

THE EFFECT OF SUSPENDED SEDIMENTS
ON THE PHOTOLYSIS OF ORGANICS IN WATER

by

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August 1978

ABSTRACT

An assessment of the role of suspended sediments and clays on the rate and mechanism of photolysis of pollutants in water was carried out. It was found that even though semiconductor powders such as TiO_2 could photocatalyze the decomposition of organics such as methyl alcohol and p-dichlorobenzene in water, no such reaction occurred with naturally occurring suspended sediments or clays. The sediments and clays were found to decrease the rate of photolysis of pollutants such as methoxychlor by shielding the pollutant from the available light.

Photolysis is an important route of environmental degradation for many organic pollutants such as pesticides¹. To date most research has been focussed on measuring photolysis degradation rates in mixed solvents and distilled water². However, in the environment varying amounts of suspended sediments are present in the water and this sediment could change the rate of mechanism of photolysis of a pollutant in several ways. Suspended sediment may reduce the photolysis rate by either shielding the organic from the available light or by quenching the excited states of the organic molecules before they react to form products. It is also possible for suspended particulates to enhance the rate of organic photolysis if sediment absorption of light produces excited states or free radicals which can then react with the organic. In this way it is possible for organic materials which do not absorb sunlight to be photolyzed indirectly.

This type of indirect photolysis does occur with semiconductors such as TiO_2 which are common constituents of clays, sediments and soils³. In the presence of O_2 , ultraviolet (UV) irradiation of TiO_2 photooxidized alkanes to alcohols, aldehydes and ketones⁴. Also UV irradiation of aqueous TiO_2 slurries results in the dehalogenation of fluorinated benzenes⁵ and polychlorinated biphenyls⁶. Similar reactions have also been observed for some semiconductors such as ZnO ⁷. It has been reported that the speed of photolysis of certain pollutants is much higher in natural waters than in distilled water due to the presence of unknown sensitizers^{8,9}. This paper reports studies designed to elucidate whether suspended sediments accelerate the photolysis of aqueous organics by a mechanism analogous to photosensitized semiconductor reactions or whether they slow down photoreactions by shielding or quenching.

EXPERIMENTAL

Some commonly found clays (montmorillonite, kaolinite, bentonite, dolomite and illite) were obtained from Ward Scientific and several samples of suspended sediments from rivers flowing into the Great Lakes were collected and freeze-dried. For comparison purposes a sample of TiO_2 (anatase) powder was obtained from Fisher Scientific. The ultraviolet-visible absorption spectra of the clays, sediments and semiconductors was measured using a Pye-Unicam SP 1700 spectrophotometer equipped with a diffuse reflectance attachment. All spectra were referenced to magnesium oxide.

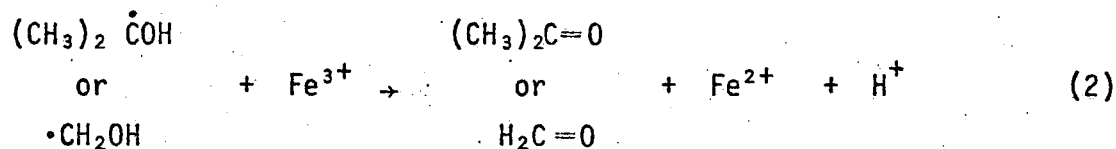
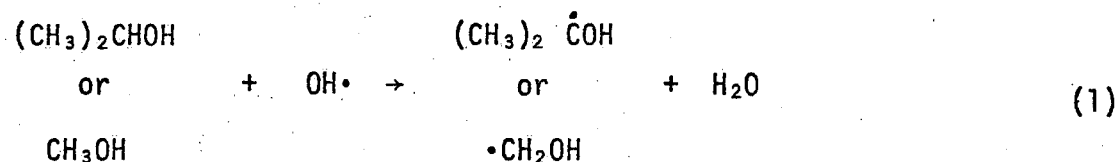
Aqueous solutions were irradiated as 1.0% slurries in a stirred quartz reaction vessel in a Rayonette photoreactor equipped with 300 nm or 350 nm ultraviolet lamps. The intensity of light impinging on the cell was 4.3×10^{-5} Einsteins/min at 300 nm and 6.3×10^{-5} Einsteins/min at 350 nm as measured by ferrioxalate actinometry¹⁰.

