Titration

1. Add 100 mL of a diluted sample to a 250 mL Erlenmeyer flask.
 - a. The diluted sample must have a chlorine residual below 4 mg/L as Cl₂ (0.056 mM).
 - b. You can assure this by adding ***10 mL of your sample*** and ***90 mL of deionized (DI) water*** to the flask and swirling to mix.
2. Record the initial level of the titrant (ferrous ammonium sulfate) in the buret.
 - a. Add more if there is less than 4.5 mL remaining.
3. Add 5 mL of DPD buffer from auto pipet bottle to the Erlenmeyer flask with the diluted sample
4. Add 5 mL of DPD indicator solution from the other auto pipet bottle to the flask
5. Titrate with the Ferrous Ammonium Sulfate until the pink color just disappears and record the final level in the buret.
6. The chlorine residual in mg/L as Cl₂ in your diluted sample is equal to the number of mL of titrant used. Back calculate to the original sample taking into account the degree of dilution (10x).

D. All data must be shared with the other groups before leaving the lab.

Data Sheet

Test #1 Test start time: _____ :
 Absorbance before chlorine
 addition: _____
 Temperature: _____

Recommended time (min)	Tested time	Real time (min)	Absorbance (cm-1)
0	:		
6	:		
13	:		
22	:		
32	:		
44	:		
60	:		
80	:		
120	:		

Residual Chlorine (mL of
 titrant used):

Test #2 Test start time: _____ :
 Absorbance before chlorine
 addition: _____
 Temperature: _____

Recommended time (min)	Tested time	Real time (min)	Absorbance (cm-1)
0	:		
6	:		
13	:		
22	:		
32	:		
44	:		
60	:		
80	:		
120	:		

Residual Chlorine:

Test #3 Test start time: _____
 Absorbance before chlorine
 addition: _____
 Temperature: _____

Recommended time (min)	Tested time	Real time (min)	Absorbance (cm-1)
0	:		
6	:		
13	:		
22	:		
32	:		
44	:		
60	:		
80	:		
120	:		

Residual Chlorine:

Test #4 Test start time: _____ :
 Absorbance before chlorine
 addition: _____
 Temperature: _____

Recommended time (min)	Tested time	Real time (min)	Absorbance (cm-1)
0	:		
1.5	:		
3	:		
5	:		
7	:		
10	:		
15	:		
20	:		
30	:		

Residual Chlorine:

Test #5 Test start time: _____ : _____
Absorbance before chlorine
addition: _____
Temperature: _____

Recommended time (min)	Tested time	Real time (min)	Absorbance (cm-1)
0	:		
0.25	:		
0.75	:		
1.25	:		
2	:		
3	:		
5	:		
8	:		

Residual Chlorine:

Kinetic Analysis

In your results section, be sure to:

- Present your data (absorbance vs time; chlorine residuals, pH, temperature) in a logical tabular format. You should also graph your absorbance (y-axis) data versus time (x-axis). You can connect the data points with straight lines, but always show the data points themselves. To save space, you may want to plot more than one set (i.e., test #) on the same set of axes.
- Take at least one of the data sets (test #s) and compare its fit to a 0-order, 1st order and 2nd order linearized model. Note that the chlorine is in great excess as compared to the Naproxen, so this would really be called pseudo-nth order kinetics. ***Before you can do the kinetic analysis you will need to subtract the absorbance of the final organic products (sometimes called the asymptotic absorbance or Abs_{∞}) of Naproxen oxidation from each of the timed absorbance measurements.*** Since we don't know exactly what these are, you will have to guess at the Abs_{∞} . For the purpose of this experiment, you should assume it is 23% of the starting absorbance of the buffered Naproxen solution at time zero. Comment on the relative fit for the three types of plots.
- Plot all 5 sets of data using the linearized pseudo-1st order model. Tabulate the "best-fit" slope for each. Remember to include units. These are what we call the "observed rate constants" or k_{obs} . These are 1st order rate constants that can be converted to the pH-dependent "apparent rate constants" or k_{app} by dividing each by the average molar concentration of the aqueous chlorine. The k_{app} values are 2nd order rate constants and they should have dimensions of reciprocal concentration x reciprocal time. Tabulate each of these with the appropriate units and conditions (pH, temperature, chlorine dose). Comment on the differences between the 5 tests. Should the k_{app} be similar for #3 and #4?
- Plot the $\log k_{app}$ vs pH for the three at the standard temp and chlorine dose (Test #1, 4 & 5). Present the equation of the best-fit straight line for this plot. Comment on the effect of pH on the reaction rate.
- Using k_{app} values for Tests #2 and #4 solve the Arrhenius equation for the activation energy (E_a) and pre-exponential factor (A) and the Engineering equation for its temperature coefficient (Θ). Tabulate these values showing their proper units.

Include as a separate subsection as part of your results and discussion: Design Problem

You've been hired as a consultant by a pharmaceutical firm that produces Naproxen. They have a production facility that discharges its wastewater into a municipal sewer. Your client's facility discharges 350,000 gallons per day at a temperature of 25°C. The city requires that 99% of the Naproxen be destroyed in your client's effluent prior to discharge. You are asked to analyze and compare total costs of the pre-treatment system that use chlorine to achieve this goal. Consider only the cost of construction of an appropriately-sized chlorine contact tank and the cost of sodium hypochlorite that must be added. Look at 3 pHs (6, 7 and 8) and a range of chlorine concentrations (0.3 – 30mg/L). The recommended steps:

- Using the rate data you developed in the laboratory portion, estimate the 2nd order apparent rate constant (k_{app}) for pH 6.0 and 25°C. From this, calculate the time required for 99% removal in a PFR (recognizing that a PFR will be superior to a CMFR for this process) under these conditions (i.e., pH 6.0 and 25°C) presuming a chlorine residual of 30 mg/L. You should also presume that chlorine is always in great excess over Naproxen so you should still use a pseudo-first order equation. This means that you take the k_{app} you calculated and multiply it by your chlorine dose (moles/L) to get the new pseudo-1st order "k" for your design calculation (i.e., the k in $C=C_0e^{-kt}$).
- Calculate the tank volume needed in cubic meters
- Determine the 1978 construction cost
- Update that cost to the 2016 construction cost
- Determine the CRF and then the EAC assuming a 20 year payback period and a 5% annual interest rate

- f) Calculate the annual usage rate of chlorine in kg/yr
- g) Calculate the annual cost for that chlorine
- h) Add this to the EAC to get the total annual project cost
- i) Repeat steps “a” through “h” for a range of chlorine concentrations from 0.3-30 mg/L. It would be worthwhile to set up a spreadsheet to do this, so you can determine many values along this range.
- j) Plot total annual project cost (in \$/yr) vs chlorine dose (in mg/L)
- k) Repeat “a” through “j” for pH 7.0 and again for pH 8.0.
- l) Comment on your calculations. Which design do you prefer? What else would you want to take into consideration before adopting a target pH? Are there any other design or operating variables you’d like to consider?