



Photodegradation using TiO₂-activated borosilicate tubes

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Abstract

This study examines the photocatalytic activity of titanium dioxide (TiO₂) semiconductor supported on borosilicate tubes (cut-off 290 nm) towards removal of a mix of persistent organic pollutants (POPs) from water. For this purpose, two widely used analgesic and anti-inflammatory drugs (NSAIDs), ibuprofen (IBU) and mefenamic acid, along with MCPA sodium monohydrate, which is a common herbicide frequently used in the agricultural activities, were selected as a case study. Borosilicate tubes were coated with titanium oxide through two different approaches: sol-gel dip-coating and a hybrid nanoparticle dip-coating and plasma-enhanced chemical vapour deposition (PECVD) process. The photochemical reactor that hosts the titania-coated tubes was designed to permit continuous throughput of liquid feed stream. The photodegradation experiments were performed in laboratory conditions under artificial irradiation simulating solar light. The efficiency of direct photolysis and heterogeneous photocatalysis (TiO₂) was investigated, and the performance of each coating method was evaluated. Kinetic studies for each experiment were accomplished, the overall results showed poor efficiency and insufficient removal for NSAIDs through direct photolysis, whereas applying heterogeneous photocatalysis with TiO₂ coated on borosilicate tubes was found to accelerate their degradation rate with complete decomposition. Concomitantly, kinetic experimental results showed a critical difference of performance for the two coating methods used; in particular, the degradation rates of pollutants by the sol-gel-coated tubes were much faster than the degradation by the nanoparticle/PECVD-coated tubes. Using TiO₂ supported on borosilicate tubes appears to be a promising alternative to conventional TiO₂ suspension and avoid post-separation stages. The results achieved in this study can be used to optimise large-scale applications, and expanding the study to cover a wide range of pollutants will lead to achieve more representative results.

Keywords Ibuprofen · Mefenamic acid · MCPA · AOPs · Wastewater · Photocatalysis · Sol-gel coating · PECVD · Borosilicate tubes · TiO₂ · Photo-degradation · Emerging contaminants

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Introduction

Advanced oxidation processes (AOPs) have been proved as innovative and promising alternative route for the treatment of wastewater containing recalcitrant organic compounds such as pesticides, pharmaceuticals, surfactants, colouring matters and endocrine-disrupting chemicals. Some of these compounds pose severe problems in biological treatment systems due to their resistance to biodegradation, and in many cases show a toxic effect on microbial processes (Stasinakis 2008). Therefore, application of advanced oxidation processes (AOPs) becomes of a great importance for their potential to oxidise a wide range of organic compounds, which are difficult to degrade biologically in wastewater, leading to the complete mineralisation of pollutants or to the formation of more biodegradable intermediates (George et al. 2003). Among AOP technologies widely employed in recent year for water

purification and wastewater treatment, heterogeneous photocatalysis with semiconductors was the most popular and effective one (Ibhadon and Fitzpatrick 2013). In heterogeneous photocatalysis, dispersed solid particles of semiconductor efficiently absorb large fractions of the UV spectrum and generate chemical oxidants from dissolved oxygen or water in situ (Zhu et al. 2005) such as hydroxyl radicals ($\cdot\text{OH}$), which are able to oxidise and mineralise almost all kinds of organic compounds (Lin et al. 2011) yielding CO_2 and inorganic ions, and as a result, leading to the destruction of target pollutants (Malato 2008; Maria et al. 2008). TiO_2 was generally demonstrated to be the most active semi-conducting material, due to its strong resistance to chemical and photo corrosion, safety and low cost. On other hand, TiO_2 exhibits an appropriate energetic separation between its valence band (VB) and conduction band (CB), which can be surpassed by the energy of a solar photon. The VB and CB energies of the TiO_2 are estimated to be + 3.1 and - 0.1 V, respectively, which means that its band gap energy is 3.2 eV and absorbs in the UV light (wavelength < 387 nm) (Wu 2008; Rana 2009).

