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Photocatalytic inactivation of bacteria in water using suspended and immobilized silver-TiO_2

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ABSTRACT

Incorporation of silver to titanium dioxide is of great interest for photocatalytic disinfection applications since in addition to the enhancement of the electron–hole separation and interfacial charge transfer and the increase in the visible light response, silver compounds present a strong bactericidal effect. Ag/TiO_2 materials used in suspension and immobilized in two different configurations (catalytic wall and fixed-bed reactors) have been prepared, characterized and tested using *Escherichia coli* as model microorganism. Although the incorporation of silver to powdered Degussa P25 TiO_2 increases the activity, the thermal treatment required for the stabilization of the supported metal particles reduces the global efficiency. The comparison with experiments of dye photodegradation indicates that the activity of Ag/TiO_2 is mainly due to the bactericidal role of silver and not to the enhancement of the photocatalytic mechanism. The best tested system has been proved to be the Ag/TiO_2 catalytic wall reactor with a 0.6 wt.% of Ag loading, showing a high activity both in relative (per gram of TiO_2) and absolute terms, an optimal use of the radiation source, and a good stability of the film with negligible silver lixiviation, allowing the continuous treatment of water.

1. Introduction

Oxidation technologies such as chlorination and ozonation have long been used for the disinfection of water. However, several concerns have emerged regarding these treatments, mainly due to the formation of potentially harmful disinfection by-products such as trihalomethanes and haloacetic acids upon reaction with the naturally occurring organic matter and halide ions [1–3].

Advanced oxidation processes (AOP) have been extensively investigated for the treatment of wastewater [4–6]. Among them, TiO_2 photocatalysis has emerged as a promising alternative technology for the disinfection of water with purposes of drinking water supply or reuse of wastewater plant's effluents [7,8]. In addition to the high photostability and low cost of the catalyst, the heterogeneous photocatalytic technologies have several advantages over other AOPs such as working under ambient conditions of temperature and pressure, the use of air as oxidant reactant, and the possibility of using solar light to drive the process, all items very interesting from the energy consumption and environmental impact viewpoints.

One of the main drawbacks of TiO_2 photocatalysis is the relatively high band gap energy of the semiconductor (above 3.0 eV for rutile and 3.2 eV for anatase, corresponding to UV-A radiation) what limits the absorption of light to only approximately 3–5% of the solar spectrum [9]. In addition to that, the quantum yield of the process is in the order of 4% [10] what means that only 1 of every 25 electron–hole pairs generated upon radiation absorption are successfully leading to the desired reaction, whereas the remaining recombine releasing heat. For those reasons, important research efforts have been devoted to the improvement of the photocatalytic efficiency by doping or metallization of the catalyst surface [11,12]. Among the metallic species usually incorporated to TiO_2 surface, silver has shown an enhancement of the electron–hole separation and interfacial charge transfer [13,14], increasing the visible light excitation of TiO_2 [15]. In addition to that, the strong bactericidal power of silver compounds makes Ag/TiO_2 materials very attractive to explore the potential in photocatalytic disinfection applications, as confirmed by the enhancement for the photocatalytic inactivation of microorganisms reported by several research groups upon incorporation of silver into the catalysts [16–19]. The mechanism of the silver toxicity is still unclear, being suggested the possible alteration of the membranes properties through the degradation of lipopolysaccharide molecules and the subsequent increase in the membrane permeability or the damage of the DNA [20].

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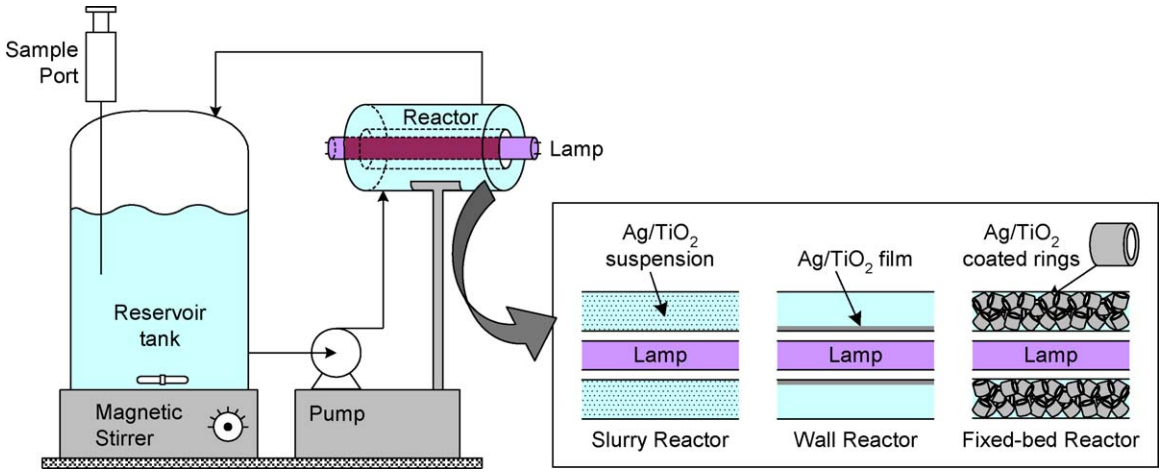

Fig. 1. Experimental setup used for the photocalytic reactions (see text for details).

