Titania nano-coated quartz wool for the photocatalytic mineralisation of emerging organic contaminants

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ABSTRACT

Many emerging contaminants pass through conventional wastewater treatment plants, contaminating surface and drinking water. The implementation of advanced oxidation processes in existing plants for emerging contaminant remediation is one of the challenges for the enhancement of water quality in the industrialised countries. This paper reports on the production of a TiO_2 nano-layer on quartz wool in a relevant amount, its characterisation by X-ray diffraction and scanning electron microscopy, and its use as a photocatalyst under ultraviolet radiation for the simultaneous mineralisation of five emerging organic contaminants (benzophenone-3, benzophenone-4, carbamazepine, diclofenac, and triton X-100) dissolved in deionised water and tap water. This treatment was compared with direct ultraviolet photolysis and with photocatalytic degradation on commercial TiO_2 micropearls. The disappearance of every pollutant was measured by high performance liquid chromatography and mineralisation was assessed by the determination of total organic carbon. After 4 hours of treatment with the TiO_2 nano-coated quartz wool, the mineralisation exceeds 90% in deionised water and is about 70% in tap water. This catalyst was reused for seven cycles without significant efficiency loss.

Key words | advanced oxidation processes, emerging organic contaminants, photocatalysis, titanium dioxide

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INTRODUCTION

The last amendment of the Water Framework Directive 2000/60/EC introduces a 'watch list' of aquatic contaminants that contains seven pesticides, six pharmaceuticals, an antioxidant, and a personal care product with the aim of monitoring them and understanding if quality standard references should be imposed. In addition to the substances regulated by the European Directives, a new group of molecules, called emerging organic contaminants (EOCs), is becoming of concern. EOCs, defined as organic compounds that have no regulatory standard, include newly commercialised chemicals just introduced in the environment, or those already monitored but whose presence and significance are not yet clear (Daughton 2004). Many pharmaceutical and personal care products, and residues of industrial activity are considered EOCs. Globally, EOC concentrations measured in the aquatic environment range from ng L^{-1} to μg L^{-1}, and only the recent development of sensitive analytical techniques has enabled the detection of such low concentrations both in surface and drinking water. The poor knowledge of EOC middle- or long-term impacts on aquatic environments and some evidence of their endocrine-disrupting activity has stimulated several surveys on their occurrence in many countries (Balmer *et al.* 2005; Loos *et al.* 2010). In some effluents from pharmaceutical manufacturing factories, and in some influents to wastewater treatment plants (WWTPs), the maximum concentration of some pharmaceuticals has been found in the order of mg L^{-1} [i.e. ciprofloxacin 31 mg L^{-1} (Larsson 2014), venlafaxine 11.7 mg L^{-1} and carbamazepine

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(CBZ) 0.84 mg L^{-1} (Lester *et al.* 2013), and diclofenac (DCF) 0.2 mg L^{-1} (Ratola *et al.* 2012)].

The WWTPs, originally not designed to handle EOCs, might be considered mainly responsible for their transfer to water bodies and consequent accumulation (Oulton *et al.* 2010). EOC removal can be accomplished only by using new technologies (Tuerk *et al.* 2010) such as the advanced oxidation processes (AOPs).

Ultraviolet (UV) radiation in the wavelength range 100–280 nm is widely used for wastewater disinfection and, in some cases, it may lead to the direct photolysis of photolabile compounds (Zuccato *et al.* 2010). The photochemical activity of UV radiation can be converted to an oxidative effect by coupling it with appropriate additives and photocatalysts (McCullagh *et al.* 2011). TiO_2 is known to be an effective water disinfection option, since it does not need the addition of chemicals which can react together to form toxic byproducts as, for instance, in the case of chlorination. The absorption of UV light by TiO_2, in O_2-saturated H_2O, produces reactive species (mainly $\cdot OH$ and $\cdot O_2^-$) capable of degrading organic molecules in solution. Since its energy gap is 3.2 eV (Oppenlander 2003), TiO_2 is able to absorb solar radiation with wavelengths shorter than 385 nm. Thus, TiO_2-based photocatalytic processes seem not only sustainable and reliable solutions for a wide variety of water-remediation issues, but also economically advantageous. In fact, with respect to the last statements, even if artificial UV radiation is energy demanding, it is preferable to solar radiation for high water loads, because it can work 24 hours per day, it allows higher light power per unit volume of water (thus avoiding huge sunlight collecting surfaces), and it induces direct photolysis on a wider group of molecules.

