# Photocatalytic Oxidation of an Organic Dye Using Titanium Dioxide

**Background:**
The removal and/or destruction of toxic materials from the biosphere is a multi-billion dollar industry. Incineration (high temperature oxidation) is the most common method but it comes at a very high cost and requires careful control and elaborate processes to scrub the effluent gases (*1*). Various *in-situ* treatments methods based on bioremediation and electro-reduction have found application in particular circumstances although each have inherent difficulties. A number of advanced oxidation processes involving photocatalysts have been investigated recently and appear to be promising alternatives, especially those employing natural sunlight as the energy input source (*2-4*). The photocatalytic method investigated in this lab employes a colloidal suspension of titanium dioxide (TiO_2) which is a readily available, inexpensive and non-toxic semi-conductor. It is produced on a large scale (30 million tons produced in 1991) for use as a paint pigment (*5*).
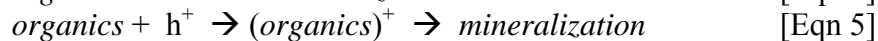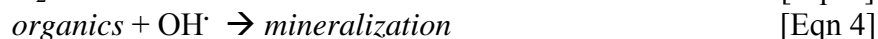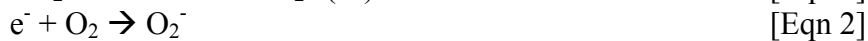
Malachite green is the common name for an organic dye developed originally for the textile industry and used more recently for the treatment of fish diseases by the aquaculture and aquarium industry. It is typically used for the control of parasites and as an anti-fungal agent in the prophylactic treatment of fish eggs. Concern about the potential for human toxicity and the presence of malachite and leucomalachite green (a metabolite) in the aquatic environment has resulted in increased monitoring especially in food supplies.

malachite green

leucomalachite green
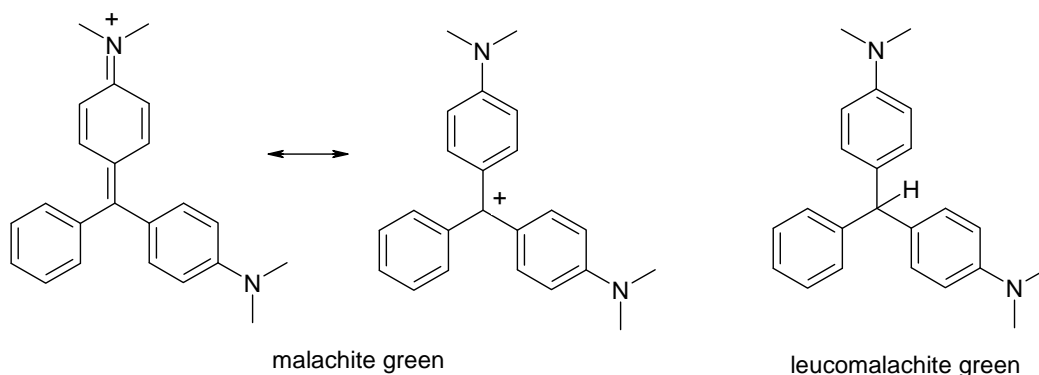
Titanium dioxide is an example of a solid state semi-conductor, characterized by two 'bands' of closely spaced electronic energy levels known as the 'valence' and 'conduction' bands. These are analogous to the <u>L</u>owest <u>U</u>noccupied <u>M</u>olecular <u>O</u>rbital (LUMO) and the <u>H</u>ighest <u>O</u>ccupied <u>M</u>olecular <u>O</u>rbital (HOMO), respectively. When electrons are promoted from the valence band into the conduction band they become delocalized and an electric current may be achieved. In an electrical insulator, the energy difference between these levels is very large and the movement of electrons into the conduction band does not readily occur. On the other hand, a good electrical conductor, the conduction band is very close in energy to the valence band and electrical conductance readily occurs. A semi-conductor has an intermediate band gap energy and becomes a conductor if that band gap energy is supplied, elevating electrons from the valence into the conduction band. For a certain mineral phase known as anatase-TiO_2 and colloidal size regimes, this gap is roughly 320 kJ mol^{-1} and consequently electronic excitation can be achieved by photons of light $\lambda \leq 360$ nm.
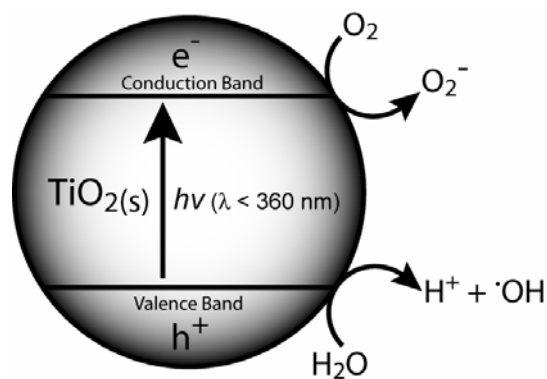
Absorption of a photon promotes an electron (*e*-) from a valence band to a higher energy conduction band. This electronic promotion simultaneously creates a localized electron hole (h$^+$), which is highly oxidizing and a mobile electron (*e*-), which is a delocalized reducing agent (Eqn 1). The electron-hole pair may recombine or be captured by other species in close proximity. For example, molecular oxygen, which is known to be required for this reaction to proceed is readily reduced to form superoxide ion (O_2^-), Eq. 2. At the same time, water is oxidized (losses an electron) at the site of the photogenerated electron holes to produce hydroxyl radical (OH), Eqn 3. The hydroxyl radical is a very powerful oxidizing agent ($E^o = 2.56V$) and will rapidly mineralize organic compounds, Eqn 4. Alternatively, an organic pollutant present on the solid semi-conductor surface, may be directly oxidized by transferring one or more of its electrons to the h$^+$, Eqn 5. Several other processes are thought to be involved in the formation and cycling of oxidants (Eqn 6 – 8).