To date, the vast majority of the investigations and applications on heterogeneous photocatalysis (TiO_2) have employed the suspension form of semiconducting particles, and the performance of such systems was well documented. Fixation or immobilisation of catalyst over a stationary substrate would circumvent the need for post-treatment stages to recover the catalyst from the reaction mixture. In the past years, several research groups have supported TiO_2 on glass beads or glass surfaces. Both systems exhibited efficacious and stable catalysts for photodegradation of the organic compounds tested (Serpone et al. 1986; Matthews 1987; Matthews 1989). In another study, the photocatalytic oxidation of some classes of hydrocarbons was performed over an anatase- TiO_2 catalytic bed in a continuous flow photoreactor system (Formenti et al. 1971; Formenti et al. 1972a; Formenti et al. 1972b; Behnajady et al. 2007). Recent examples of TiO_2 immobilised include immobilisation on alumina, polyvinylidene difluoride, cellulose fibres and glass through various immobilisation techniques, such as sol-gel techniques, chemical vapour deposition, electrospinning and film casting (Romanos et al. 2012; Damodar et al. 2009; Liu et al. 2012; Bedford et al. 2012). Immobilisation of TiO_2 on rigid substrates is mostly done on glass due to the transparency of the system that will be obtained after the immobilisation. This can facilitate the penetration of light which can result in improved photocatalysis (Chen and Dionysiou 2008, Chen et al. 2008; Pelaez et al. 2010; Costacurta et al. 2010).

In the present work, the immobilisation of TiO_2 over borosilicate tubes has been investigated to assess the potential of such a technique for removal of a group of emerging pollutants in water systems. Borosilicate was chosen for its relative transparency to light irradiation; since the measured cut-off of borosilicate material used for our tubes and reactor was 290 nm, light transparency 91%, sodium release $5 \mu\text{g}/\text{dm}^2$ as Na_2O ,

potassium release minor than $5 \mu\text{g}/\text{dm}^2$ as K_2O . Selected pollutants consist of two widely used analgesic and anti-inflammatory drugs: ibuprofen (IBU) and mefenamic acid (Khalaf et al. 2013a, b), along with sodium (4-chloro-2-methylphenoxy) acetate (MCPA sodium monohydrate), which is a common herbicide frequently used for agricultural purposes (Baelum et al. 2006) (Scheme 1). To this scope, two different titanium oxide (TiO_2)-coated borosilicate tubes were obtained from Veneto Nanotech ScpA (Padova, Italy). The tubes were prepared using two diverse immobilisation techniques. Sol-gel process with subsequent treatment steps was employed to prepare the first tube starting from a titania sol precursor, whereas the TiO_2 coating on the second tube was applied by using a nanoparticle dip-coating followed by a plasma-enhanced chemical vapour deposition (PECVD) process of a SiO_2 layer to immobilise the TiO_2 particles. This research focusses on examining the photocatalytic activity of TiO_2 catalyst immobilised over such substrates through a continuous flow photochemical reactor system in laboratorial conditions under artificial irradiation simulating solar light. This research is aiming also at the evaluation of the immobilisation technique that could better achieve the desirable photocatalytic properties, determining the rate of photodegradation of ibuprofen, mefenamic acid and MCPA sodium monohydrate. The herbicide MCPA sodium was chosen for this case study due to its very high solubility in water and its toxicity to aquatic life. The novelty in this work with respect to the previously coating processes using TiO_2 is that we immobilised the semiconductor on macro-tubes instead of plates or nanotubes (Byrne et al. 2018). For this reason, it was impossible to provide direct SEM or X-ray inspection of the tube surfaces without destroying the realised materials, but the manufacturer prepared some plane samples with the same technology used for tube coatings to provide the characterisation of coated surfaces.

The results can be regarded as representative of a wide range of such pollutants and could be used to optimise large-scale applications.

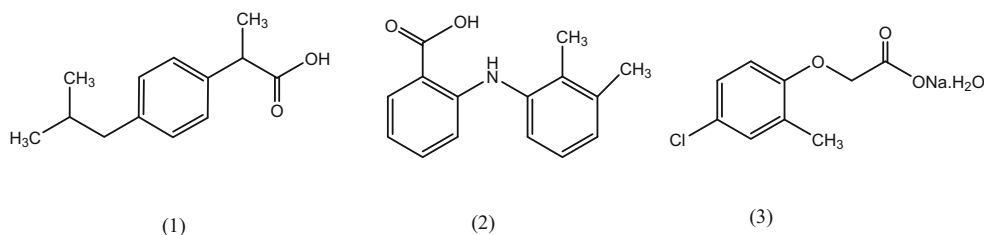
Experimental

Chemicals

The herbicide MCPA sodium salt monohydrate (sodium (4-chloro-2-methylphenoxy) acetate pure standard (99% purity), pharmaceutical compounds ibuprofen and mefenamic acid and all reagents including phosphoric acid, HPLC grade water and acetonitrile were purchased from Sigma-Aldrich Corporation (USA). All the solutions were daily prepared in ultra-pure water from a Milli-Q® purification system (Merck-Millipore, USA).

