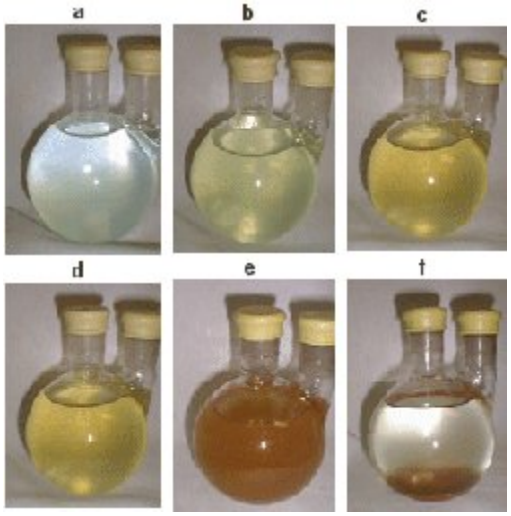
Argonne NATIONAL LABORATORY

Energy Systems Division

Removal of Heavy Metals from Waters by Using Organically Modified Nanosized Titanium Dioxide Colloids

Heavy metals, such as lead, cadmium, mercury, and copper, are toxic contaminants that must be removed from wastewaters before discharge. Conventional wastewater treatment processes to remove aqueous metals, such as precipitation, ion exchange, and electrowinning, have several limitations and drawbacks. They may require pretreatment, their by-products are often considered hazardous, and their disposal is costly. We have developed a new photocatalytic method for removing and chemically reducing metals such as lead, copper, cadmium, and mercury that may prevent the problems associated with conventional methods.



Wastewater containing copper sulfate and modified titanium dioxide (a) wastewater is continuously mixed and illuminated in (b)-(e). The change in color corresponds to the reduction of copper from Cu^{2+} to Cu^{o}. In (f), the solution has been settled for 2 minutes, with elemental copper at the bottom of the flask.

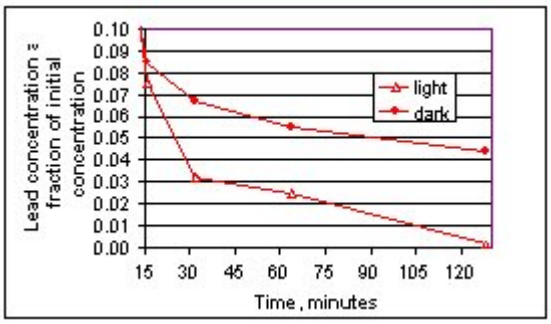
Photocatalysis using titanium dioxide (TiO2) has been extensively studied for oxidation and is known to be effective for destruction of organics. Work on photocatalytic metal removal has been much less extensive. A process that can remove metals and destroy organics at the same time would represent a significant breakthrough for the treatment of heavy-metal-contaminated waters at U.S. Department of Energy and industrial sites. In addition, metals deposited on the photocatalyst particle surface could be recovered or used directly as high-surface-area metal catalysts.

Our approach uses a wide-gap semiconductor TiO2, a nontoxic material widely used in paint and cosmetics. The surfaces of colloidal nanosized TiO2 crystals (~5 nanometers [nm]) are modified with various organic compounds that alter TiO2 reduction/oxidation properties, enabling photocatalytic reduction of certain heavy metals. Metal removal from water solutions occurs in two steps. First, metal ions in the solution are adsorbed to the TiO2 surface. Then, when illuminated with light of frequency greater than the bandgap energy, the adsorbed metal ions are photoreduced to their metallic form. Three mechanisms contribute to the enhanced metals removal/reduction:

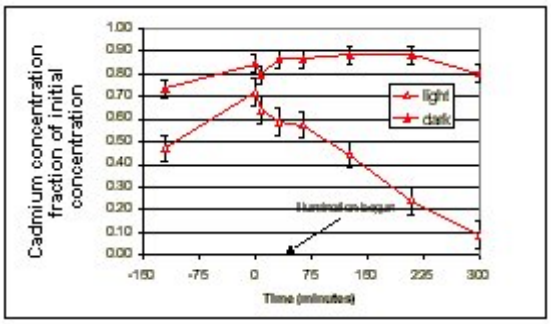
1. The modifiers promote sorption of the metal to the semiconductor crystal surface.
2. They create new trapping sites on the crystal, thus allowing a two-electron transfer to occur to the sorbed metal upon illumination.

3. They physically separate photogenerated electrons and holes, preventing their recombination.

Thiolactic-acid modified TiO2 is very effective in removing and reducing lead and cadmium, as shown below.



Residual lead concentration as a function of illumination time: 100 parts per million (ppm) of lead was removed/reduced to below detection limits.



Residual cadmium concentration in the filtrate as a fraction of initial cadmium concentration. The reagents were equilibrated under aerobic conditions and switched to anoxic conditions for the reaction.

In a 65 ppm cadmium solution, 75% of cadmium ions were removed and reduced. The result for cadmium is particularly significant because there is no other known method that can accomplish these results.

Alanine-modified TiO2 is effective for copper removal/reduction. In a 100 ppm copper solution with methanol as a hole scavenger; 50% removal was achieved after 60 minutes of illumination.