

# Photodegradation of Methylene Blue

## Using Solar Light and Semiconductor (TiO<sub>2</sub>)

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There is an increasing interest in nonconventional methods for destruction of potentially toxic organic compounds (PTOC) present in both potable water and waste water. Heterogeneous photocatalysis is receiving increasing attention as a process of water detoxification because of its low cost when using solar light as a source of radiation. A recent report from The National Council calls for the Department of Energy to continue to support fundamental research in the oxidative destruction of organic contaminants in water using solar light (1).

Semiconductors such as metal oxides (TiO<sub>2</sub>, ZnO) or metal sulfides (CdS) usually are used as photocatalysts in the degradation of PTOC (2-4).

### Theory of Semiconductors

Electronic conduction in a solid can be explained with the help of the Molecular Orbital (MO) Theory. In isolated atoms, the energy of electrons are defined by the energy of the atomic orbitals (AO). In a solid, however, considering the possibility of overlap among *n* atomic orbitals, electrons will be distributed among the same number of MO formed as a linear combination of AO. These molecular orbitals have such a small difference in energy levels that they can be treated as bands instead of discrete levels of energy.

In solid semiconductors such as TiO<sub>2</sub>, electrons occupy these energy bands according to their energy. The occupied bands are called valence band (VB), and the next band above, or the conduction band (CB) is totally empty. Between these two bands there is a region with no orbitals, or a band gap. The size of this band gap is used to characterize materials as semiconductors or insulators, because it can act as a barrier to electronic mobility.

In the valence band, the highest occupied orbital at absolute zero is called the Fermi level and lies near the center of the band. As the temperature increases, or upon optical excitation by photons with energy exceeding the band gap, electrons can be promoted to the conduction band, and the resulting vacancy in the valence band is called a hole (or positive charge). The mechanism is shown schematically in Figure 1. For TiO<sub>2</sub>, this band gap corresponds to a radiation of 388 nm (3.23 eV), e.g. in the near-UV range.

It is interesting to emphasize that optical absorption in colloidal semiconductors may differ from that observed for bulk material. As particles become smaller (~100 Å), the adsorption edge becomes diffuse, with a blue shift and adsorption peaks that correspond to electronic transitions between discrete levels of energy. More detailed aspects concerning physicochemical aspects of semiconductors are discussed in reference (5).

### Photodegradation of Organic Compounds

Because electrons and holes are present in the semiconductor surface, the particle shows both reducing and oxidizing sites (Fig. 1). Once a suitable redox couple is pro-

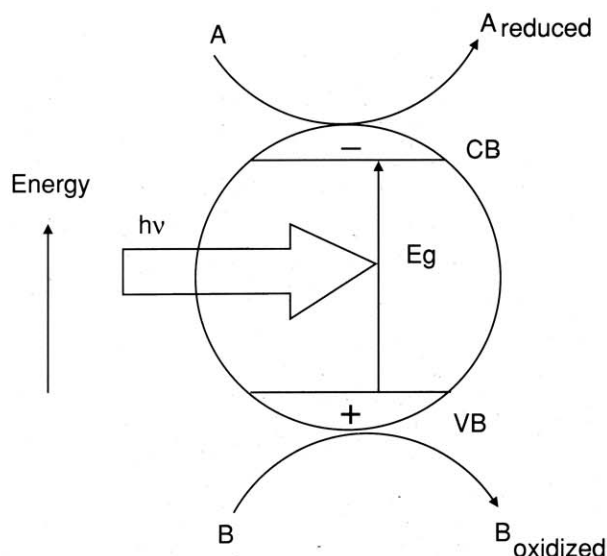
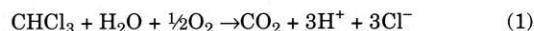


Figure 1. Schematic representation of the semiconductor particle showing the pair electron/hole formed in the conduction band (CB) and valence band (VB), respectively. Band gap energy is represented by  $E_g$ .

vided in the solution and allowed to reach the semiconductor surface, the particle behaves as in a short circuit, and the reaction goes on until one of the compounds or ion is consumed totally.

Many mechanisms involved in these redox reactions still are obscure. Adsorption of the substrate onto the semiconductor surface seems to be the first step in most cases (6). Total oxidation to CO<sub>2</sub> and H<sub>2</sub>O is rarely achieved with 100% efficiency, and intermediate products often are found in the reactional medium. According to Pruden and Ollis (7) and Hsiao et al. (8), chloroform can be mineralized totally to CO<sub>2</sub> and HCl according to the reaction:



Organochlorides are not the only class of PTOC that can be destructed using light and semiconductors. TiO<sub>2</sub> has been investigated extensively by many workers in the photodegradation of organic contaminants such as phenols, aromatics, and alcohols (6, 7). The oxidation of alcohols shows more complex pathways, depending mainly on the nature of the electron scavenger (usually dissolved oxygen).

Perhaps one of the most interesting ways of evaluating the photocatalytic activity of metal oxides is in the degradation of organic dyes. Most of these compounds show a high molar absorptivity ( $\epsilon$ ) allowing the rate of bleaching to be computed easily by colorimetric measurements.

In this paper, we present a simple experiment in which Methylene Blue (MB) is photodegraded using solar light in conjunction with TiO<sub>2</sub>. The extent of degradation is moni-

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tored at 660 nm following the rate of mineralization of MB ( $\epsilon = 66700 \pm 350 \text{ L cm}^{-1} \text{ mol}^{-1}$ ).