$$TiO_2 + h\upsilon \rightarrow e^- + TiO_2^+ (h^+) \qquad\qquad \text{[Eqn 1]}$$
$$e^- + O_2 \rightarrow O_2^- \qquad\qquad \text{[Eqn 2]}$$
$$H_2O + h^+ \rightarrow OH^\cdot + H^+ \qquad\qquad \text{[Eqn 3]}$$
$$organics + OH^\cdot \rightarrow mineralization \qquad\qquad \text{[Eqn 4]}$$
$$organics + h^+ \rightarrow (organics)^+ \rightarrow mineralization \qquad\qquad \text{[Eqn 5]}$$
$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad\qquad \text{[Eqn 6]}$$
$$H_2O_2 + O_2^- \rightarrow OH^\cdot + OH^- + O_2 \qquad\qquad \text{[Eqn 7]}$$
$$H_2O_2 + e^- \rightarrow OH^\cdot + OH^- \qquad\qquad \text{[Eqn 8]}$$

The term mineralization refers to the complete chemical oxidation resulting in the formation of carbon dioxide and water, Eqn 9. (In the case of an organic molecule that contains nitrogen and chlorine a stiochiometric amount of ammonium hydroxide and hydrogen chloride are also produced).

$$organics + [Ox] \rightarrow CO_2 + H_2O \qquad\qquad \text{[Eqn 9]}$$

The complete mechanism to mineralize an organic substrate will necessarily involve numerous steps and intermediates. Although a kinetic analysis for such a reaction may be complex depending on a number of experimental conditions (*6*), quite often one of the reagents will be much lower in concentration than the others. As a result, the reaction rate will appear to depend on only the concentration of this reactant since the change in the concentrations of the other reactants will be negligible (i.e., their concentrations will remain essentially constant). The observed rate constant will appear to be first order and the k_{obs} is called the *pseudo* first order rate constant. A number of applications of heterogeneous photochemical reactions have appeared in the literature including several involving undergraduate teaching labs (*7-9*).
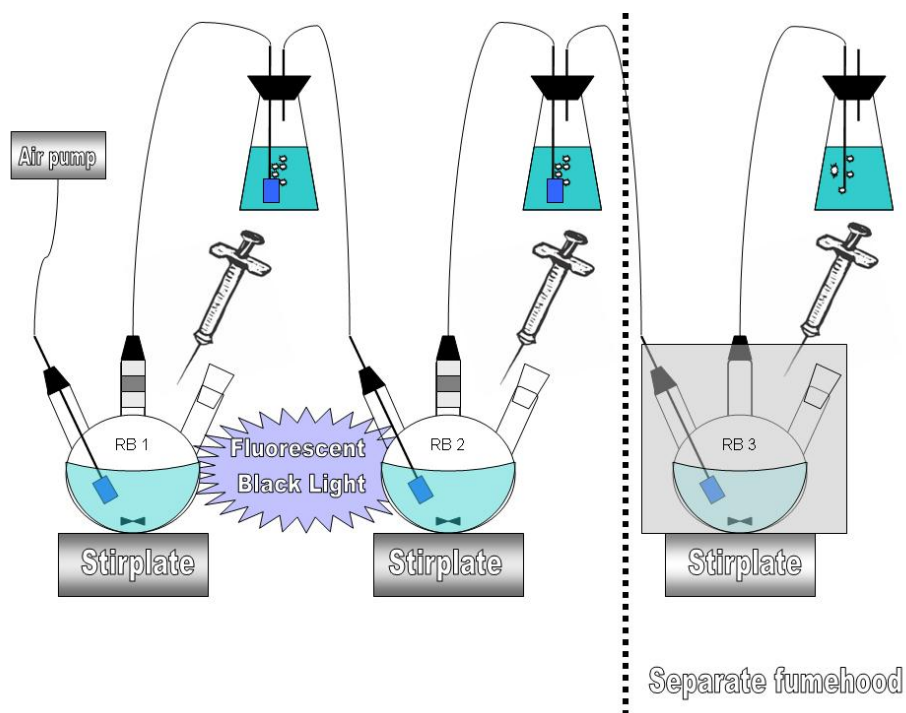
EXPERIMENTAL

