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Photocatalytic method for removal of mercury from contaminated water

K. Tennakone [1,*], U.S. Ketipearachchi

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

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Abstract

Inorganic mercury complexes with citrate ions. In oxidative photodegradation of this complex with TiO_2, metallic mercury is found to become deposited on TiO_2. The reaction is sufficiently sensitive to sunlight and for practical application TiO_2 can be confined in a transparent dialysis bag to facilitate the disposal of extracted mercury.

Keywords: Citrate complexes; Mercury removal; Photodegradation; Titania; Water

1. Introduction

Heterogeneous photocatalysis is becoming recognized as a promising method for destroying and totally mineralizing organic pollutants in water [1–8]. Aqueous oxygenated suspensions of TiO_2 oxidatively degrade a large number of potential organic water contaminants [1–8] (e.g., phenols, carboxylic acids, organo-chloro and organo-phosphorus compounds). As the inert photocatalyst can be physically separated, photocatalytic mineralization of organic pollutants is considered to be practically viable.

The other severely hazardous water contaminants are heavy metals, notably mercury [9,10]. Both inorganic and organic mercury are cumulatively toxic [9,10]. Effluents from a number of industries [9,10] are contaminated with mercury and there is an urgent necessity for developing cheap methods to decontaminate mercury polluted water. TiO_2 is also known to act as a photocatalyst to remove mercury and other (e.g., lead) heavy metal ions from aqueous solutions [11–19]. In methods

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[*] Corresponding author.

[1] Sumanasekara Chair in Natural Sciences

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reported in the literature [12–19], any significant degree of metal removal by deposition in TiO_2 occurs only in the presence of hole-consuming sacrificial agents and in the absence of oxygen. The suggested reaction mechanism is

$$h\nu \xrightarrow{TiO_2} \underset{\text{conduction band}}{e^-} + \underset{\text{valence band}}{h^+} \tag{1}$$

$$Hg^{2+} + 2e^- \rightarrow Hg \tag{2}$$

$$h^+ + OH \rightarrow OH^0 \tag{3}$$

$$nOH^0 + \text{sacrificial agent} \rightarrow CO_2 + H_2O \text{ etc.} \tag{4}$$

In the presence of oxygen, the above reaction is suppressed, as oxygen is also an efficient electron acceptor. For practical applications deoxygenation of polluted water is prohibitively expensive and it is essential to develop cheap techniques that work effectively even in oxygenated solution. We have found that in the presence of citrate ion (which complexes with Hg^{2+}), metallic mercury is readily photodeposited on TiO_2 from an oxygenated solution. Evidence is presented to show that the reaction mechanism here is not electron transfer to Hg^{2+} with hole consumption by citrate, but electron transfer to oxygen with hole consumption by the (citrate–Hg^{2+}) complex. Thus the complex is oxidised with deposition of metallic mercury on TiO_2. The reaction is sufficiently sensitive to sunlight so that ca. 20 ppm Hg^{2+} was removed in ca. 30 min exposure to sunlight. In order to simplify the separation of mercury coated TiO_2, the experiment was conducted by confining the catalyst to a transparent dialysis bag immersed in the solution.