## Experimental Detail

### Reagents

Titanium dioxide (Degussa P 25) was used as a 1.0 g/L suspension. Methylene blue was supplied by Merck and used in a concentration of  $10^{-4} \text{ M}$ .

### Equipments

Micronal B-382 spectrophotometer was used in the determination of MB at 660 nm and 1 cm optical path. Solar light intensity at 365 nm was measured using a Cole Parmer Radiometer 9811-50.

## Results

### Testing the Photocatalytic Activity of $\text{TiO}_2$

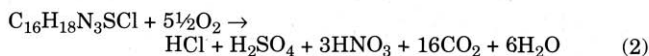
To evaluate the  $\text{TiO}_2$  photocatalytic activity, three Petri dishes (10 cm dia) each containing 25 mL of a  $10^{-4} \text{ M}$  solution of methylene blue were used. To two of them, 25 mg of  $\text{TiO}_2$  was added. One of these suspensions was wrapped in a black plastic bag before exposure to the sun. In this way, two types of control were used. One Petri dish with just the MB solution was used because MB is a sensitizer. Some degradation caused by UV/visible light absorption was observed. A second suspension of  $\text{TiO}_2$  in MB solution left in the dark acted as a control to compute adsorption losses of MB onto  $\text{TiO}_2$ .

Under the experimental conditions used in Campinas (latitude  $24^\circ$  south,  $3.4 \text{ mW/cm}^2$ ), it was observed that evaporation losses can reach up to 10% in 60 min. In order to correct the data obtained in the MB photometric readings, the Petri dishes were weighed immediately before and after exposure. Losses due to evaporation were corrected by dropwise addition of distilled water.

The suspensions were filtered using  $0.22 \mu\text{m}$  membranes and the absorbance measured at 660 nm (tenfold dilutions were necessary for some samples). Readings were converted to concentrations with the help of calibration curve using MB standards. The results obtained are shown in the table. The photocatalytic activity of  $\text{TiO}_2$  can be seen easily by the fact that the extent of degradation reaches nearly 99% in just one hour. As shown in the table, the net value of 99% includes the contribution of some adsorption as well as direct destruction of the organic dye.

### Kinetics of Methylene Blue Photodegradation

According to Matthews (9), MB can be mineralized totally according to the equation:



### Photodegradation of MB Exposed to Sunlight

Condition	$C_0$ (mM)	$C_{60}$ (mM)	losses(%)
MB solution	0.1	0.082	17.7
MB sol. + $\text{TiO}_2$ (light)	0.1	0.015	98.4
MB sol. + $\text{TiO}_2$ (dark)	0.1	0.083	17.4

$C_0$  = initial concentration;

$C_{60}$  = concentration after 60 min. exposure.

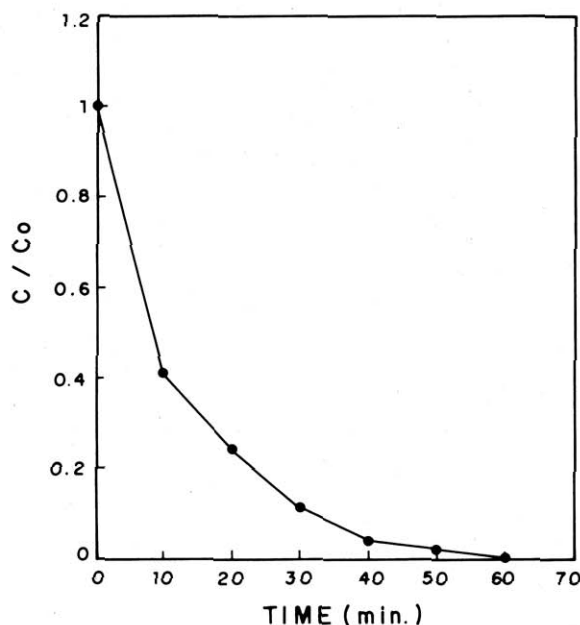


Figure 2. Degradation of methylene blue by solar light irradiation using  $\text{TiO}_2$  as photocatalyst.

The author mentioned also that "the rate of destruction obeys first-order kinetics with reasonable precision". In terms to evaluate the rate of mineralization under sunlight, both the constant  $k$  and the half-life ( $t_{1/2}$ ) of MB were calculated using the following procedure. Seven Petri dishes containing  $\text{TiO}_2$  suspended in MB solution (same concentration as used in the previous section) were exposed to sunlight for 60 min. At 10-min intervals, one Petri dish was withdrawn, weighed to correct losses due to evaporation, filtered, and analyzed for MB. The results are shown in Figure 2.

When plotting  $\ln C/C_0$  as a function of time, a straight line yield  $k = 0.078 \text{ min}^{-1}$  (slope) and  $t_{1/2} = 8.88 \text{ min}$ . The values are in good agreement to the same parameters determined by Matthews (9) using artificial UV lights ( $k = 0.070 \text{ min}^{-1}$  and  $t_{1/2} = 9.90 \text{ min}$ ) to the same concentration of MB used in this experiment.

## Conclusion

The experiment proposed in this paper can be used either to introduce or to explore further the numerous fundamental concepts necessary in modern chemistry courses. They include classical and environmental photochemistry, valence and conduction bands in semiconductors, light interactions with solids, adsorption phenomena, and kinetics.

The experiment also provides students the opportunity of dealing with nonconventional (and, in this case, low-cost) alternatives used to solve or ameliorate environmental problems.

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