The immobilisation of a photocatalyst on a UV-transparent solid is an advantage for practical use; some research has been devoted to TiO_2 immobilised on mineral fibres. Wang & Ku (2003) studied the coating of TiO_2 on a single quartz fibre for the abatement of benzene in air. Hue & Hang (2013) performed the degradation of 0.44 mg m^{-3} benzene in air with TiO_2-coated quartz cotton irradiated with 40 W UV light (400–315 nm), achieving the total decomposition of the contaminant in 4.5 hours, due to the transparency and the high surface area of the substrate. Horikoshi *et al.* (2002) achieved the partial photocatalytic mineralisation of a 0.1 mmol L^{-1} nonylphenol polyetoxylate aqueous solution after 6 hours of UV irradiation by using TiO_2 immobilised on fibreglass cloth by the sol-gel method.

The aim of the present study was to evaluate the possibility of producing large batches of photocatalyst nanolayers immobilised on a high-surface-area (per unit of volume) solid substrate potentially transparent to UV light. The present work reports on the synthesis and the use of a TiO_2 nano-layer on quartz wool (TiO_2-qw) for the degradation of a mixture of five EOCs: benzophenone-3 (BP3), benzophenone-4 (BP4), CBZ, DCF and triton X-100 (TRX). Furthermore, this study was carried out both on deionised water (DW) and tap water (TW), in order to understand the degradation parameters of standardised samples before use on real WWTP effluents. The performance of TiO_2-qw was compared with that of commercial TiO_2 micropearls (TiO_2-mp), up to now considered the most efficient on the market (Kanakaraju *et al.* 2014a, 2014b), and with that of direct UV photolysis. The TiO_2-qw life cycle was also evaluated.

The five EOCs selected for the present study, besides being some of the most frequently detected pollutants, belong to categories showing different water affinities, and containing different chemical groups. Their structures and a short description of their use and occurrence in water bodies are reported in the Supporting Information (available with the online version of this paper).

METHODS

All chemicals were reagent grade and were used without any further purification. TiO_2 VP Aeroperl P25 20 from Evonik is the new brand of the well known Degussa P25. The average geometrical area has been estimated as 0.2 m^2 g^{-1}. Quartz wool (density 2.2–2.6 g cm^{-3}) was supplied by Carlo Erba.

DW was produced by a MilliRO 15 water purification system (Millipore). TW was collected from municipal waterworks of Bologna, Italy, and the concentrations of the main metals and anions are listed in Table SI2 (available with the online version of this paper) with total organic carbon (TOC), light absorbance and conductivity.

TiO_2-qw was produced by the deposition of a TiO_2 thin film on quartz wool by the sol-gel technique. The sol was obtained by mixing titanium tetraisopropoxide, absolute ethanol, acetylacetone and 1 mol L^{-1} HCl aqueous solution in 1:0.5:3:34 ratios. Acetylacetone was used as a complexant in order to avoid the precipitation of titanium byproducts, whereas HCl was added in order to introduce the required amount of water and to promote the polymeric sol synthesis by acidic catalysis.

Four specimens of the sol were dried under atmospheric conditions up to sol-gel transition and the solvent evaporation was completed under infrared lamp, then the solids were treated for 30 min at 350, 400, 450, and 500 °C, respectively.

The quartz wool (Figure SI1, available with the online version of this paper) was soaked in the TiO_2 sol previously diluted in ethanol with a volume ratio of 1:5. This dilution ratio was chosen in order to avoid a thick deposition on the fibres, which would exhibit fragile behaviour and low adhesion. The solvent was then evaporated under atmospheric conditions for about 20 min and the densification was performed for 30 min at 450°C (the temperature selected after X-ray diffraction (XRD) studies of the above-mentioned four specimens). The obtained samples were washed with water to remove the unbound TiO_2 and dried at 120°C for 20 min. A loading of 35 mg of TiO_2 per gram of TiO_2-qw was determined by weight.

The scanning electron microscopy (SEM) observations were performed on TiO_2-qw with the scanning electron microscope Leo 438 VP, using both secondary electrons and backscattering electron detectors, in partial vacuum conditions, with and without sample metallisation. Absorbance was evaluated by Perkin-Elmer Lambda 9 spectrophotometer.

