

Immobilization of TiO₂ nanopowders in multilayer fluorinated coatings for highly efficient clear and turbid wastewater remediation

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ABSTRACT

The use of nanosized photocatalytic TiO₂ in suspension or slurry type reactors is well reported. However, the industrial feasibility of such systems is limited, on account of the low quantum efficiency reported for slurry processes and of the need for a post-treatment catalyst recovery stage, which may present poor efficiency, with the double drawback of dispersing nanoparticles in the environment and losing precious photocatalyst.

In this work, the photodegradative activity of titanium dioxide immobilized into a multilayered transparent fluoropolymeric matrix has been studied. Several TiO₂ nanostructured powders featuring different primary particle size, crystalline phase and specific surface area have been produced by the flame spray pyrolysis (FSP) of organic solutions containing titanium (IV) isopropoxide. The activity of such powders has been tested and compared to that of TiO₂ P25 by Evonik Degussa, which is the reference nanopowder commonly employed in the evaluation of the photocatalytic activity of non-commercial TiO₂. A multilayer ionomeric-perfluorinated matrix has been used to immobilize the powders, having high chemical resistance and transparency towards UV light, good permeability to oxygen and good wettability to favor interactions with the polluted aqueous solutions.

Keywords: nanoparticles, titanium dioxide, flame spray pyrolysis, photocatalysis

1 INTRODUCTION

The photocatalytic activity of titanium dioxide (TiO₂) – i.e., its ability to accelerate chemical reactions by absorption of light, which is exploited in the degradation of water and air pollutants – has been subject of studies, experimental investigations and optimization since its first observation in 1970s [1,2], and has now reached the maturity of a commercial technology [3,4]. A large amount of photocatalysts has been proposed and studied, but the most interesting system is still represented by TiO₂, and especially in nanostructured form – nanopowders, nanotubes – which largely enhances the surface area

available for the reactions, increasing photodegradation efficiency [5].

Yet, particular attention has to be paid to the nanometric size of the catalyst particles that may be used in direct contact with air or dispersed in water: in fact, a growing number of specific restrictions are being proposed to take into account the negative impact of nanoparticles on human health, as underlined by several research works [6].

For these reasons, this work tries to combine the beneficial effect of TiO₂ nanopowders with an immobilization system based on a perfluoropolymeric coating where TiO₂ nanoparticles are dispersed [7]. In this frame, the photocatalytic activity of immobilized nanopowders was first compared with that of the same amount of powders dispersed in solution, in order to prove the actual efficiency of the immobilization system and discard any shielding effect of the polymer on the photoactivity of TiO₂. To produce the powders, flame spray pyrolysis (FSP) was used, a well known gas phase combustion synthesis method which can be used to prepare several metal oxides (e.g. SiO₂, TiO₂ and Al₂O₃) in the form of nanocrystalline powders with high surface area with precise control over the powder structural characteristics [8,9]. Nanopowders of different size and crystallinity were produced, and their photocatalytic activity was compared with AEROXIDE® TiO₂ P25 powders (P25 hereon), as representative of a standard material commonly utilized in studies on titanium dioxide photoinduced properties.

2 EXPERIMENTAL

2.1 Coating production and first validation

First, the viability of powders immobilization in a perfluorinated polymer coating was investigated by preparing a coating containing P25 nanopowders, and testing its photocatalytic activity in the photodegradation of the dye Rhodamine B (RhB) as model water pollutant.