2. Experimental

TiO_2 (99.9%) purchased from Aldrich was used in all experiments. The deionized distilled water used was tested for organic matter by the permanganate decoloration test. Weighed quantities of TiO_2 were dispersed in water by sonication, and in order to obtain reproducible results, sonication was continued until the particle size distribution remained independent of the time of sonication. Photolysis experiments 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. A pyrex thimble filtered out light of wavelength < 300 nm. Photolysis solutions (350 ml) contained different concentrations of $HgCl_2$ (BDH) and citrate (Trisodium citrate, Aldrich) at a pH of ca. 7. pH adjustments were made using sodium hydroxide and citric acid. Solutions were kept purged with carbon dioxide free air (bubbling rate ca. 20 ml min^{-1}). For comparison, experiments were repeated by replacing air with argon (99.99%). In both sets of experiments, the outgoing gas was monitored for carbon dioxide by gas chromatography (Shimadzu GC-9AM gas chromatograph, activated charcoal column, thermal conductivity detector). Mercury depletion in the solution was determined as follows: Aliquots of solution drawn at different intervals of time were centrifuged to remove the catalyst; mercury in the clear solution was determined by the dithiazone method [20]. The residual catalyst was washed and the nitric acid extract was tested for mercury by the same method. The deposit on TiO_2 is soluble in nitric acid, but insoluble in strong sulphuric acid, indicating that the deposit is metallic mercury but not the oxides. X-ray diffractometry (Shimadzu XD-7A X-ray diffractometer) confirmed that the deposit is metallic mercury. On prolonged exposure of the used catalyst to the atmosphere, oxides of mercury were also detected.

To devise a practical method, the following experiment was carried out. 400 ml of water containing 20 ppm Hg^{2+} and $2\cdot10^{-4}$ *M* citrate were placed in a cylindrical glass vessel (diameter 4 cm). A portion of the same solution and 0.05 g of TiO_2 was kept in a transparent cellulose dialysis bag (Spectrapor) of 2.8 cm diameter. The vessel was exposed to sunlight and the TiO_2 inside the bag was agitated by purging air (Fig. 4). At different intervals of time aliquots of solution drawn from the beaker (outside the bag) were quantitatively estimated for mercury (dithizone method [20]). The average solar intensity during the period of exposure as measured with an Eko Pyranometer (Model SBP-801) was 0.7 kW m^{-2}. For confirmation a blank experiment was also conducted in the dark.

3. Results and discussion

Fig. 1 shows the time variation of the rate of carbon dioxide liberation ($R[CO_2]$) at different Hg^{2+} concentrations, when the citrate ion concentration ($2\cdot10^{-4}$ *M*) and the TiO_2 concentration (0.25 g l^{-1}) were kept fixed. Curve 5 of this figure gives the rate of carbon dioxide liberation when Hg^{2+} is absent. It is clear that the presence of Hg^{2+} greatly enhances $R[CO_2]$. When $[Hg^{2+}]$ is increased, $R[CO_2]$ initially increases and then begins to decrease as $[Hg^{2+}]$ is further increased. Fig. 2 shows a similar set of curves for the argon purged solution. As in the previous case, the presence of Hg^{2+} greatly increases $R[CO_2]$. Furthermore as $[Hg^{2+}]$ is increased, $R[CO_2]$ initially increases and begins to decrease. Compared to the air purged system $R[CO_2]$ continues to increase until a higher $[Hg^{2+}]$ is approached (ca. $7.5\cdot10^{-4}$ *M* and $1.5\cdot10^{-3}$ *M*, respectively, in the air and argon purged systems).

Our observation that the rate of mineralization of citrate (in the presence of O_2) is enhanced by Hg^{2+}, can be explained on the basis of the following argument. The citrate ion ($Cit^{3-}=C_6H_5O_7^{3-}$) forms complex anions of the form $[Hg^{2+}nCit^{3-}]^{-3n+2}$ with Hg^{2+} and a number of other heavy metals [21,22], where *n* is dependent upon pH and citrate concentration. During irradiation, photogenerated holes in TiO_2 are transferred on to OH^- to generate OH^0 free radicals, which react with the complex, i.e.