Ibuprofen (IBU) or (RS)-2-(4-(2-methylpropyl) phenyl) acid (Structure 1 in Scheme 1) is one of the most potent nonsteroidal anti-inflammatory drug (NSAID). It works by reducing

Scheme 1 Chemical structures for ibuprofen (1), mefenamic acid (2) and MCPA sodium monohydrate (3)



hormones that cause inflammation and pain in the body, reduces fever and treat pain or inflammation caused by many conditions such as headache, toothache, back pain, arthritis, menstrual cramps or minor injuries.

About the potential acute health effects, ibuprofen is considered very hazardous in case of ingestion or inhalation, eye contact (irritant), slightly hazardous in case of skin contact. An overdose of ibuprofen can cause damage to human stomach or intestine. Molecular formula: $C_{13}H_{18}O_2$, MW: 206.29.

Mefenamic acid or [(2,3-dimethyl diphenyl) amino-2-carboxylic acid] (Structure 2 in Scheme 1) is a member of the fenamate group, which includes potent nonsteroidal anti-inflammatory drugs (NSAID) including meclofenamate sodium monohydrate and mefenamic acid belonging to the acidic NSAIDs. Mefenamic acid is used for the relief of short-term moderate pain lasting less than 1 week, such as muscular aches and pains, menstrual cramps, headaches and dental pain. It is typically prescribed for oral administration. About the potential acute health effects of mefenamic acid, symptoms of overdose may include severe stomach pain, coffee ground-like vomit, dark stool, ringing in the ears, change in amount of urine, unusually fast or slow heartbeat, muscle weakness, slow or shallow breathing, confusion, severe headache or loss of consciousness. Molecular formula: $C_{15}H_{15}NO_2$, MW: 241.285.

MCPA sodium monohydrate is a common herbicide in the phenoxy or phenoxyacetic acid family, designated chemically as sodium (4-chloro-2 methylphenoxy) acetate (Structure 3 in Scheme 1). MCPA herbicide is used to control broadleaf weeds, but its use poses a high risk to percolate through the soil due to its anionic nature, high solubility and low sorption to soil colloids. Synthesis: chlorination of *o*-cresol to produce *p*-chloro-*o*-cresol followed by coupling with monochloroacetic acid in an alkaline medium (WSSA 1994). MCPA sodium monohydrate is sold in the form of white crystalline powder or flakes, freely soluble in water. Molecular formula: $C_9H_8ClNaO_3 \cdot H_2O$, MW: 240.62.

Apparatus

A schematic diagram of the photodegradation system is shown in Fig. 1. The reacting fluid flows continuously into the photochemical reactor (Fig. 2), assembled such as the active coated borosilicate tube that can be fixed inside it. The flow of liquid through the reactor provides both a continuous

fresh feed and complete immersion of the titanium oxide-coated tube inside the reactor, and thus, the solution is in contact with both the internal and external surfaces of the tube. The diameter and length of the photochemical reactor are 5 and 19 cm, respectively. The diameter and length of the borosilicate tube inside the photochemical reactor are 3.3 and 14.9 cm, respectively, and the thickness is 3 mm. The photochemical reactor can load up to 420 ml of the treating water. A peristaltic pump (Autoclave model V, Velp Scientifica Usmate, Milano, Italy) recirculates the reactant solution from a storage tank to the photochemical reactor placed in the chamber of a solar simulator device (Heraeus-Atlas Suntest CPS+, Chicago, USA). A 1.8-kW xenon arc lamp was employed as the irradiation source. The lamp was protected with a quartz filter. Taking into account the borosilicate filtration effect, the flux of photons with wavelengths between 300 and 580 nm entered the photochemical reactor and passed through the solution. The photochemical reactor (exposed area $\approx 149.2 \text{ cm}^2$) inside the chamber of the solar simulator device was irradiated with 500 W/m^2 (7.46 W irradiated the solution in the reactor).