The Fe(II) yields were determined from the absorbance at 510 nm ($a = 1.09 \times 10^4$) using o-phenanthroline and a neutralization/dilution technique¹¹. Formaldehyde concentrations were measured colorimetrically ($a = 1.8 \times 10^4$ at 570 nm) using a modified chromatographic acid technique¹². After extraction of the 100 ml of slurry into 20 ml of pentane the dichlorobenzene concentrations were measured using a Tracor 550 gas chromatograph equipped with an electron capture detector. A glass column, packed with 10% OV-1 on Gas Chrom Q, was used isothermally at 130°C for the analysis. Methoxychlor was determined using the same extraction and gas chromatographic procedure except the temperature of the column was programmed from 230°C to 330°C at a rate of 5°C/min with a final hold of 4 min.

RESULTS AND DISCUSSION

The absorption spectra of a typical suspended sediment, clay and, semiconductor are shown in Fig. 1. All the materials absorbed light strongly in the ultraviolet spectral region but the semiconductor (TiO_2 , anatase) showed a sharp cut-off in absorption at about 400 nm corresponding to the band gap energy, whereas, the suspended sediment and clay continued to absorb a significant amount of light in the visible region of the spectrum. These spectra were typical of various materials studied although the wavelength dependence of the extinction coefficients varied significantly for the different suspended sediments and clays. To examine whether light absorption by these solids could lead to photoreactions, experiments were carried out with various scavengers which react with the photochemically produced free radicals to give readily identifiable products.

The first scavenger system employed was a degassed aqueous solution of isopropyl alcohol (0.26 M), methyl alcohol (0.49 M), ferric perchlorate (0.01 M), and perchloric acid (0.5 M). This system was chosen because the solution absorbs minimally at the irradiation wavelength (350 nm) and because alcohols are excellent scavengers for most oxygen containing free radicals^{13,14}. From studies of iron photochemistry¹¹ alcohol concentrations were selected that were large enough to scavenge all free radicals in the solution. Typical reactions of hydroxyl radicals in this solution are:



It can be seen that the production of one hydroxyl radical in the system eventually leads to the production of one Fe^{2+} molecule. Thus the addition of ferric perchlorate at concentrations large enough to react with all the alcohol radicals formed, suppresses chain reactions and provides a simple analytical system (Fe^{2+} analysis). Perchloric acid must be added to prevent dimerization and polymerization of the hexaquo iron (III) to species that absorb light at the irradiation wavelength¹¹. Unfortunately this strongly acidic solution caused decomposition of some of the materials under study (all suspended sediments, some clays), but some useful information was obtained.

Table 1 shows the Fe(II) quantum yields for the stable materials. There is a small but measurable Fe^{2+} yield in the scavenger solution in the absence of solids due to a small amount of light absorption of the hexaquo iron (III) charge transfer band which produces hydroxyl radicals¹¹. The semiconductor, TiO_2 , gave Fe^{2+} quantum yields well above the blank, whereas the montmorillonite and kaolinite clays gave Fe^{2+} yields below the blank. This indicates that the semiconductor is producing free radicals which are being scavenged in the system and that the clays are photochemically inactive in this solution.

Table I. Iron II quantum yields of 1% slurries of clays and TiO_2 in the aqueous solution $[\text{HClO}_4] = 0.5 \text{ M}$, $[\text{CH}_3\text{OH}] = 0.49 \text{ M}$, $[(\text{CH}_3)_2\text{CHOH}] = 0.26 \text{ M}$, $[\text{Fe}^{3+}] = 0.01 \text{ M}$. (Irradiation wavelength, 350 nm)

<u>Material</u>	<u>FeII Yield</u>
Blank	0.032
TiO_2 (anatase)	0.200
Kaolinite	0.0022
Montmorillonite	0.0048

The next scavenger system tested was an aqueous solution of 10% methanol. Methanol should react with oxygen containing free radicals to produce formaldehyde for which a very sensitive analytical technique is available¹². Formaldehyde quantum yields at 300 nm are reported for a few materials in Table II. Again there is a small but measurable yield with the scavenger solution in the absence of solids due to the photolysis of methanol. The addition of suspended sediments to the solution resulted in a reduction in the formaldehyde yield. The addition of the semiconductor TiO_2 led to large increases in the formaldehyde yield. When oxygen, an excellent electron scavenger, is added to the system (air saturated) the formaldehyde yields in all cases are increased substantially over the degassed solutions. Again, the semiconductor, TiO_2 , appears to be the only photoactive material with this scavenger system.