The light source was a Multilamp Rayonet provided with 16 lamps (Sylvania G8 W) with emission maximum centred at 254 nm and absorbed power 8 W (UV flux in the centre of the reactor was 25 mW cm^{-2}) and an air blowing cooler. The experiments were carried out in a quartz tube (diameter 4 cm) equipped with a condenser, a thermometer, and a Teflon capillary pipeline to supply the air bubbles that provided the stirring and suspended the catalyst particles. The tube was filled with 0.25 L of the DW or TW solution containing $C_0 = 5$ mg L^{-1} of each contaminant, that is the same order of magnitude of the highest concentration detected in effluents of pharmaceutical manufacturing (Ratola *et al.* 2012; Lester *et al.* 2013; Larsson 2014). Three samples of the solutions were treated as follows: (i) UV radiation and air; (ii) UV radiation, 25 mg TiO_2-mp and air; and (iii) UV radiation, 1 g TiO_2-qw and air. 5 mL samples were withdrawn at specific times and stored in the dark at 4 °C before the analysis. In the case of the TiO_2-mp suspension, the samples were centrifuged before the analysis.

The concentration of the contaminants was determined using a high performance liquid chromatograph (HPLC) Agilent 1260, equipped with a diode array detector and a luminescence detector. Sample injection volume was 40 μL and analytes were separated on a reverse phase Zorbax C8 column (4.6 × 150 mm, 5 μm). A linear gradient from 0.1% trifluoroacetic acid in water to 100% acetonitrile at 1.0 mL min^{-1} flow rate was used. The detection was carried out at 285 nm for all the compounds, with the exception of TRX which was detected by using the in-line Varian Pro Star 363 fluorescence detector ($\lambda_{ex} = 229$ nm and $\lambda_{em} = 302$ nm).

TOC concentration was measured by means of a Hach-Lange DR5000 spectrophotometer and LCK-385 test-in-cuvette with limit of quantification (LOQ) 3 mg L^{-1} and uncertainly 15%. The pH was measured by an Orion Research Expandable Ion analyzer EA940 equipped with a Hanna Instruments HI 1111 electrode. When possible pH was reported as the average value of several different solutions with its standard deviation (SD).

RESULTS AND DISCUSSION

TiO_2-qw studies

In the four powder specimens, the two main TiO_2 phases, anatase and rutile, were confirmed by XRD (Figure SI2, available with the online version of this paper). Anatase, the phase with the most promising photocatalytic activity (Oppenlander 2003), appeared after treatment at 350 °C, but mainly in amorphous form. The rutile phase was detected at 500 °C together with anatase of the highest crystallinity compared to that observed after thermal treatment at lower temperatures. On the basis of the XRD results, a temperature of 450 °C was chosen for the densification of TiO_2 nano-coating on a relevant amount of quartz wool (about 50 g), in order to obtain anatase with the highest crystallinity together with the minimum content of the rutile phase.

The SEM characterisation of the TiO_2-qw was done on specimens with and without gold sputtering. In both cases, very good resolutions were obtained, but observations without sputtering and using the secondary electron partial vacuum detector were preferred, in order to avoid any possible interference from gold deposition. The backscattering electron detector was used to find the coating defects, exploiting its sensitivity to the mean atomic weight, which is lower for quartz than for titania. Some micrographs of the obtained coated quartz fibres before use are shown in Figure 1. The diameter of the fibres spans from 6 to 20 μm, consequently the TiO_2-qw geometric surface is estimated in the range 0.28–0.08 m^2 g^{-1}, which is comparable to that of TiO_2-mp. Because of the characteristics of the quartz substrate and because of the coating method (dipping in a precursor solution, gelling and drying), very variable coating thicknesses and also defects were observed. In particular, some fibres show crystallites grown perpendicularly to the fibre axis and, sometimes, mass accumulation appears near the fibre crossings. Finally, some collar-shaped defects appear, showing the presence of the coating and its

