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Advanced oxidation of organic matter in natural waters with TiO₂ immobilized films

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Abstract: The purpose of this paper is to report the development of a laboratory-scale pilot based on the use of TiO₂ photocatalytic thin films for degrading organic matter and pollutants from natural water. The photoreactor consists of a channel inclined with a glass plate coated by TiO₂ in both faces and fixed at 1 cm from the bottom. The thin film was immobilized on the glass plates by *Sputtering* technique. The reactor was designed to be able of reproduce the hydraulic conditions of a water treatment plant. In experimental testing of degradation of organic matter with solar irradiation maximum efficiency of 50% was achieved. At optimal conditions it was possible to exceed the efficiencies of a full scale preozonation in a water treatment plant, thus providing a more sustainable process.

Keyword: Advanced oxidation - TiO₂, NOM-removal, hydraulic effects

Introduction

A natural organic matter (NOM) has a significant impact on drinking water quality and it is always present in water. For this fact the NOM should be completely removed in water treatment plant (WTP). Ozonation is a common pre-treatment in WPT combining high oxidizing potential of NOM with an efficient bactericidal action. This process and others (e. g. membrane technologies) have high operating costs and/or generating sub products. Advanced oxidation processes (AOP) like heterogeneous photocatalysis with TiO₂, with capacity in removing NOM and micropollutants using solar radiation as a source of energy (Chong *et al.*,2010). This process is able to oxidize and mineralize almost any organic molecule, yielding CO₂ and inorganic ions as final products. Another characteristic of TiO₂ is it highly reactive, nontoxic relatively inexpensive and chemically stability (García *et al.*,2011). The purpose of this work was to study the performance of a laboratorial pilot, a continuous flow reactor, with TiO₂ immobilized on a glass by *Sputtering*.

Material and Methods

The photodegradation process was performed on a laboratory-scale pilot presented in Figure 1.1. with and without the contribution of TiO₂ sputtered thin films. The experiments with the pilot were carried outside of Hydraulics and Environment Laboratory at Minho University (Latitude: N 41° 27 '07.60" and Longitude: 8°O 17'

31.93"), under clear sky conditions between June and October 2012. The incident visible-light (I_{vis} , $400 < \lambda < 700 \text{ nm}$) irradiance was measured using a Radiometer *OHM – HD 902*. As shown in Figure 1.1 the plate with TiO_2 coating on both sides is placed at a depth of 1 cm. In Figure 1.2 it is shown the scanning electron micrograph (SEM) of the TiO_2 film cross-section on the upper surface of the plate. The degradation tests were accomplished with three concentrations of humic acid (HA) from Aldrich, CAS: 1415-93-6, which simulates NOM. The solution of HA flowed inside the reactor with two different flow rate, 3 and 6 L/h. A sample was collected every 5 min and the absorbance was measured on an *Unicam UV2 Spectrophotometer* at the wavelength of 254 nm.

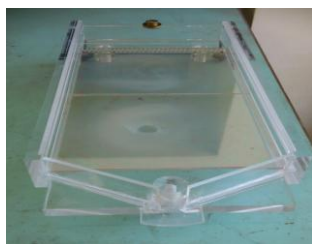


Figure 1.1 Laboratorial pilot

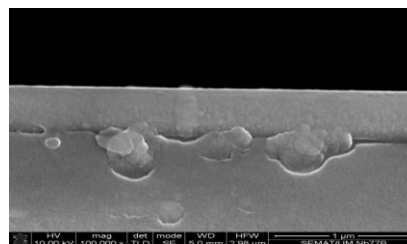


Figure 1.2 SEM image of TiO_2 coating

Results and Conclusions

The best removal efficiency obtained with and without TiO_2 under solar light was 39% and 49%, respectively (Figure 1.3). The kinetics of photodegradation of NOM follows

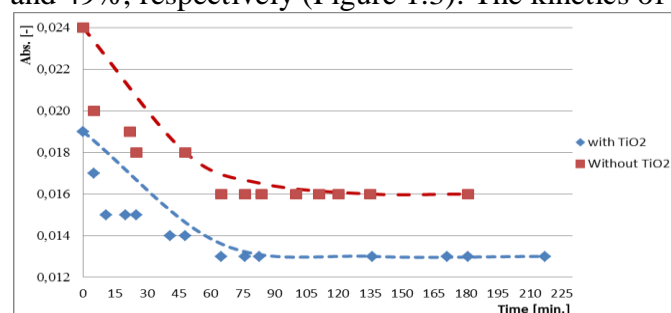


Figure 1.3 NOM degradation over time

Langmuir-Hinshelwood model with an apparent first order rate constant (K_{app}) of 0.006 min^{-1} . The maximum efficiency was obtained after 77 kJ/L irradiation, for a contact time of 1h09min and a surface area of 0.14 m^2 .

The HF with TiO_2 immobilized presents higher efficiencies than the preozonation process of a local WPT that has an annual average efficiency of NOM's degradation of 47%. According to the toxicity tests performed, it was found that the byproducts generated are not potentially toxic. The advantages of using TiO_2 films are: (i) oxidation potential of NOM; (ii) protection of the public health of the effects to direct/indirect TiO_2 nanoparticles exposure when used in suspension (EPA, 2010); (iii) does not require the solid-liquid separation; (iv) lower energy costs in relation to preozonation. This study is the initial phase of technological development of a new innovative technology that can solve economic, environmental and social problems.

References

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