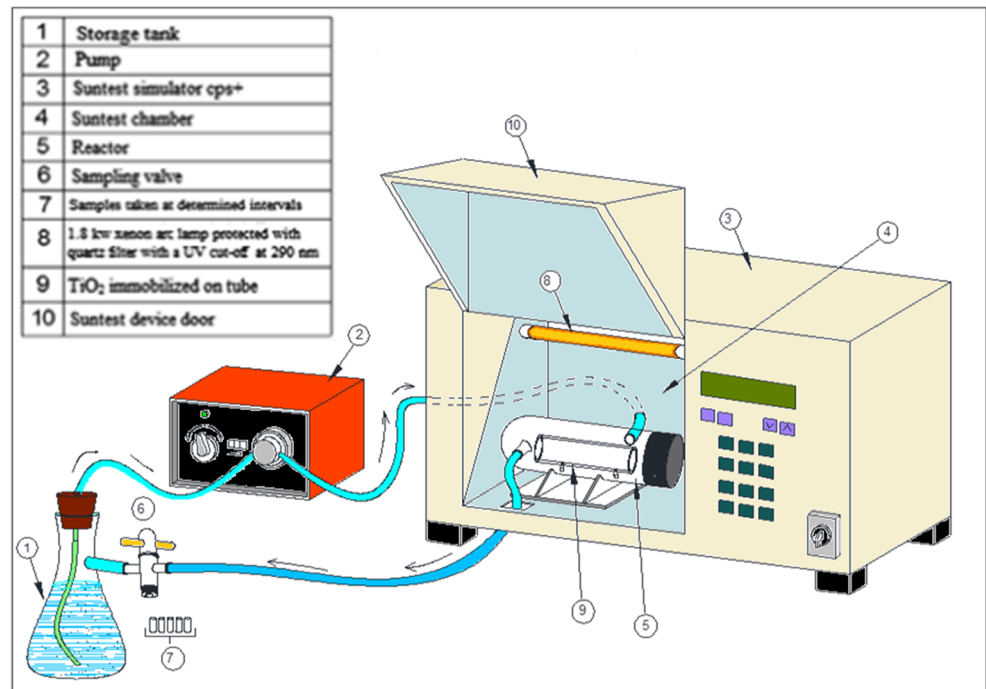
TiO₂ immobilised on borosilicate tube surfaces

Sol-gel coating

The borosilicate tubes were dip-coated using a titania sol obtained through the sol-gel process. The TiO₂ precursor sol was prepared by mixing titanium isopropoxide (98%, Acros Organics), absolute ethanol (Carlo Erba reagents), HCl (1 M solution, Carlo Erba) and H₂O (18 MΩ) in the molar ratios 1:100:0.06:3.4. The sol was stirred for 1 h before coating. The borosilicate tubes were dip-coated in the fresh sol at 10% relative humidity at the pulling rate of 100 mm min^{-1} . After an intermediate thermal treatment at 230 °C for 20 min, the tubes were submitted for a second dip-coating using the same sol and were finally treated at 500 °C for 3 h to allow titania crystallisation in its anatase form (Falcaro et al. 2014).

The total thickness of the TiO₂ coating was $40 \pm 6 \text{ nm}$, as measured using a stylus profilometer (Alpha-Step IQ) on the coating deposited on flat silicon wafer substrate, using the same titania sol and process parameters. Due to the curve

