

# REMOVAL OF METHYLMERCURY FROM WATER BY HETEROGENEOUS PHOTOCATALYSIS

J. Aguado<sup>a</sup>, M.J. López-Muñoz<sup>a</sup>, A. Arencibia<sup>b</sup>, R. Pascual<sup>a</sup>,

<sup>a</sup> Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain ([mariajose.lopez@urjc.es](mailto:mariajose.lopez@urjc.es))

<sup>b</sup> Department of Chemical and Energy Technology, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain

## Abstract

The feasibility of heterogeneous photocatalysis using TiO<sub>2</sub> for the removal of methylmercury from wastewater has been evaluated under different experimental conditions. The influence of pH, and the presence or absence of oxygen on the efficiency of Hg(II) reduction and methyl group oxidation has been investigated. The results obtained prove that the photocatalytic treatment is efficient to achieve the disposal mercury concentrations currently legislated

Keywords: methylmercury; organomercurial compounds; heterogeneous photocatalysis; TiO<sub>2</sub>

## Introduction

Pollution of water with mercury is a worldwide problem because mercury and its compounds have adverse effects in both the human health and the environment, due to their toxicity and high tendency to bioaccumulate. Mercury enters the environment from a large number of human activities including industries such as chloro-alkali factories, agricultural applications, mining, thermometers, dental and electrical products (Global Mercury assessment, 2002). The extent to which mercury is harmful depends on the form of mercury present in the ecosystems. Besides the elemental state, mercury can be found in waters as either inorganic mercury, such as mercury chloride or mercury sulphide, or organic mercury as for example methylmercury or phenylmercury. In general terms, the toxicity of the organomercurial compounds is much higher than the inorganic mercurial compounds (Patra and Sharma, 2000), being methylmercury one of the most toxic forms because it is efficiently retained and bioconcentrated by organisms at various levels in the food chain.

It is therefore urgent to develop appropriate technologies for the treatment of waters polluted with mercury before being discharged to aquatic systems. The techniques currently used to remove mercury from wastewater include precipitation, ion exchange, chemical reduction, membrane separation and biological detoxification (U.S. EPA, 1997). However, some of them require high costs and large treatment times to achieve the legislated concentration limits, which are increasingly restrictive (European Parliament and of the Council, 2008).

In a previous study we have demonstrated the feasibility of heterogeneous photocatalysis for uptake of aqueous inorganic mercury Hg(II), achieving the currently established disposal limits (100–200 mg L<sup>-1</sup>

<sup>1)</sup> (López-Muñoz et al.). The objective of the present work has been to investigate the scope of organic mercury uptake by photocatalytic treatment of aqueous solutions of CH<sub>3</sub>HgCl with TiO<sub>2</sub>. The influence of pH, and the presence of oxygen or nitrogen on the efficiency of Hg(II) reduction and the methyl group oxidation has been studied.

## Methods

Mercury adsorption, photolysis and photocatalytic reactions were performed separately to evaluate the effectiveness in removal methylmercury from water at different pH values with TiO<sub>2</sub> Degussa P25. Batch experiments were carried out in a thermostated 1 L batch annular reactor provided with an axially immersed medium pressure Hg lamp (150W, Heraeus TQ-150) for UV irradiation. Methylmercury(II) chloride (CH<sub>3</sub>HgCl) was used to prepare organic solutions of 10 mg·L<sup>-1</sup> concentration. Different reactions were carried out under air-equilibrated conditions or in the absence of oxygen by bubbling a nitrogen stream. Influence of pH was evaluated in the range 2 to 10, by adjusting the pH with HNO<sub>3</sub> or NaOH.

Mercury concentration in solution was analyzed by a PSA Analytical, Millenium Merlin cold vapor atomic fluorescence spectroscopy (CV-AFS). Additionally, anion concentration was measured by ion chromatography using a 732-IC-Detector and a Metrosep A Supp 5-250" column.

Samples recovered after photocatalytic reactions were filtered and analyzed by XRD (Philips X'PERT MPD equipment) to characterize the mercury crystal phases.

## Results and discussion

Preliminary adsorption experiments were performed in the dark using a CH<sub>3</sub>HgCl solution of 10 mg·L<sup>-1</sup> concentration at different initial pH values. Mercury adsorption on the titania surface was scarce at all pH values, evidencing a negligible affinity of the organomercurial for the catalyst surface at pH 2 and natural pH. At alkaline pH conditions slight increments in the adsorption were detected, achieving mercury uptake percentages of 7.9 % and 13.4 % at pH 7 and 10, respectively.

Figure 1 shows the kinetic profiles of photocatalytic removal of aqueous mercury under nitrogen flow at acidic and alkaline pH conditions. It is evidenced the strongly dependence of the photocatalytic reaction on the solution pH, being the process enhanced by increasing the initial pH of the solution. An efficient uptake of aqueous mercury was achieved in the reactions performed at initial pH 5, 7 and 10. Under these experimental conditions the concentration of mercury remaining in solution at the end of the reaction was lower than 100 ppb (legislated limit).

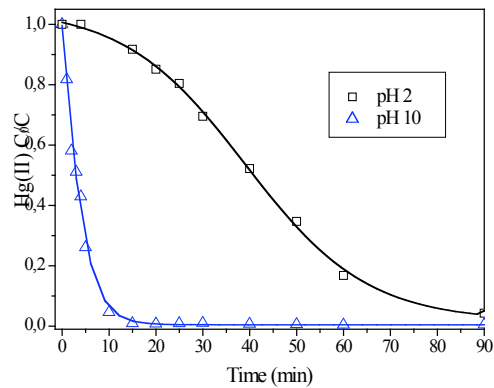


Figure 1. Kinetics of photocatalytic removal of methylmercury

Some reactions were carried out in the presence of oxygen in order to promote the oxidation of the methyl group and simultaneously favour the reduction of Hg(II). The presence of oxygen, however, was found to be detrimental for the overall process, the negative effect so much evident as lower the pH of the solution.

The characterization of the catalysts recovered after performing the reactions, showed that mercury is mainly deposited as elemental mercury on the catalyst, from where it can be recovered by treatment with nitric acid.

## Conclusions

It is plausible to achieve the removal of methylmercury from aqueous solutions by heterogeneous photocatalysis with titanium dioxide. This treatment allows achieving the disposal mercury concentrations currently legislated.

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