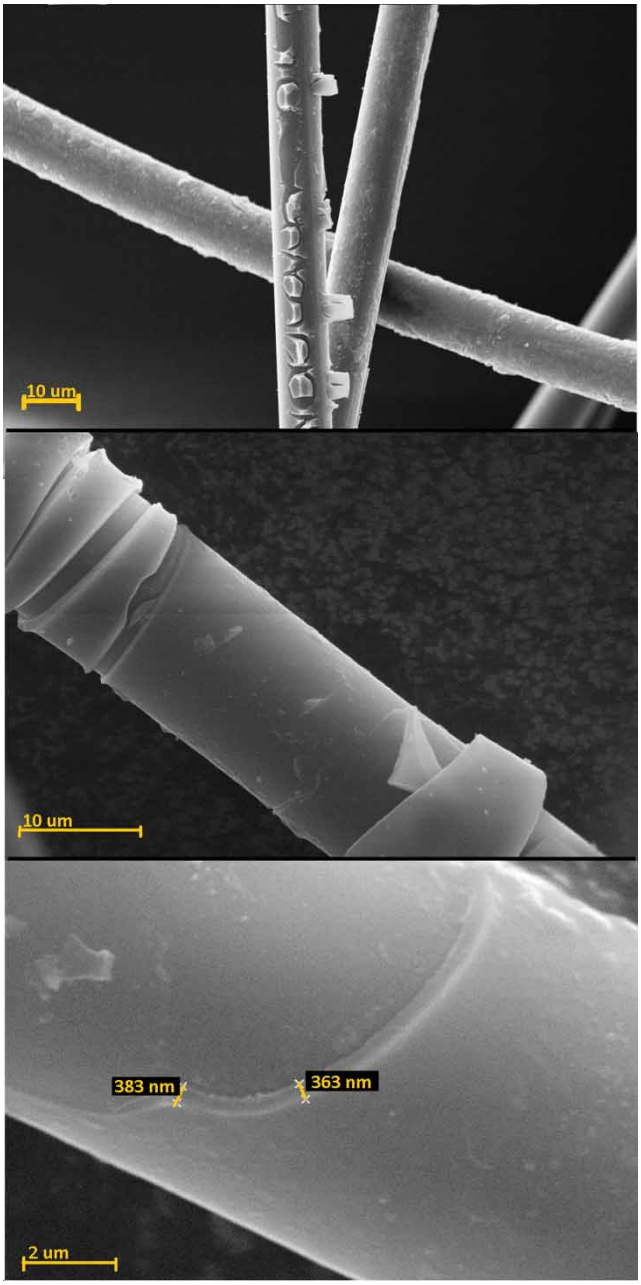

Figure 1 | SEM images of TiO_2-qw before use (secondary electron detector in partial vacuum conditions). Thickness data are reported on a sample without gold coverage.

occasional collapse along the fibre axis during the early deposition phase. In the region without defects, the thickness of the TiO_2 coating is about 400 nm.

Degradation of the EOCs

Figure 2 shows the percentage ratio of the residual concentration C_t and the initial concentration C_0 of the five EOCs

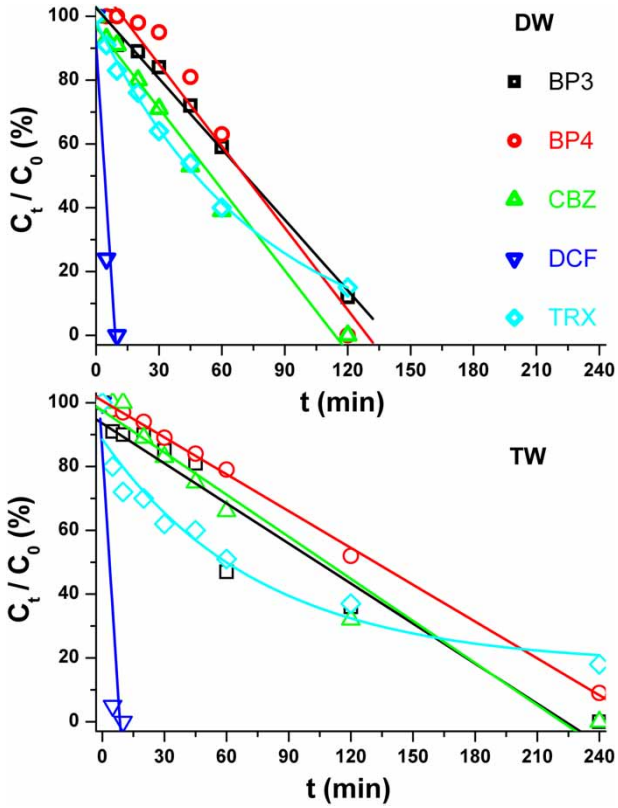

Figure 2 | Residual content of the five EOCs treated with UV light and air in DW and TW.

after UV irradiation and is considered the reference experiment for the following photocatalytic treatments. DCF, due to its photosensitivity, completely disappears after 5 min of irradiation both in DW and TW. The concentration of the other EOCs in DW show decreases of about one order of magnitude after 120 min, roughly following zero-order kinetics. All these five molecules, like many other EOCs, contain UV-sensitive aromatic systems whose excited species may start photochemical reactions involving dissolved O_2.

