

# TiO<sub>2</sub>-catalysed oxidative photodegradation of mercurochrome: an example of an organo-mercury compound

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## Abstract

Irradiation of mercurochrome in an aqueous medium containing TiO<sub>2</sub> caused the complete mineralization of this compound with deposition of metallic mercury on TiO<sub>2</sub>. It is suggested that the photocatalytic decontamination of water would lead to the removal of highly toxic organo-mercury compounds.

## 1. Introduction

Aqueous oxygenated suspensions of semiconductor particles (e.g. TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>) are known to catalyse oxidative mineralization of organic solutes [1–7]. A large number of potential water contaminants (e.g. phenols, organo-chloro and organo-phosphorus compounds) undergo complete mineralization (i.e. decomposition to CO<sub>2</sub>, N<sub>2</sub>, Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> etc.) in this process [1–7]. As the inert catalyst can be physically separated, the photocatalytic decontamination of water has potential practical applications. Heavy metals (e.g. Hg, Pb, Cd) constitute another class of water contaminants. They can occur in either the inorganic or organic forms [8, 9]. Inorganic forms of heavy metals (i.e. the ionic species) cannot be removed from solution by photocatalytic methods in the presence of oxygen. The electrons that are photogenerated in the catalyst are accepted by oxygen to yield O<sub>2</sub><sup>-</sup>, which combines readily with photogenerated holes or OH free radicals on the surface of the catalyst (OH free radicals are formed by hole capture of OH<sup>-</sup> adsorbed at the surface of the catalysts). In the absence of oxygen, electrons can be accepted by heavy metal cations resulting in the deposition of the metal on the surface of the catalyst [10]. A sacrificial agent that consumes holes greatly enhances the deposition of the metal.

The situation with respect to organic forms of heavy metals is different. In this case the oxidation of the organic components may result in the deposition of the metal on the surface of the catalyst.

As an example of such a compound, we have studied the oxidative photocatalytic degradation of the dye mercurochrome (merbromin) and have found that it is completely mineralized with deposition of metallic mercury on TiO<sub>2</sub>.

Mercury compounds are extremely hazardous and are known to contaminate water [8, 9]. Anthropogenic and natural processes can result in the mercury pollution of water. Both inorganic and organic mercury are cumulatively toxic and the latter form is known to be more virulent. This study suggests that photocatalytic methods may be adopted to remove organic mercury from water.

## 2. Experimental details

TiO<sub>2</sub> (99.9%) was purchased from Aldrich and the surface area was estimated using a Horiba particle size distribution analyser CAPA 700 (3.9 m<sup>2</sup> g<sup>-1</sup>). Deionized distilled water was used in all experiments. It was free from organic matter as tested by permanganate decoloration. Mercurochrome was used as purchased from Aldrich without further purification. Mercurochrome (0.15 mg) dissolved in 400 ml of water was ultrasonically agitated with 0.2 mg of TiO<sub>2</sub> for 45 min to obtain a uniform dispersion. Irradiations were carried out in a 500 ml water cooled (26 °C) cylindrical photochemical reactor (Applied Photophysics), with a 400 W medium pressure mercury lamp housed in an inner quartz jacket. In some experiments, a Pyrex thimble was used to cut off light of less than 300 nm. The suspension was purged continuously with air (4 ml min<sup>-1</sup>), the

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lamp was switched on and the outgoing gas was monitored for carbon dioxide (Shimadzu GC-9AM gas chromatograph, activated charcoal column, thermal conductivity detector). The gas chromatograph was calibrated using 99.9% carbon dioxide. Aliquots of solution drawn from the reactor at different intervals of time were centrifuged to remove the catalyst and the depletion of mercurochrome was determined spectrophotometrically at 498 nm (absorption spectrum and structural formula of mercurochrome are shown in Fig. 1). After prolonged irradiation, *i.e.* when carbon dioxide liberation had ceased, a sample of the solution was centrifuged to remove the catalyst and tested for mercury by passing  $H_2S$  and for bromide with silver nitrate. The residual catalyst was washed and a nitric acid extract was tested for mercury with  $H_2S$  and also ethylenediamine. The deposit on  $TiO_2$  was insoluble in a saturated solution of KI which confirmed that it was metallic mercury not oxides (oxides of mercury are soluble in saturated KI).

