Iron Wall Kinetics:
Zero Valent Metal Groundwater Remediation[1]

Wastes from chemical manufacturing processes were routinely discharged with little or no treatment or concern for potential environmental damage. Legislation aimed at curtailing or eliminating discharge of manufacturing wastes has dramatically lowered the input of these chemicals into the environment, but already existing groundwater contamination is widespread, necessitating development of new **remediation** technologies. One of the methods involves **permeable reactive barriers (PRBs).** A PRB consists of immobile solid materials placed in the subsurface to extract or chemically degrade groundwater contaminants on contact (Figure (1)).

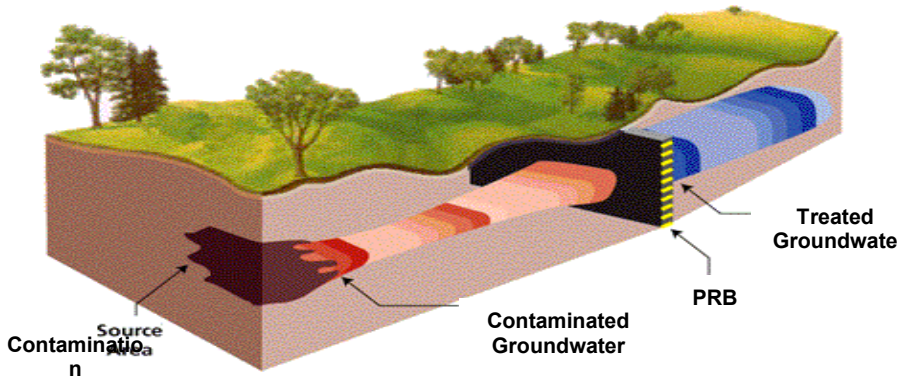


Figure 1: Water infiltrating soil contaminated with chemical waste forms a plume of contaminated groundwater. When the plume is directed through a **permeable reactive barrier**, contaminants are chemically converted to less hazardous or non-hazardous products. The groundwater is then considered remediated.

In a well-designed PRB, groundwater passing through the barrier emerges free of hazardous substances. Because the method has considerable cost advantages over traditional pump-and-treat technologies, interest in PRBs is growing. They are already widely used to control halogenated organic solvent contamination in groundwater, and application has been extended to treatment of other organics, metal, and radionuclide contaminants.

In this experiment, you will study the feasibility of using **iron PRBs** - also known as **iron walls** -- to remediate water contaminated with a common dye, indigo carmine (Figure (2)). The

[1] Bumpus, J.A., et. al., JCE, 76(1999), 1680

iron PRB-contaminant reaction can be explored by simple kinetics experiments. Indigo carmine is chosen as the model contaminant in part because its

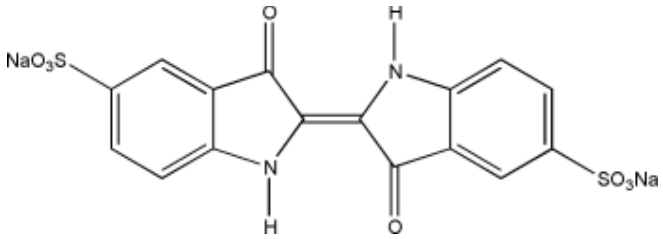


Figure (2): Indigo Carmine (FD&C Blue #2), a derivative of the more familiar indigo, is used in dyeing textiles, as a food coloring, and as a biological stain.

intense color makes spectrophotometric monitoring of its degradation possible. The overall goal is to obtain useful information about this reaction so that you can make recommendations about whether an iron wall would be a suitable remediation strategy for contaminated groundwater at an indigo carmine manufacturing site.

Iron PRB Electrochemistry

Remediation involving iron PRBs is a redox process; the iron metal undergoes oxidative dissolution while the contaminant is reduced. It has long been known that the oxidation (i.e., corrosion) of **zero valent metals** such as Fe^0, Sn^0, and Zn^0 can bring about the reduction of many organics, but only recently has this chemistry been applied to the problem of contaminated groundwater. PRBs filled with granules of one or more zero valent reducing metals are quite effective in degrading halogenated organic solvents, common industrial pollutants. Today, iron is the metal of choice for PRBs because it is readily available, inexpensive, nontoxic, and a good reducing agent. PRBs have many advantages over more traditional groundwater remediation technologies. First, iron walls are able to remediate many contaminants in addition to halogenated solvents, such as pesticides, nitrates from fertilizers, and heavy metals (e.g., chromium). Second, iron walls are a passive technology, requiring little maintenance after installation. Because of these advantages, as well as the prevalence of contaminants that iron walls are capable of removing, iron PRBs are now widely used in North America and Europe to clean up contaminated sites.