Fig. 1 Schematic diagram of the photodegradation system

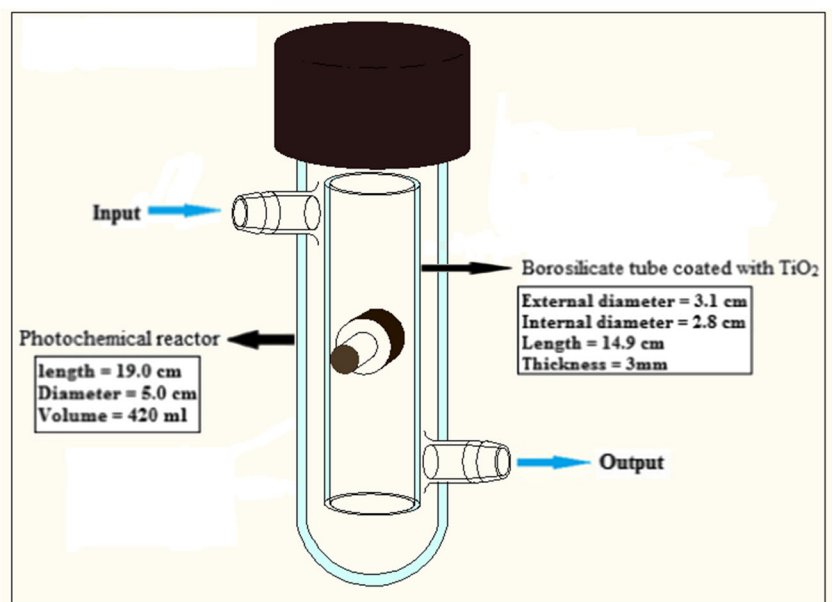


surface of the tubes and to avoid breaking them, XRD and SEM measurements were performed on the flat surface of the silicon wafer substrate. To be noted that, as the borosilicate tubes were dip-coated in the sol, both the inner and the outer walls of the tubes were coated.

Before coating with the TiO₂ sol, the borosilicate tubes were pre-coated with a SiO₂ interlayer, which functions as a barrier coating, since the formation of the TiO₂ anatase phase could be inhibited by the migration of cations from the glass to the sol-gel titania coating during the thermal treatment

(Atkarskaya 1998). The SiO₂ sol was prepared mixing ethanol, tetraethyl orthosilicate (98%, purchased from Acros Organics), H₂O (18 M Ω) and HCl in the molar ratios 18:1:4.2:0.025. The sol was 1 h stirred at room temperature; then, the tubes were dip-coated at the pulling rate of 90 mm min⁻¹ with 10% relative humidity. The samples were fired at 400 °C for 1 h to allow for the inorganic silica condensation. The thickness of a single coating was 200 ± 20 nm, as measured using a stylus profilometer on coatings deposited on flat silicon substrates.

Fig. 2 Schematic diagram for photochemical reactor and borosilicate tube coated by TiO₂ placed inside it



PECVD photocatalytic coatings on borosilicate tube

Deposition of nanoparticle titanium oxide thin films was performed using modified plasma-enhanced chemical vapour deposition (PECVD) process. As a first step, TiO₂ anatase nanocrystal dispersion was prepared by mixing a commercially available dispersion (Degussa VP Disp. W 740 X) with ethanol, reaching a final solid content of 1%. The commercial dispersion has an anatase/rutile phase weight ratio of 80/20 and a solid concentration of 40%wt in water; the average particle diameter is 20 ± 1 nm with agglomerates no larger than 100 nm. The borosilicate tubes were dip-coated in the ethanol dispersion at 100 mm min⁻¹ and dried at 110 °C for 15 min. In the second step, a PECVD silica coating deposition process was used to fix the TiO₂ nanoparticles on the tube walls. The silica coatings were deposited by radio frequency plasma-enhanced chemical vapour deposition (RF-PECVD) in an industrial apparatus with a vacuum chamber of 1 m³, using O₂ (99.999%) and hexamethyldisiloxane (HMDSO, purchased from Acros) as the precursor gases at the constant flow rate of 300 and 50 sccm, respectively, and at the working pressure of about 7.5 Pa. The substrates were positioned on the cathode (0.5 m²) and the RF power was set to 450 W, corresponding to 0.1 W cm⁻². The thickness of the final film was measured with a stylus profilometer (Alpha-Step IQ) on the coating that was deposited on flat silicon wafer substrate and was found to be about 100 ± 10 nm.