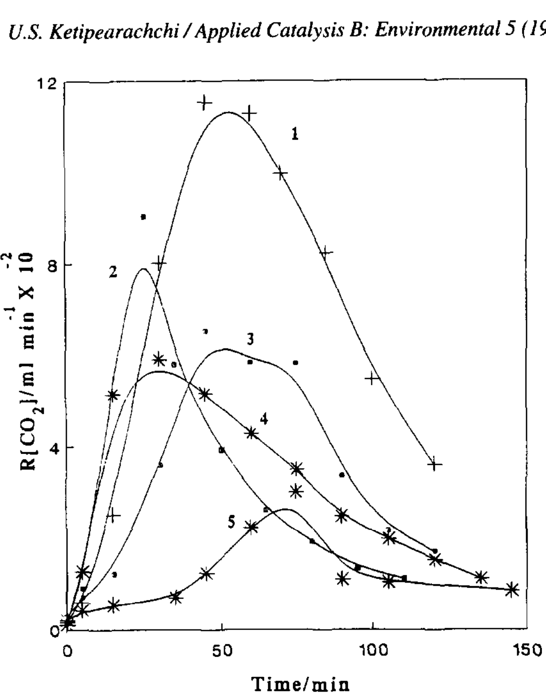

Fig. 1. Plot of rate of carbon dioxide generation ($R[CO_2]$) from a air purged solutions (350 ml) containing $2\cdot10^{-4}$ *M* citrate, 0.25 g l^{-1} TiO_2 and Hg^{2+} concentrations of (1) $7.5\cdot10^{-4}$ *M*, (2) $2.5\cdot10^{-4}$ *M*, (3) $1.5\cdot10^{-3}$ *M*, (4) $5\cdot10^{-4}$ *M* and (5) in the absence of Hg^{2+}.

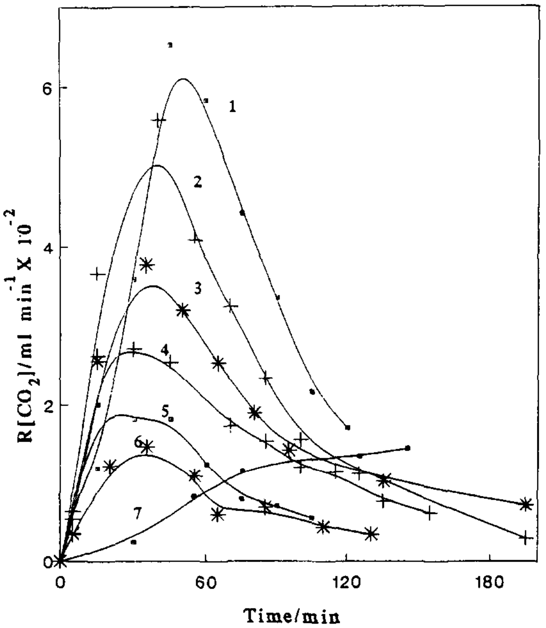

Fig. 2. Plot of rate of carbon dioxide generation ($R[CO_2]$) from argon purged solutions (400 ml) containing $2\cdot10^{-4}$ *M* citrate, 0.25 g l^{-1} TiO_2 and Hg^{2+} concentrations of (1) $1.5\cdot10^{-3}$ *M*, (2) $3.0\cdot10^{-3}$ *M*, (3) $7.5\cdot10^{-4}$ *M*, (4) $5\cdot10^{-4}$ *M*, (5) $2.5\cdot10^{-4}$ *M*, (6) $1.25\cdot10^{-4}$ *M* and (7) in the absence of Hg^{2+}.

$$Hg^{2+} \cdot nCit^{3n-} + (3n-2)H^+ + (18n-2)OH^0$$
$$\rightarrow 6nCO_2 + (13n-2)H_2O + Hg \quad (5)$$

Mercury formed in the reaction (5) is deposited onto TiO_2. Photogenerated electrons are accepted by oxygen and the charge transfer cycle is completed via

$$O_2 + e^- \rightarrow O_2^{0-} \quad (6)$$

and the protonation of the superoxide anion, i.e.

$$H^+ + O_2^{0-} \rightarrow OOH^0 \quad (7)$$

The species OOH^0 could directly attack the sacrificial agent or dismutate to yield hydrogen peroxide.