In TW: BP3, BP4, and CBZ need about 240 min to decrease their concentration by one order of magnitude, whereas TRX does not reach this goal. The slower degradation in TW is likely to be due to inorganic ions which inhibit the process by scavenging the active radicals.

During the UV treatment in DW, as well as during the photocatalytic ones described below, pH decreases from neutral values (average 7.8, SD 0.5) to a value ranging from 4.3 to 5.6, typical values of the carboxylic acid solutions. On the other hand, in TW the initial pH (average 7.9, SD 0.3) is similar to that in DW, but it increases to about 8.3–9.2 (after the treatment with TiO_2-qw in TW average pH was 8.3, SD 0.3) indicating that the scavenging of the active radicals opens alternative pathways to the formation of carboxylic acids.

The samples irradiated up to about 60 min show a yellowish coloration, and the corresponding HPLC analysis have a slightly increased baseline signal, indicating the presence of byproducts. However, their concentrations were too low to be detectable by our analytic procedure.

UV irradiation in the presence of 0.1 g L^{-1} suspended TiO_2-mp in DW – that is reported as one of the best TiO_2 concentrations (Mendez-Arriaga *et al.* 2008) – if compared to UV radiation alone, does not enhance appreciably the disappearance rate of DCF and CBZ, but speeds up the degradation of BP3 and BP4, shifting the disappearance half-life from 72 min to 56 and 63 min, respectively; and that of TRX from 56 min to 46 min (Figure 3 DW). Also the use of TiO_2-mp in TW generally speeds up the disappearance rate of the contaminants, but it also seems to change the kinetics from zero-order to pseudo-first-order (Rizzo *et al.* 2009) or to a mechanism combining two consecutive steps with different kinetics (Figure 3 TW). The kinetics of Degussa P25 photocatalysis has been clearly explained elsewhere (Xiong & Hu 2012).

In a recent study (Kanakaraju *et al.* 2014a, 2014b), 30 mg L^{-1} of DCF in distilled water were subjected to a

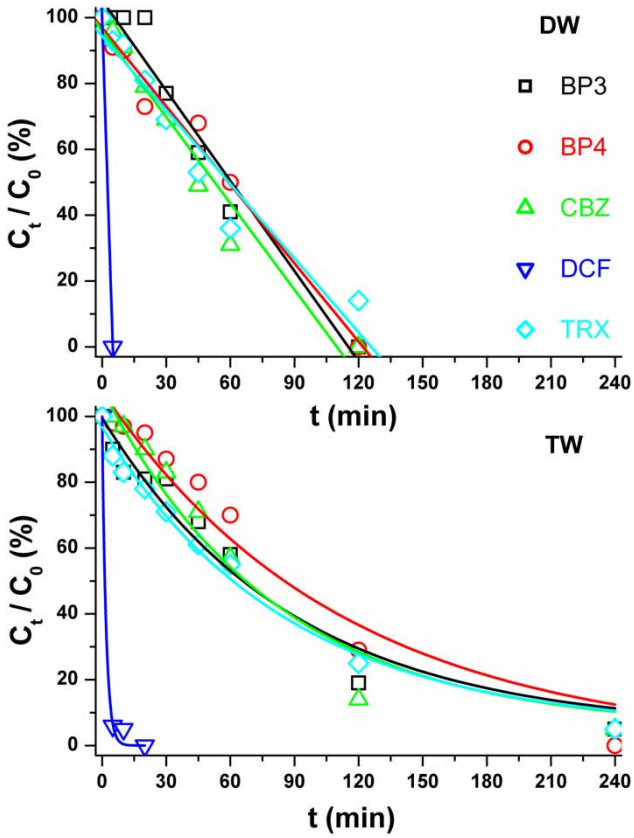

Figure 3 | Residual content of the five EOCs treated with TiO_2-mp, UV light and air in DW and TW.