### 3. Results and discussion

Figure 2 shows the variation of the dye concentration in the solution with time during photolysis in the absence and presence of the filter. The corresponding carbon dioxide generation rates are shown in Fig. 3. The rate of disappearance of the dye in the solution and the rate of  $CO_2$  evolution are not identical at a given instant of time because of the dissolution of  $CO_2$  in water and the existence of initial steps of partial degradation. However, the total amount of  $CO_2$  liberated is in good agreement with the carbon stoichiometry of mercurochrome. The amount of  $CO_2$  liberated (*i.e.* when purging was continued until the gas chromatograph gave a signal close to the background level of  $CO_2$ ) was  $3.4 \times 10^{-4}$  mol. The theoretical yield expected from the mercurochrome content in the solution is  $3.9 \times 10^{-4}$  mol. Although the reaction rate is slower, a similar

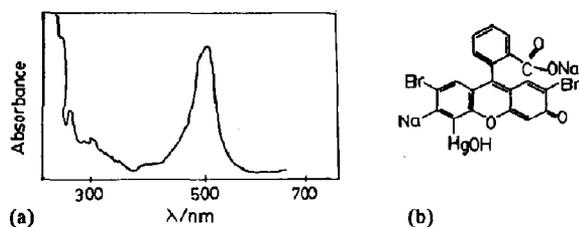


Fig. 1. (a) Absorption spectrum of mercurochrome. (b) Structural formula of mercurochrome.

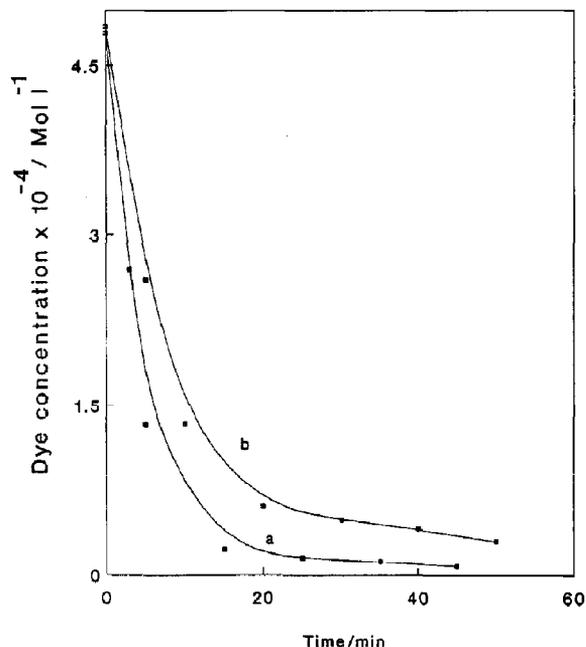


Fig. 2. Variation of the dye concentration in the solution with time during photolysis in the absence (a) and presence (b) of the filter.

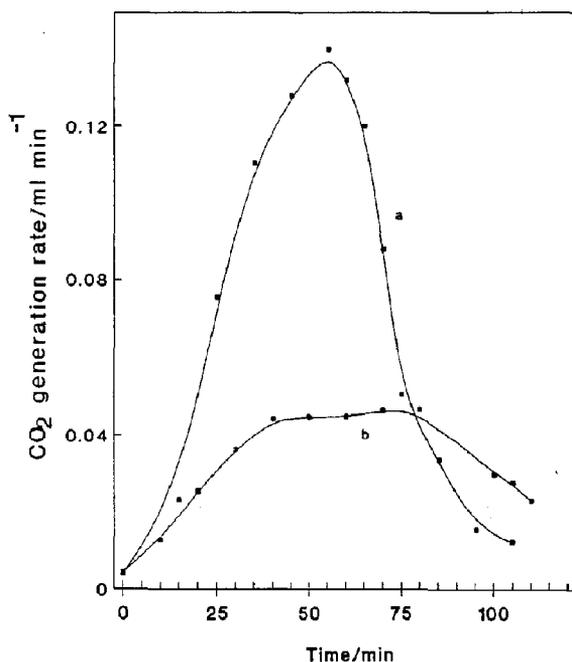


Fig. 3. Variation of the  $CO_2$  content in the air leaving the reactor with time in the absence (a) and presence (b) of the filter.