More in details, the photoactive coatings were realized in a multilayer fashion with AQUIVION® D83-06A (AQ) and HYFLON® AD60 (AD); both fluoropolymers are produced, commercialized and supplied by Solvay

Specialty Polymers. Two different perfluoropolymer solutions were employed: a 10%_{wt} solution of AD in Galden® HT110 perfluoropolyether and a 6%_{wt} solution of AQ in a hydroalcoholic solvent (water/*i*-propanol/*n*-propanol 20:40:40) containing 0.6%_{wt} of dispersed TiO₂ nanopowders. The first two layers in contact with the substrate consisted in AD – one to provide a hydrophobic primer, thermally cured as described in previous work [7], the other – not cured – to allow adhesion between the perfluorinated hydrophobic layer and the AQ ionomeric hydrophilic layer. This was the actual photoactive layer, where the fine dispersion of TiO₂ nanostructured powders was obtained by ultra-sonication for 30 min at room before its application on glass. Subsequently, it was thermally cured with a specific heating program described in previous work to evaporate solvents and promote adhesion between perfluoropolymeric layers [7].

Both AD and AQ layers are chemically stable towards the TiO₂ photocatalytic degradation effects and to UV-Vis light [10]; moreover, AQ is permeable to aqueous pollutants which can diffuse towards the photoactivated TiO₂ powders, being therefore degraded.

As abovementioned, at first coatings were produced by using P25; the photoactive coatings was deposited on the quartz sheath (thickness: 2 mm) of a stirred semi-batch 0.5 l photocatalytic reactor equipped with a low pressure Hg UV lamp (4 W Engelhard Hanovia®, emitting light at wavelengths of 240-300 nm with irradiation intensity of 0.2 W/m²). The UV lamp was cooled with a flux of nitrogen in order to maintain constant the solution temperature (25 ± 3°C). Photocatalytic activity was evaluated by monitoring the trends of RhB abatement, i.e., by monitoring RhB color intensity in time, as it is proportional to its concentration as already presented in previous works [7,11]. Oxygen is required in the photocatalytic reaction and it was fed at the bottom of the reactor. The oxygen flux was regulated at 7 NI/h in the presence of constant magnetic stirring. Tests were repeated by adding barium sulfate microparticles to the RhB diluted, in order to create a turbid solution and observe the efficiency of anopowders in presence of such an obstacle to TiO₂ photoactivation.

2.2 Nanopowders production

After this validation test on the coating production method, different nanopowders were produced and tested. TiO₂ nanostructured powders were produced from the gas-phase in a commercial FSP system (NPS10, Tethis S.p.A., Italy) by the flame spray pyrolysis of titanium (IV) isopropoxide (TTIP, Aldrich, purity >97%) dissolved in xylene solvent. The TTIP precursor/solvent mixture was injected in a water-cooled nozzle and dispersed into fine droplets by a coaxial oxygen gas flow. The spray was ignited by a pilot methane/oxygen flamelet with 1.5 and 3 L min⁻¹ of CH₄ and O₂ flow rate, respectively, to burn the

organic part and grow the metal oxide nanoparticles. Different TiO₂ powders were produced varying the TTIP concentration (0.45 or 0.8 M) in the precursor solution, the feed flow rate (1 or 4 ml/min) of the precursor solution and of the oxygen dispersion gas (5 or 8 l/min). These parameters are known to significantly affect the synthesis conditions enabling the production of nanopowders with tunable specific surface area [8]. Nanopowders were collected using a watercooled, stainless-steel filter housing located downstream the FSP reactor at distance of ca. 640 mm from the nozzle of the burner.

2.3 Nanopowders photocatalysis tests

The coating procedure was then repeated on different glass slides for each of the nanopowders described in the following. In this case, the photocatalytic activity tests were different, in order to allow a quick screening of the different nanopowders efficiencies. The glass slide was immersed in distilled water to release the coating, which was cut in squares and inserted in a Teflon® frame to prevent it from bending and winding up, leaving a 1 cm² surface exposed. The sample was then placed on the bottom of a 100 ml beaker containing 15 ml of 10⁻⁵ M RhB solution. Irradiation was achieved from top by using a solar spectrum lamp (a 300 W Osram Vitalux®, UVA irradiation of 10 W/m² on the exposed coating. Dye absorbance was monitored in time for 6 h by means of an absorbance spectrophotometer as reported in previous work [11], using the peak at 550 nm as proportional to RhB concentration.