Table 1 | Variation of the concentration of some inorganic ions before and after treatment with TiO_2-mp, UV light and air in TW

Parameter	Before treatment	After 240 min	Units
pH	7.6	9.0	–
CO_3^{2-}	0	3.6	mg L^{-1}
HCO_3^-	226.5	49.9	mg L^{-1}

UV photocatalytic treatment (TiO_2 Degussa P25 loading 0.1 g L^{-1}), achieving complete removal after 15 min, when sunlight photochemical degradation required up to 360 min of exposure. TOC was not evaluated but six photoproducts were detected. Also in this study, DCF in TW showed higher pseudo-first-order rate constants, confirming matrix effect on the degradation rate. Similar confirmation comes from a study on a photocatalytic process (TiO_2 0.02–0.5 g L^{-1}; light 400–315 nm, 250–400 W) where the removal efficiency of the 5 mg L^{-1} CBZ alone declined by 30% when the matrix was changed from distilled water to a groundwater having pH 7.5 and conductivity 0.79 mS cm^{-1} (Shirazi *et al.* 2013).

The inorganic components of TW before and after the treatment with TiO_2-mp under UV irradiation remain almost unaltered except for those reported in Table 1. On the other hand, the concentrations of carbonate and bicarbonate are in the same order of magnitude of EOC concentrations but are several orders of magnitude higher than that of halides (Table SI2). We observe the increase of pH and the decrease of HCO_3^- concentration that we explain with CO_2 evolution that consumes the H^+ produced in the oxidation processes. On the other hand, the scavenging converts ·OH to OH^-, increasing the alkalinity (Buxton *et al.* 1988; Grebel *et al.* 2010). Other authors report that CO_3^{2-} is also responsible for a slower absorption of EOCs on the TiO_2 surface (Guillard *et al.* 2005).

The use of 1.0 g TiO_2-qw per experiment, corresponding to an estimated maximum value of 0.14 g L^{-1} of TiO_2, almost doubles the disappearance rate of the EOCs (Figure 4), both in DW and TW, with respect to the TiO_2-mp treatment (Figure 3). For example, the time for the 50% removal of TRX in DW shifts from 56 to 12 min, and in TW from 61 to 26 min.

Only the DCF degradation rate was not enhanced because direct photolysis largely remains faster than photocatalysis. The TiO_2-qw samples are in the shape of a wool ball with a diameter of 4 cm and an apparent density of about 30 mg cm^{-3}. The TiO_2-qw absorption and scattering of the 254 nm light increased by about 10% per mg cm^{-3} of apparent density. With this geometry a fraction of the

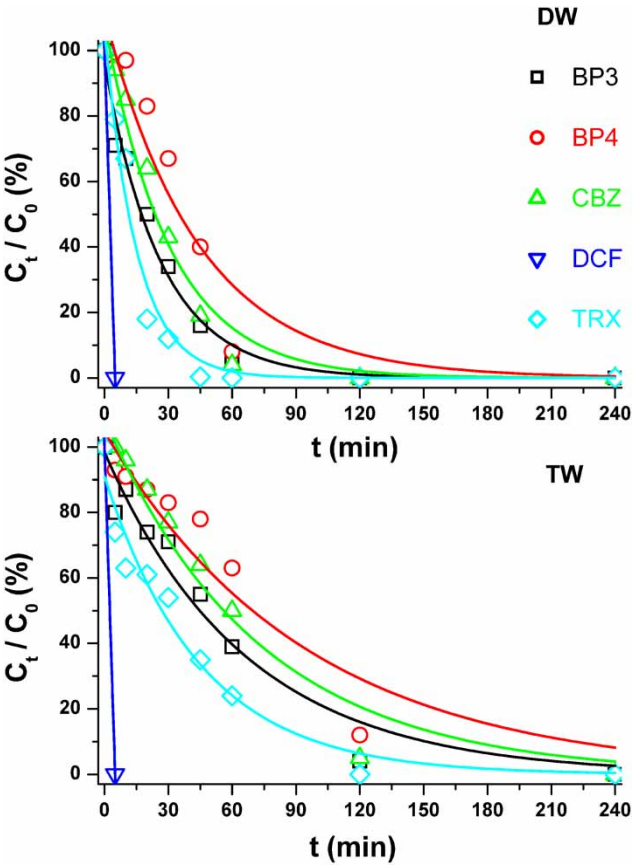

Figure 4 | Residual content of the five EOCs treated with TiO_2-qw, UV light and air in DW and TW.