On the other hand, another important limitation of the photocatalytic technologies using titanium dioxide suspensions is the need of a post-treatment separation stage [21,22]. Consequently, the treatment of water in continuous reactors require the development of immobilized TiO_2 systems to avoid the recovery stage and the losses of catalyst [23], being this aspect particularly important when silver or other expensive metals have been incorporated into the TiO_2 [24]. However, the use of immobilized photocatalysts usually introduces mass transport limitations that reduce the global efficiency of the reaction, a feature that could be particularly significant in disinfection processes due to the high size of microorganisms [25]. Moreover, the adhesion between bacteria and catalyst has been shown to play a crucial role on the efficiency of the process [26–28].

This work is focused on the development of Ag/TiO_2 materials with enhanced photocatalytic efficiency for the disinfection of water. Two different silver-modified titania immobilized systems have been used (catalytic wall and fixed-bed reactors), comparing their activity with that corresponding to powder Ag/TiO_2 in suspension and with bare TiO_2. *Escherichia coli* has been selected as model microorganism, due to its wide use as indicator of faecal contamination.

2. Experimental

2.1. Photoreactor

The photocatalytic experiments have been carried out in the experimental setup schematized in Fig. 1. The annular photoreactor (15 cm long, 3 cm inner diameter and 5 cm outer diameter) operates in a closed circuit with a reservoir tank, recirculating at 2.5 L min^{-1} of flow rate, being the total working volume of 1 L. A Philips TL6-W black light with an emission maximum at 365 nm was placed in the axis of the annulus to irradiate the reactor with a stationary UV-A incident photon flow of 2.8×10^{-6} Einstein s^{-1} (calculated by ferrioxalate actinometry). In all cases, the lamp was switched on 15 min before the reaction starts to stabilize its emission power and spectrum.

The Ag/TiO_2 photocatalysts were tested in three different reactor configurations previously tested using pure TiO_2 photocatalysts [23] to investigate the role on the photocatalytic reaction of the silver incorporated into the materials:

(i) Slurry reactor, in which the 0.1 g L^{-1} Ag/TiO_2 particles are suspended in the whole liquid volume of the recirculation system. This catalysts concentration has been selected as optimum according to previous studies with pure TiO_2 suspensions [23].
(ii) Wall reactor, in which the Ag/TiO_2 photocatalyst is immobilized as a film in the inner-tube wall of the annular photoreactor.
(iii) Fixed-bed reactor, in which glass rings coated with the Ag/TiO_2 material are placed in the whole annular reactor volume.

2.2. Catalysts preparation and characterization

Degussa P25 titanium dioxide was immobilized onto the glass substrates by a dip-coating procedure schematized in Fig. 2. All the materials used in the present work have been prepared following three coating cycles. More details of the method can be found elsewhere [23].

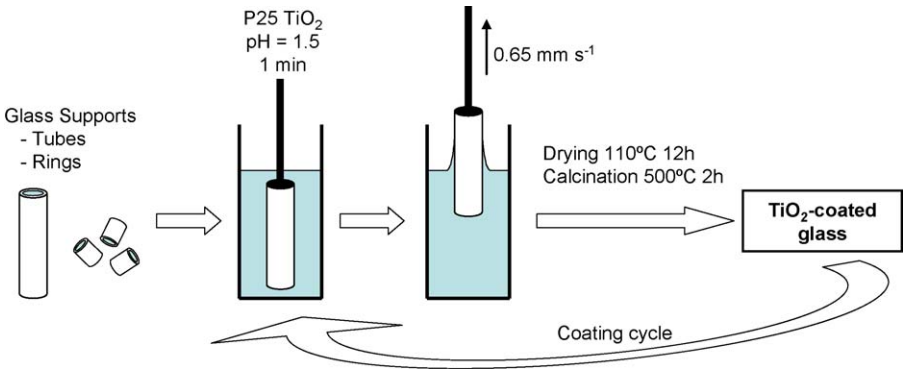

Fig. 2. Schematic representation of the immobilization of TiO_2 onto the glass supports.