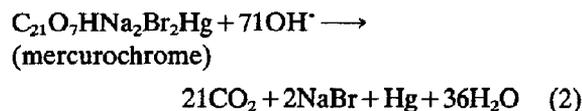
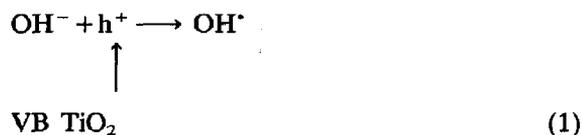
result was noted in the presence of the filter. The total amounts of  $CO_2$  obtained at different time intervals are presented in Table 1. When a solution

TABLE 1. Total amount of CO<sub>2</sub> liberated at different intervals of time

t (min)	CO <sub>2</sub> (mol)
25	0.5 × 10 <sup>-4</sup>
50	0.1 × 10 <sup>-4</sup>
100	2.1 × 10 <sup>-4</sup>
150	3.9 × 10 <sup>-4</sup>

of mercurochrome was irradiated with the full spectrum of the mercury lamp in the absence of TiO<sub>2</sub>, the colour faded owing to partial degradation. Carbon dioxide was detectable, but the yield was far below the value corresponding to complete mineralization. When the filter was used, there were no signs of degradation (partial or complete) in the absence of TiO<sub>2</sub>. In experiments with TiO<sub>2</sub>, analysis of the solution (subjected to irradiation) revealed the presence of bromide and sodium ions but not mercury. The used catalyst was ash coloured and readily sank to the bottom of the reactor. The ash colour was cleared by dilute nitric acid with the emission of nitric oxide. The nitric acid extract was found to contain mercury. These experiments prove that metallic mercury is deposited on TiO<sub>2</sub>.

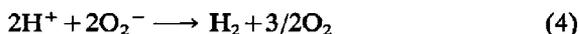
The reactions of the photogenerated electrons and holes leading to degradation can be understood as follows. Holes react with OH<sup>-</sup> ions to form hydroxyl free radicals, that accumulate as adsorbed species on the surface on the catalyst particles. Subsequently, hydroxyl free radicals oxidize mercurochrome, *i.e.*



Electrons in the conduction band react with O<sub>2</sub> to yield O<sub>2</sub><sup>-</sup>, *i.e.*



and the charge transfer cycle is completed by H<sup>+</sup> ions accepting electrons to form O<sub>2</sub>, *i.e.*



It is probable that these reactions involve several intermediate steps and products.

#### 4. Conclusions

In TiO<sub>2</sub>-sensitized photocatalytic oxidative degradation of mercurochrome, metallic mercury is deposited on TiO<sub>2</sub>. The situation with respect to ionic mercury is different. Mercury ions (Hg<sup>2+</sup>, Hg<sup>+</sup>) are not photoreduced and deposited as metal on TiO<sub>2</sub> in an oxygenated solution. In the absence of oxygen there is partial deposition, and complete deposition becomes possible only in the presence of a reducing agent [11]. The Hg<sup>2+</sup> ion forms organometallic complexes with citric acid; in the presence of citric acid, metallic mercury is photodeposited on TiO<sub>2</sub> from oxygenated solutions of Hg<sup>2+</sup>. Although generalizations are not possible from the results based on one or two compounds, it is probable that most organo-mercury compounds, in which mercury is covalently linked, will behave in the same manner. Experiments with many organo-mercury compounds are needed to arrive at a general conclusion. The result is encouraging, because photocatalytic oxidative water purification could automatically remove any organic mercury from the aqueous phase.

#### References

- 1 T. Hissanaga, K. Harada and K. Tanka, *J. Photochem. Photobiol. A: Chem.*, 54 (1990) 113.
- 2 R. W. Mathews, *Water Res.*, 20 (1986) 569.
- 3 S. Ahmed and D. F. Oillis, *Sol. Energy*, 32 (1984) 597.
- 4 C. H. Langford and H. Carey, in W. J. Cooper and R. G. Zika (eds.), *Photochemistry of Environmental Aquatic Systems*, ACS Symposium Series No. 327, American Chemical Society, 1991.
- 5 J. C. D. Oliveira, G. Al. Sayed and P. Pichat, *Environ. Sci. Technol.*, 24 (1990) 990.
- 6 H. Ohinishi, M. Matsumura, H. Tsubomura and M. Iwasaki, *Ind. Eng. Chem. Res.*, 28 (1989) 719.
- 7 N. Duran, M. Dezotti and J. Rodrigues, *J. Photochem. Photobiol. A: Chem.*, 62 (1991) 269.
- 8 G. Kaiser and G. Tolg, in O. Hutzinger (ed.), *Environmental Photochemistry*, Vol. 3, Part A, Springer, Berlin, 1980, pp. 1-101.
- 9 F. M. D'Itri, *The Environmental Mercury Problem*, Chem. Rubber Co., Cleveland, OH, 1972.
- 10 J. M. Herrmann, J. Disdier and P. Pichat, *J. Catal.*, 113 (1988) 72.
- 11 K. Tennakone, *Sol. Energy Mater.*, 10 (1984) 235.