Iron PRB Kinetics

The degradation of a typical organic contaminant, R, by Fe^0 usually obeys the following rate law:

$$\text{Rate} = -d[R]/dt = -k[\text{Fe active sites}]^m[R]^n \qquad (4)$$

Where n is equal to one, and first order kinetics with respect to the contaminant "R", though zero order kinetics are observed at very high contaminant concentrations. The number

of active sites at the Fe surface depends greatly on its history (e.g., the method of manufacture, storage conditions, etc.) However, since in most experimental systems it has been found that the concentration of iron active sites does not vary significantly during the course of the degradation reaction, it is possible to simplify (5):

$$-d[R]/dt = -k_{obs}[R]^n \quad (5)$$

where k_{obs}= k[Fe active sites]. Thus, the kinetics of degradation of groundwater contaminants by iron metal generally are **pseudo first order, "n" is one.** It should be emphasized that k_{obs} is not a true first-order rate constant and it *will* depend on the concentration of active sites on the iron metal. Consequently, k_{obs} should be affected by both the mass and the surface area of the iron particles since both of these factors influence the number of active sites. The goal of this lab is to determine the reaction order for the mock contaminant indigo carmine "R".

Preparing for Lab

In this lab, you will simulate the iron PRB remediation of indigo carmine contaminated groundwater. For part I you will design various control experiments and construct a Beer's Law plot for the model contaminent , indigo carmine. In Part II you will work out the details for a standard spectrophotometric kinetics experiment in which you measure the rate constant for dye degradation by following the change in the absorbance of a dye solution. Assuming Beer's Law is followed, the solution absorbance will be proportional to the dye concentration. By selecting the proper kinetics relationship to plot (see Table 1), it is possible to deduce the rate constant, k_{obs}. You are expected to draw on your laboratory experience as you work out the details. **There is no prelab for Part 1 as you will work in a team to discuss ideas for experiments to address each of the controls Read the instructions below how to use the Vernier Visible Spectrophotometer below BEFORE coming to lab. Review Table 1: Summary of Kinetics Plots BEFORE coming to lab.**

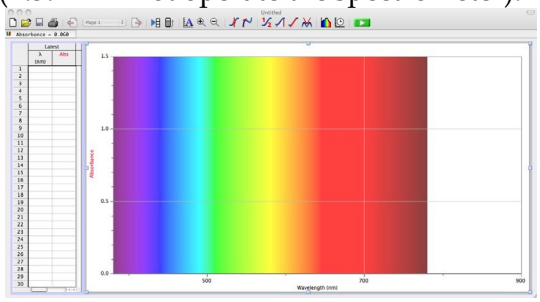
Table 1: Summary of Kinetic Relationships, rate = $k_{obs}[R]^n$

if reaction order is	straight line plot is	integrated rate law	find k_{obs} from
zero order	[R] vs. time	$[R]_o - [R] = k_{obs}t$ $[R] = - k_{obs}t + [R]_o$	- slope of [R] vs. time
first order	ln [R] vs. time	$\ln [R]_o - \ln [R] = k_1 t$ $\ln [R] = - k_{obs}t + \ln [R]_o$	- slope of ln [R] vs. time
second order	1/[R] vs. time	$1/[R] - 1/[R]_o = k_{obs}t$ $1/[R] = k_{obs}t + 1/[R]_o$	slope of 1/[R] vs. time

Instructions for Taking a Spectrum with the *SpectroVis Plus* Spectrometer:

This requires LoggerPro 3.8 or higher.

1. Attach the SpectroVis Plus unit to the laptop via a USB cable.
2. Open ***LoggerPro.*** Within a few minutes, you should see a spectrum window. If not, check the version of ***LoggerPro*** (v.3.7 will not operate the spectrometer).