3 RESULTS

3.1 Coating validation

Figure 1 reports the variation in the concentration of RhB contained in the photocatalytic reactor, in presence either of a photoactive coating (PC) obtained by immobilizing TiO₂ nanopowders as previously described, or of TiO₂ nanopowders dispersed free in the RhB solution (TiO₂ slurry). The overall quantity of TiO₂ was the same in both conditions, i.e., in coating or as slurry. It is immediately observed the excellent photocatalytic degradation of the coating. RhB molecules were homogeneously dispersed in the aqueous solution and they could reach the aqueous solution-polymer interface due to simple convection and diffusion; then, the acidic sulfonic side chain terminals of AQ promoted RhB transfer into the water phases within the ionomeric matrix, and therefore towards TiO₂. This ensured the possibility for RhB to come into contact with the photoactive ingredient of the coating, and therefore its degradation.

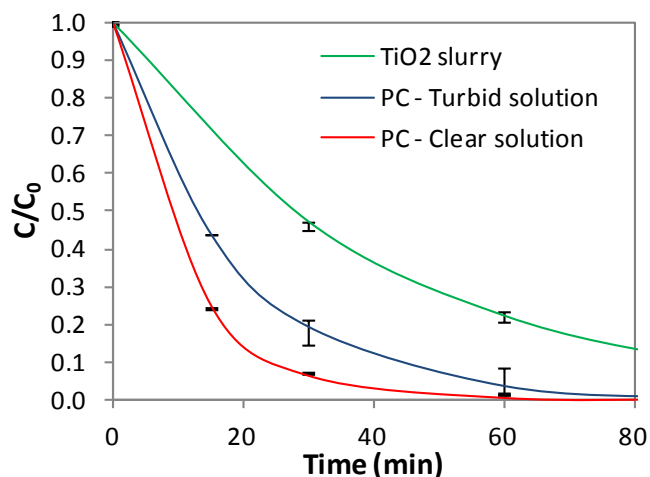


Figure 1: Variation in concentration of RhB under photocatalytic degradation in presence of immobilized or dispersed P25 nanopowders.

The enhanced interactions of RhB with the acidic terminals of the ionomer actually produced an enhancement of photocatalytic activity compared with that observed on dispersed nanopowders, making the coating more effective than the slurry configuration. This is of extreme interest, as usually nanoparticles immobilization is considered to reduce their photoactivity with respect to free particles – generally on account of a reduced exposed surface area – while in this case no such effect is observed, on the contrary, activity is enhanced by immobilization.

The same diagram reports the photocatalytic activity of the same photoactive coating (PC) in presence of a turbid solution, obtained by mixing barium sulfate to RhB. Also in this case activity is maintained: on the contrary, in presence of dispersed photocatalytic particles we would have expected a large decrease in photoactivity on account of the lower light absorbed by TiO₂ nanoparticles, due to the solution scattering. Since nanoparticles are immobilized and irradiation comes from the side which is not in contact with the solution, this problem is solved, making this reactor geometry particularly appealing for the purification of turbid waters.

3.2 FSP nanopowders

FSP nanopowders are labelled hereon as a function of the operative parameters used in their production, in the following order: TTIP (titanium precursor) concentration, in moles per liter; precursor flow, in ml/min; O₂ dispersion, in l/min. Therefore, sample F-0.45-4-5 represents nanopowders obtained by flame spray pyrolysis with 0.45 M TTIP injected with a flow rate of 4 ml/min in presence of an oxygen flow of 5 l/min. The specific surface area, measured by BET and reported in Table 1, of as prepared nanopowders ranges from 90 to 250 m²g⁻¹ according to the synthesis conditions.

The kinetics of degradation of RhB under solar spectrum irradiation in presence of TiO₂ nanopowders is reported in Figure 2, and is given as $\ln(C/C_0)$, with C concentration at the time of measurement, and C_0 initial concentration; in figure 3, the kinetic constants of the degradation reaction are given, using the reactivity of P25 as comparison. It is possible to see that in all cases RhB degradation follows a linear trend in time, confirming the pseudo-first order degradation kinetics often observed in literature.