TiO_2-qw does not receive light, however, better performances could be achieved by changing the reaction geometry or by reducing the apparent density of the catalyst substrate composite.

Mineralisation and catalyst life-cycle

Figure 5 compares the average residual content of the five EOCs after 120 min (initial EOC concentration $C_0 = 25\ mg\ L^{-1}$) and the residual TOC after 240 min (theoretical initial TOC $C_0 = 15.9\ mg\ L^{-1}$), in the two water matrices. The temperature during all six experiments increases in the same way from $24 \pm 2\ ^\circ C$ to $53 \pm 2\ ^\circ C$, making a homogeneous contribution to the degradation rates. In DW the three treatments, after 120 min, reduce the total EOC concentration by one order of magnitude or more, but in TW, only the AOP treatment with TiO_2-qw is able to reach this goal (Figure 5(a)). Also the opposite trends of pH in DW and TW suggests different degradation pathways depending on the matrices.

In the case of TW, the EOC mineralisation needs longer times than in DW (Figure 5(b)). Even if in DW the three mineralisation processes can be considered satisfactory after 240 min, in TW, UV mineralises only the 30% of the EOCs. However, photocatalysis significantly enhances the EOC mineralisation process, achieving the best performance with TiO_2-qw (residual TOC about 30%). The advantage in this case is that a larger photocatalytic area is exploited, compared with the same amount of TiO_2-mp. Furthermore, the use of a solid support facilitates the recovery and reuse of the catalyst itself.

Figure 6 shows the performance of TiO_2-qw in TW on TOC (dots) and EOC average concentration (squares) over repeated cycles of UV irradiation in the presence of air bubbling. After every 240 min long treatment, TiO_2-qw was recovered, washed three times in DW to remove residual salts and organic matter, dried at 120 °C for 18 hours and weighed. The weight loss after every cycle was less than 0.5%. The fitting to a constant residual content shows that the average EOC residual after 120 min (12%) stays within the confidence band (confidence level 95%), but TOC residual after 240 min (45%) at the eighth cycle exceeds the confidence band. The energy spent to degrade a gram of EOCs, evaluated after Bolton *et al.* (2001), was 47 ± 2 kWh g^{-1}, and the energy spent to mineralise a gram of

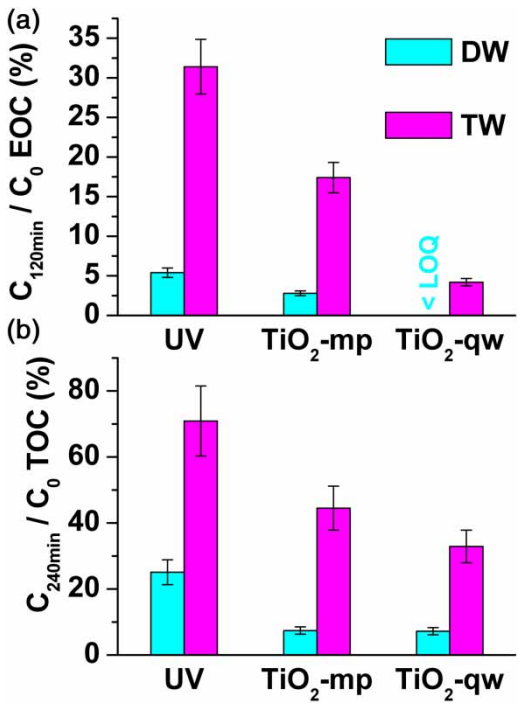

Figure 5 | Residual EOC content after 120 min (a) and residual TOC content after 240 min (b) of the three treatments.

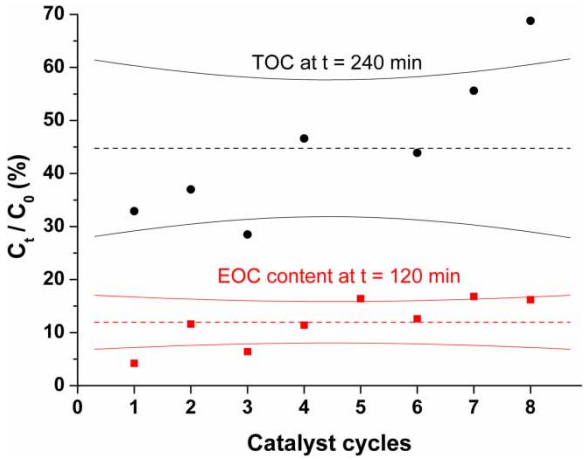

Figure 6 | Residual EOC content after 120 min and residual TOC after 240 min of repeated treatments with TiO_2-qw, UV light and air in TW. The dashed lines show the linear fitting to constant residues and the curves the related confidence bands.