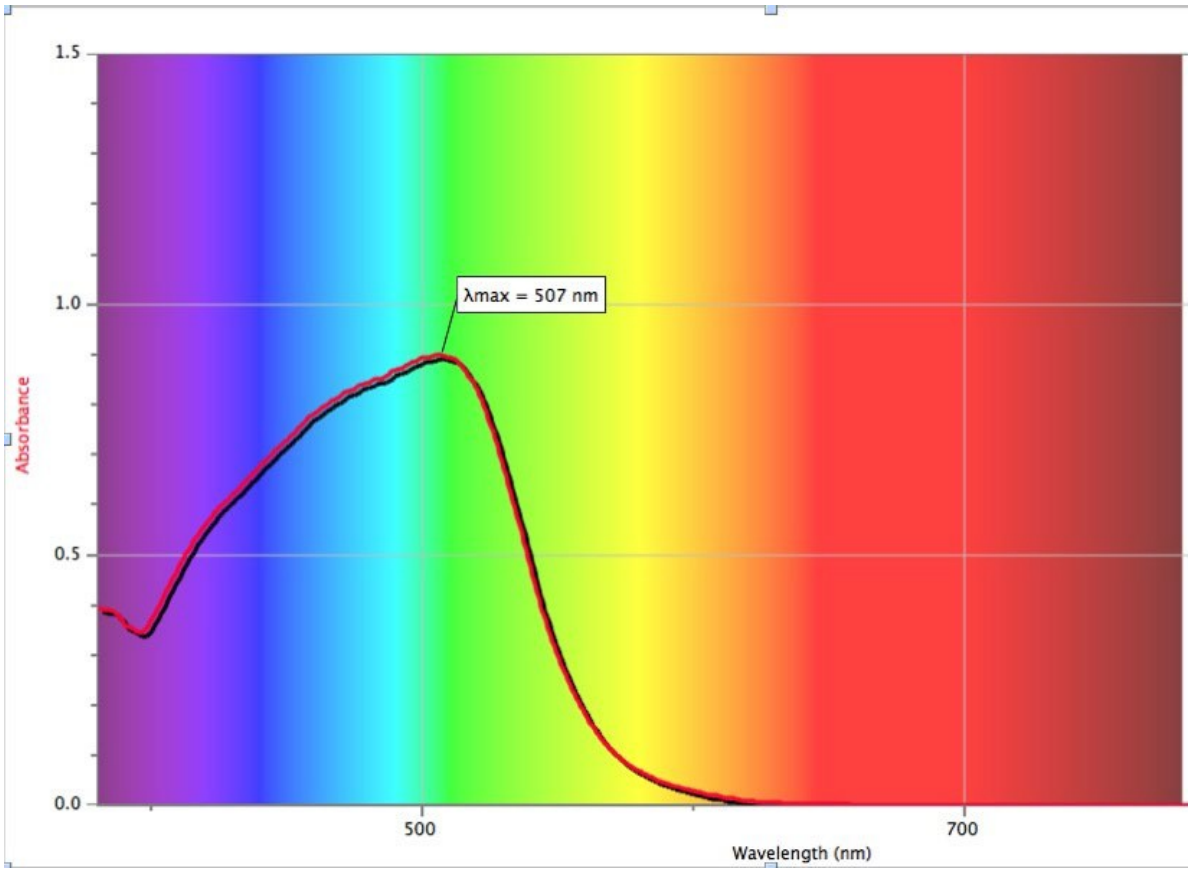


3. Blank the spectrophotometer:
   a. From the **Experiment** menu → **Calibrate** → **Spectrometer**. Allow a 90 second warmup of the lamp.
   b. When prompted, pace a blank (a square cuvet filled ~3/4 with distilled water) with the clear sides in line with the white triangle and white lamp icons (that is, cuvet clear sides oriented left and right as shown below). The frosted sides should be oriented to the top and bottom.

c. Click **Finish Calibration**. When complete, click **O.K.**

4. Run the sample:
   a. Remove the blank cuvet and insert the sample cuvet. Click on the collect button  at the top of the window to begin data collection.
   b. Allow the sample to run for ~30 seconds (to average signals); click 

   c. If necessary, to delete a bad spectrum, go to **Edit** menu → **Undo Collect**.
   d. To find the λ_{max}, move the cursor to the peak absorbance (highest y value) and then note the corresponding wavelength (x value). The x,y values are shown in the spectrum window near the origin. Alternatively, read the λ_{max} from the data table. Record the value in yoru lab notebook.
   Example spectrum: This could probably use more scale divisions on the wavelength axis and a title.