	Surface area (m ² /g)
F-0.45-4-5	113
F-0.8-4-5	90
F-0.45-1-5	250
F-0.45-4-8	161

Table 1: Surface areas of FSP nanopowders.

Only one powder, F-0.45-1-5, showed a photocatalytic efficiency close to that of P25, while all other synthesized nanopowders exhibited higher performances. An increase in the quantity of oxygen and precursor conveyed in the flame allows to improve the efficiency of the nanopowders. This underlines the importance of the overall synthesis conditions and of the synergistic effect of the nanopowder characteristics (e.g. crystallite size and crystalline phase) on the photocatalytic efficiency of the coating, even in spite of the overall surface area.

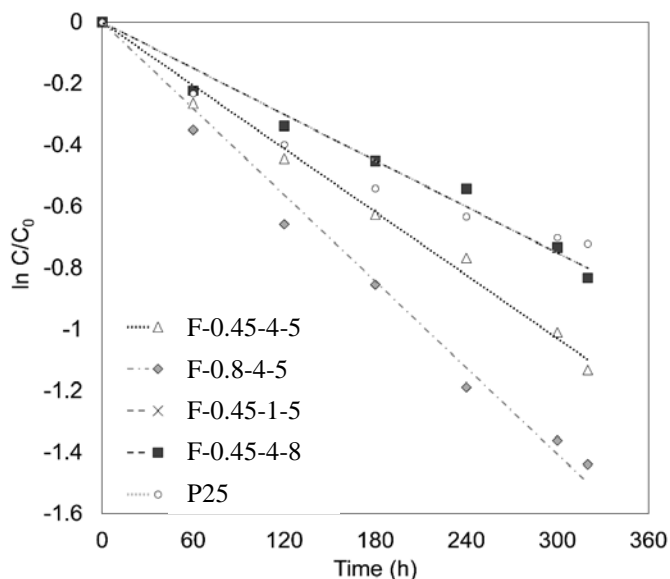


Figure 2: Variation in concentration of RhB under photocatalytic degradation in presence of immobilized FSP nanopowders.

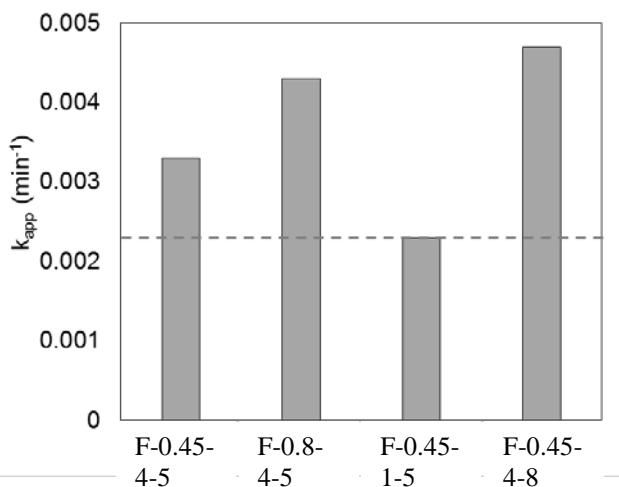


Figure 3: Kinetic constant of the reaction of RhB degradation in presence of immobilized FSP nanopowders (dashed line: P25).

4 CONCLUSION

In this work, an effective method for the immobilization of TiO_2 nanopowders was presented, and TiO_2 nanopowders of different structure and dimension were produced and tested in order to obtain a highly photoactive coating for water purification. Results show that the P25 containing coating has higher photocatalytic activity than dispersed TiO_2 P25, and maintains its efficiency also in turbid solutions. Tests performed on coatings containing TiO_2 nanopowders produced by FSP show an increase in photocatalytic efficiency from 40% to 100% with respect to P25 depending on powders particle size.

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