Table II. Formaldehyde quantum yields for 1% slurries of suspended sediments and TiO_2 in the aqueous solution 10% methanol (Irradiation wavelength, 300 nm).

<u>Material</u>	<u>Formaldehyde Quantum Yield</u>	
	Degassed	Air Saturated
Blank	0.00038	0.00058
TiO_2 (anatase)	0.0034	0.0821
Black River S.S.	0.00028	0.00041
40-Mile Creek S.S.	0.00015	0.00023

Since many of the persistent pollutants in natural waters are chlorinated compounds, an experiment was performed to see whether a chlorinated compound that did not absorb sunlight could be photodegraded when suspended sediment or clays were present. P-dichlorobenzene (pDCB) was chosen for

study since it has an absorption maximum of 275 nm and does not absorb significantly at the wavelength of irradiation (300 nm). A saturated aqueous solution of p DCB (47 ppm) was irradiated at 300 nm in the Rayonette photoreactor with 1.0% TiO_2 (anatase) and the p DCB degraded rapidly with a half-life of approximately 5 min. When saturated aqueous solution of p DCB were irradiated as 1.0% slurries with the clays, montmorillonite, kaolinite, bentonite, illite and dolomite, and with the suspended sediments from the Ausable, Grand, Black and 40-Mile Rivers, no decomposition of the p DCB was observed even after irradiation periods up to 4 hours in the photoreactor. The irradiation of slurries of the naturally occurring titanium containing ores, rutile, and ilmenite, again resulted in no decomposition of the p DCB from saturated aqueous solutions. Therefore, even though ultraviolet irradiation of the semiconductor, TiO_2 , can result in the photodecomposition of non-light absorbing organics in water, naturally occurring suspended sediments and clays do not appear to be capable of undergoing this type of photocatalytic reaction.

To find out what effect suspended sediments have on the photolysis rate of a compound that absorbs sunlight, the degradation rate of methoxychlor in the Rayonette photoreactor at 300 nm was studied as a function of suspended sediment concentration. Fig. 2 shows that the rate of photodecomposition of methoxychlor from a saturated aqueous solution (0.12 ppm) is considerably reduced in the presence of the suspended sediments. The half-life of methoxychlor in the photoreactor seems to increase linearly with suspended sediment concentration but at different rates for the two sediments studied. Although there is a large difference in organic carbon content between the two sediment (40-Mile Creek, 21%; Black River, 4.1%),

the major reason for the difference in behavior appears to be differential light absorption. The extinction coefficients at 300 nm, as measured in the secondary cell compartment of the spectrophotometer close to the photomultiplier, are $13.8 \times 10^{-4} \text{ L mg}^{-1} \text{ cm}^{-1}$ for 40-Mile Creek and $4.1 \times 10^{-4} \text{ L mg}^{-1} \text{ cm}^{-1}$ for Black River sediment. The true extinction coefficients of such suspensions are impossible to measure using a standard spectrophotometer because of sample light scattering. For example, if the measurement is made using the primary sample compartment of this spectrophotometer located some 15 cm from the photomultiplier, the apparent extinction coefficients are about twice the above values. In any case, the ratio of the extinction coefficients at 300 nm (30-Mile Creek/Black River) is about 3.3. The ratio of the slopes of the half-life versus concentration plots (40-Mile Creek/Black River) is 3.8. Therefore, to a reasonably close approximation, the suspended sediments appear to be simply shielding the methoxychlor from the available light.

In summary, even though suspended sediments and clays can contain TiO_2 and other semiconductors in the 5-10% range and even though they absorb sunlight, suspended sediments and clays do not appear to photocatalyze the decomposition of organic pollutants in water but reduce the rate of photolysis by shielding the pollutant from the available light.

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FIGURE CAPTIONS

Fig. 1 Ultraviolet-visible absorption spectra of TiO_2 (anatase), Black River suspended sediment, and montmorillonite clay.

Fig. 2 The effect of suspended sediment on the half-life of methoxychlor in a Rayonette photoreactor (Wavelength of irradiation, 300 nm).

ABSORBANCE