EOCs was 230 ± 40 kWh g^{-1}. These results are evaluated on the basis of the nominal electric absorption of the UV lamps but the high power of the lamps, 128 W, was chosen in order to exceed the absorption of both the catalysts and compare them at their maximum activity. Furthermore, the geometry of the stationary photoreactor does not ensure the complete absorption of the emitted radiation. Studies with a flow reactor with optimised geometry are in progress and the use of LED UV sources is under evaluation (Xiong & Hu 2012).

After working for eight cycles, the TiO_2-qw was analysed by SEM once again and the images are shown in Figure 7. A comparison of these images with those of Figure 2 demonstrates that the coating morphology of the catalyst was essentially unchanged after eight cycles even if a loss of TiO_2 appears in the defects and thicker points.

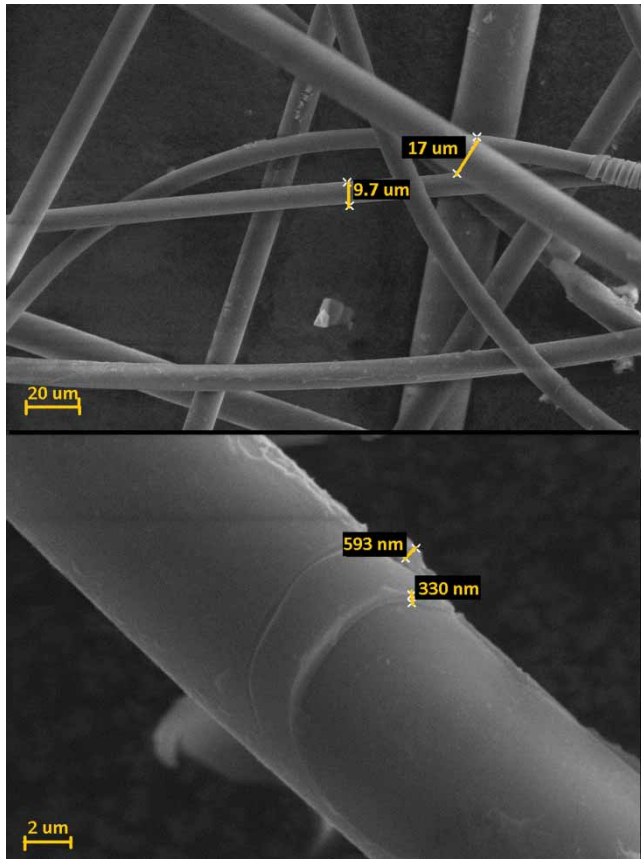

Figure 7 | SEM images of TiO_2-qw after eight treatments in TW (secondary electron detector in partial vacuum conditions).

CONCLUSIONS

The sol-gel method is suitable for producing a nanometric layer of TiO_2 on an amount of quartz wool with a satisfactory adhesion and homogeneity, which has never been reported before.

The simple treatment with UV light and air, already used as a sanitising post-treatment in WWTPs, if correctly powered and coupled with air can significantly decrease the concentration of the five molecules selected as representative of the EOC main categories, but it does not mineralise the byproducts in TW. Direct UV absorption generates excited states of EOCs which degrades them to photostable organic compounds, but photocatalysis generates radicals from water which react both with EOCs and their photostable byproducts leading to the mineralisation. In fact, it can be envisaged that an expected inhibition of the process by TW inorganic ions affects the UV radicals more strongly than the photocatalytic ones.

TiO_2-qw leads to better performances with respect to a commercial TiO_2-mp suspension of similar mass of catalytic materials, because it allows a wider distribution of the photoactive material on the substrate surface. After 4 hours of UV irradiation on pristine TiO_2-qw, the mineralisation of the five selected EOCs exceeds 90% in DW and is about 70% in TW. Furthermore, TiO_2-qw has the advantage of being easily recovered and reused seven times without a relevant efficiency loss. Repeated treatments with TiO_2-qw in TW achieves an EOC degradation of about one order of magnitude and an average mineralisation of about 55% over seven consecutive cycles, making it a promising technology to abate those EOCs shown to be refractory to conventional wastewater treatments.

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