Photodegradation procedure

Direct photolysis and photocatalytic degradation experiments were carried out in the photochemical reactor and through the system described previously. Aqueous solutions of initial concentration 1.0 mg L⁻¹ were prepared by dissolving determined quantities of each organic compound (ibuprofen, mefenamic acid and MCPA sodium monohydrate). Three experiments were performed in triplicate, direct photolysis, photocatalytic degradation using the sol-gel-coated borosilicate tubes (1 for each replicate) and photocatalytic degradation using PECVD photocatalytic coating on borosilicate tubes (1 for each replicate). One litre of prepared solution was used in each experiment. Photolysis and photocatalytic reactions were performed under light radiation inside the Suntest (solar simulator) device as illustrated in Fig. 1.

Analytical methods

The concentrations of tested compounds (ibuprofen, mefenamic acid and MCPA sodium monohydrate) were monitored using high-performance liquid chromatography (HPLC) (Agilent Technologies 1200 series, USA) equipped with an Eclipse XDB-C₁₈ (3 μm particle size, 4.6 mm × 150 mm) column (Phenomenex, USA), using a diode array

detector at a wavelength of 230 nm. The mobile phase was 50% of 0.1% phosphoric acid solution/50% acetonitrile. The flow rate was 1.0 mL min⁻¹. Several concentrations (from 0.05 to 1.0 mg L⁻¹) of mix solution containing all tested compounds were injected into the HPLC and analysed; peak areas vs. concentrations of each compound were plotted and the calibration curves were obtained with determination coefficients (*R*²) of 0.998, 0.999 and 0.998 for ibuprofen, mefenamic acid and MCPA sodium monohydrate, respectively. The limit of detection (LOD) of studied compounds for this method was ranging 0.012–0.017 mg L⁻¹, and the limit of quantitation (LOQ) was 0.03–0.05 mg L⁻¹.

Results and discussion

XRD measurements on TiO₂ particles used for the sol-gel coating process

The X-ray diffraction (XRD) pattern of the coating film performed on a silicon plate using the same titania sol and process parameters confirms the major presence of anatase in the coated surface Fig. 3 (Fig. S1 in Supporting information file provided by the manufacturer). According to preliminary results, for a thermal treatment of 500 °C, a maximum in the photocatalytic activity was observed; at this temperature, the formation of the anatase phase is favoured, whereas, according to the literature (Costacurta et al. 2010) at higher temperatures, the anatase to rutile transition causes the photocatalytic activity of the coating to decrease. Therefore, a thermal treatment of 500 °C for 3 h was chosen for the preparation of the samples. The nanocrystal size determined with the Scherrer formula $L = (k\lambda)/(FWHM \cdot \cos 2\theta)$ using the 101 peak was found to be *L* = 8.2, 8.4, 9.2, 9.8, 10.8 nm at the temperatures of 400, 450, 500, 550, 600 °C (data not shown).

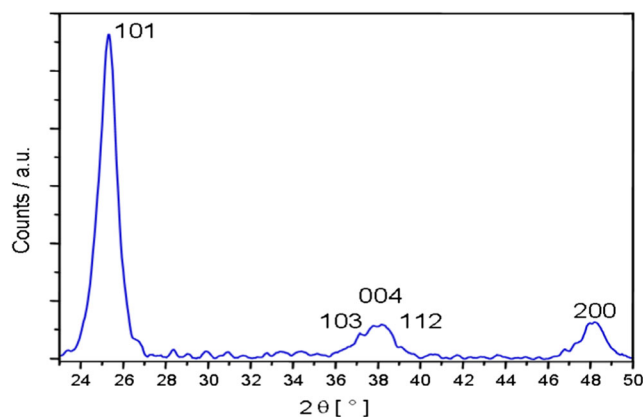


Fig. 3 XRD diffraction pattern of TiO₂ film acquired using a Bruker D8 Advance (Cu Kα, λ = 1,5404 Å) equipped with a Göbel mirror, at an acquisition speed of 5 s/step and 0.05°/step, at grazing angle (α = 0.1°)