Objectives:
- Determine the extinction coefficient of Malachite Green (MG) to relate absorbance measurements to concentration.
- Investigate the kinetics of photochemical oxidation of a 10. ppm solution of MG in an aerated aqueous solution in the presence of a heterogeneous TiO_2 photocatalyst (Degussa P25).
- Record the irradiance spectrum of natural sunlight (solar spectrum) and several other light sources.

Procedure:

Prepare a 1L of 10 ± 0.5 ppm (mg/L) stock solution of MG oxalate (the concentration must be known accurately). Prepare 10 mL of 1, 2 and 5 ppm standard solutions, determine the wavelength of maximum absorption of MG and measure the absorbance of each standard solution (including the 10 ppm stock) at λ_{max} to generate a calibration curve. Determine the extinction coefficient including units.

Set up a reaction vessel (250 mL three neck round bottom flask) in the fumehood adding enough TiO_2 to produce a 0.025% (m/v) suspension in 250 mL of a 10 ppm MG solution. You will need to set up two control reactions to monitor for direct photochemical degradation of MG (no TiO_2) and a dark reaction of MG on TiO_2 (no light). Ensure that the reaction vessel, the light control and your dark control have air bubblers purging at similar rates. Talk this over with your group and check with the lab instructor prior to running your reactions.

Set up the reaction vessels (250 mL three neck round bottom flask) in the fumehood, as shown in Figure 1, adding enough TiO_2 to produce a 0.025% (m/v) suspension in 250 mL of a 10 ppm MG solution (**RB 1**). You will need to set up two control reactions to monitor for direct photochemical degradation of MG (UV light, but no TiO_2) (**RB 2**), and a dark reaction of MG (TiO_2, but no UV light) (**RB 3**). To ensure no stray light is absorbed by **RB 3** wrap the round bottom with aluminum foil. Ensure that the reaction vessel, the light control and your dark control have air bubblers purging at similar rates. Talk this over with your group and check with the lab instructor prior to turning on the UV lamp to initiate the reaction.

Figure 1: Experimental set-up for photochemical degradation monitoring and comparison to control reactions.

You will be using fluorescent black lamps that contain potentially damaging UV-A and some UV-B light, so it is important to limit exposure to your skin and eyes. Set up your reaction vessels in the fumehood with a covered sash. Once the reagents are added to the reaction vessels, begin stirring and bubbling air through the samples. Allow to reaction to stir for 15 minutes prior to turning on the lamp and take an initial absorbance measurement (see sampling below) to determine how much MG has been adsorbed onto the surface of TiO_2. Turn on the UV lamp and continue to sample RB 1 at regular 10 minute intervals for about ~1.5 hrs (or until no further change in absorbance is observed). Sample your light and dark control reactions several times during the course of the reaction and again at the end of the photochemical reaction period.

Sampling: Stop the air bubbler, withdraw ~5 mL of sample from the reaction vessel using a 10 mL plastic syringe, then place the stopper back on the flask and start the bubbler again. Fit the syringe with a filter barrel and 0.45 µm PTFE filter membrane. Carefully rinse a cuvette with several milliliters of filtered solution. Fill the cuvette and measure the absorbance being careful to ensure fingerprints and air bubbles are removed.

Irradiance Spectra: Using the StellarNet fibre optic uv/vis spectrometer in irradiance mode (see instructor for details), record the spectra of natural sunlight and the UV lamp used in this experiment. Show these as an overlay plot of irradiance intensity versus wavelength over 200 – 700 nm for direct comparison. You may choose to record the spectra of other light sources for comparison.

Data Analysis:
- Use your absorbance versus concentration data to generate calibration plot and determine ε at λ_{max}.
- Determine the amount of MG adhered to per gram of titanium catalyst and calculate the fraction of MG adsorbed to the TiO_2, of MG that underwent direct photolysis and of MG photodecomposed by TiO_2.
- Plot MG concentration (ppm) *versus* time (starting at the time the light is turned on). Is the photodecompostion zero-order or first order? What does this tell you about the reaction mechanism?
- Suggest how you could determine the extent of mineralization for this reaction?
- Discuss several strategies to increase the rate of photodecompostion.

References:

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