An aqueous solution of Hg^{2+} and citrate contains the complex anions as well as free Hg^{2+}. Thus in the argon purged solution, the electron consumption is via (2) with (4) as the hole consuming reaction. Here both electron and hole consuming reactions lead to deposition of mercury on TiO_2. The observation that in argon purged solutions, an optimum $R[CO_2]$ occurs for higher concentrations of added Hg^{2+} can be understood, because Hg^{2+} is also needed for electron consumption. The fact that the presence of Hg^{2+} enhances carbon dioxide production from citrate in both reactions (i.e., air purged and argon purged) suggests that the mercury–citrate complex ion is more susceptible to photocatalytic degradation than the citrate ion. Presumably, the complex ion is more strongly chemisorbed on TiO_2 than the citrate ion, and reaction (5), which takes place at the catalyst surface, is enhanced.

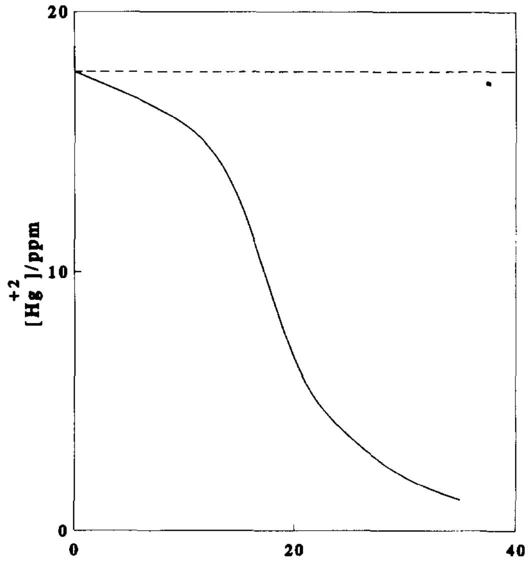

Fig. 3. The rate of depletion of Hg^{2+} in the experiment with sunlight, TiO_2 kept confined in a dialysis bag (Fig. 4). The dashed line indicates the mercury concentration in a blank test without irradiation.

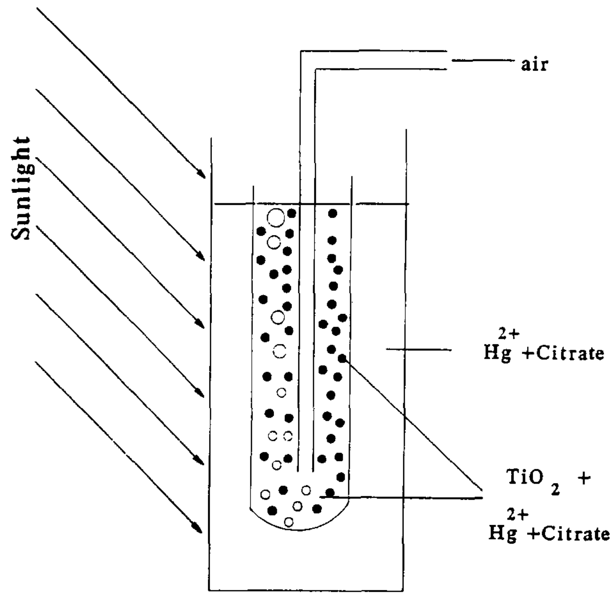

Fig. 4. Experimental set up for removal Hg^{2+} by exposure of contaminated water to sunlight.

Detailed reaction mechanisms could be more complicated than the description given above. What is important is the practical utility of the method. Fig. 3 shows the depletion of mercury in the experiment with sunlight (Fig. 4) described in the experimental section. Nearly 20 ppm of Hg^{2+} are removed in ca. 30 min. Reaction takes place inside the dialysis bag. As the reaction proceeds, Hg^{2+} in the solution outside the bag continuously diffuses into the bag. This could be readily adopted to remove mercury industrial effluents. Any remaining citrate generally causes no problem as it is non-toxic. If necessary residual citrate can be removed by further exposure to sunlight in the presence of TiO_2.

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