Part 1

Controls to Consider

There are certain potential problems that should be taken into account. Plan your experiments so that these do not affect your experiments or your conclusions in Part II. Some controls to consider are:

1. What is an appropriate wavelength to use? (See **Instructions for Taking a Spectrum with the *SpectroVis Plus* Spectrometer**)
2. Does the concentration of dye used in this experiment (20.0 ppm indigo carmine) fall within the linear range of the spectrometer? (between 0.100 and 1.100)

3. Does the dye degrade in room light (is indigo carmine 'photosensitive')? **Hint: The typical time for a kinetics experiment in Part II is ~5-15 minutes.**

4. Does the dye degrade upon exposure to the wavelengths of light used in spectrophotometry? **Hint: The typtical time a cuvette with the dye is in the spectrophotometer is ~ 30 seconds – 1 minute.**

With your team clearly design experiments to address each of the these questions. Make sure to share any data/graphs and include them in your data section of your lab notebook. In your notebook make notes and record data/observations to address each of the four control experiments.

Part II Kinetics Experiment
Part A: Protocol to Use for a Standard Kinetics Experiment

Safety*: Safety goggles must be worn when preparing solutions, filling cuvets, or doing any chemical modification of the iron filings. Goggles may be removed during spectrophotometry so long as no one around you is preparing solutions or performing chemical modifications**.** Fine grain, high purity iron is a strong reductant and can be explosive if exposed to concentrated strong oxidant. This will not be a safety hazard if you use only the small quantity of iron suggested. Reaction of iron particles and acid is exothermic, and rinsing iron particles in an acid solution may lead to foaming if the solution is too concentrated.* ***Waste disposal****: Place all indigo carmine solutions (with or without iron particles) in the waste collection container.*

1. Blank the spectrophotometer at an appropriate wavelength using distilled water in a disposable polystyrene cuvet. Wipe the outside of the cuvet with a Kimwipe tissue. the cuvet in the adaptor so that the clear sides are in the light path.

2. Weigh 0.25 g of iron filings and place into another disposable polystyrene cuvet.

3. *Quickly* fill the iron filings cuvet as completely as possible with a 20.0 ppm indigo carmine solution. It is important to minimize trapped air in the cuvet because the oxygen will oxidize the reduced form of the dye, reversing the reaction you are trying to study.

4. Fill the underside of a cuvet cap with indigo carmine solution and cap the cuvet. Wipe the outside of the cuvet with a Kimwipe tissue.

5. *Immediately* place the cuvet in the spectrophotometer (clear sides in the light path), put the holder in the spectrophotometer, and record the initial absorbance of the dye. Begin timing at the moment you take the initial absorbance reading.

6. Remove the cuvet holder from the spectrophotometer and rock it end to end to facilitate mass transport of the dye to/from the iron surface (think of some way to keep the mixing rate reasonably constant). Estimate and record the mixing rate. Maintain this mixing rate in all of your experiments.

7. Record the dye absorbance as a function of time. You should measure absorbance over *at least* three reaction half-lives (one half life is the time required for the dye absorbance to drop by 50%). You will have to determine how often to sample and how long to carry out the experiment. Initially, you may want to run through the experiment quickly just to get a sense for how long it takes to degrade the dye and then repeat the experiment more carefully.

8. Repeat the kinetics experiment if time allows.

Part B: Graphical analysis to determine the reaction order with respect to dye (this can be done anytime before Thursday's lab) save your plots for the group report

The absorbance is directly proportional to concentration, so we can simply use absorbance to create the three kinetics plots. Make the three kinetics plots described in Table 1 , where [R] is absorbance in our experiments. Determine the reaction order (zero, first or second) with respect to the dye and the observed rate constant kobs. Make sure to SAVE all three plots in your data section of your lab notebook.

No lab report for this week but make sure to save all your work to use for the Iron Wall kinetic project next lab!