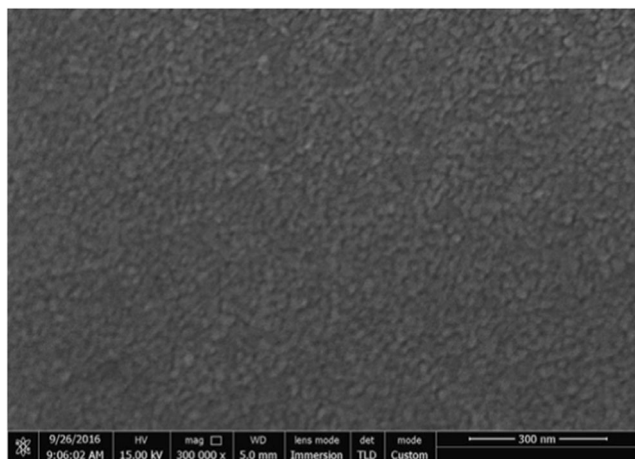


Fig. 4 Scanning electron micrograph of sol-gel coating obtained on a planar sample analysed by means of a FEI Nova NanoSEM450 Field Emission SEM (FEG-SEM), in immersion lens mode

The TiO₂ coating surface produced on the flat silicon wafer substrate appeared extremely compact and homogeneous, as evidenced in the SEM micrograph Fig. 4 (Fig. S2 in the Supporting Information file) provided by the manufacturer.

PECVD photocatalytic coatings on borosilicate tube characterisation

The deposition procedure used is similar to that presented in Costacurta et al. (2011), where the TiO₂ nanoparticles are fixed on the supporting surface by a silica PECVD layer. A SEM image of the final coating obtained on the flat silicon wafer substrate can be seen in Fig. 5 (The Supporting Information file as Fig. S3).

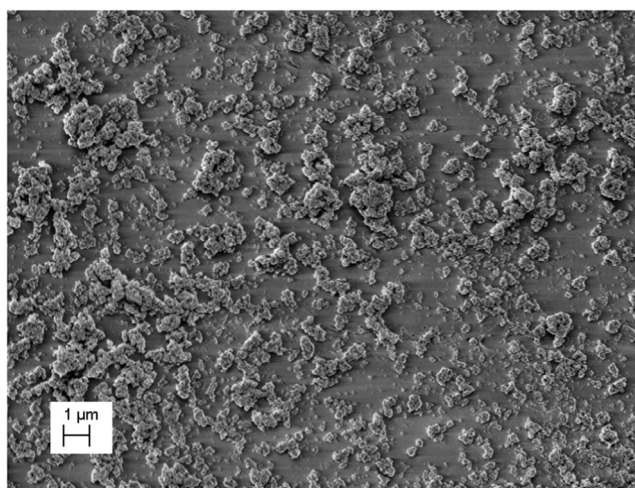


Fig. 5 SEM top view image of the deposited surface of titania nanoparticles Degussa VP Disp. W 740 X fixed with a 100-nm silica PECVD coating on a silicon substrate. Image obtained using a VEGA TS 5130 LM(Tescan) microscope equipped with a W filament and accelerating voltage of 30 kV

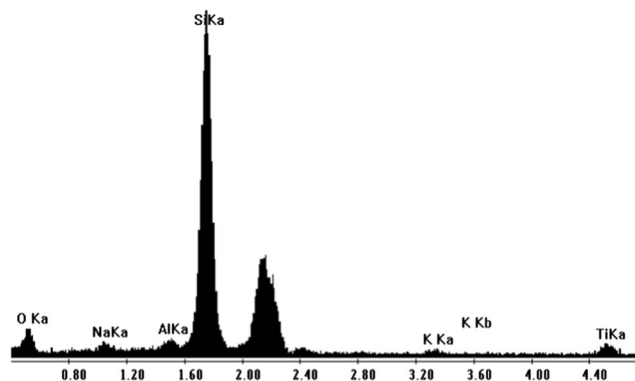


Fig. 6 ESEM microchemical analysis of the PECVD-coated silicon substrate undertaken using a XL30 Philips LaB6 ESEM instrument equipped with an energy-dispersive X-ray spectrometer (SEM-EDS)

The silica film produced on the top surface has a composition of SiO₂ with a very low Si-C content; more information on this process can be found in Patelli et al. (2009). The process adopted is able to create a very porous coating structured in two layers: the deeper is constituted of TiO₂ particles, the upper is composed of a porous film of silica. Nevertheless, the composition of the coated surface by microchemical analysis (ESEM) showed that TiO₂ is a component present with other metal oxides such as aluminium, sodium and potassium oxides Fig. 6 (Fig. S4 in the Supporting Information file).

Photolysis experiment

Direct photolysis of a diluted solution (1.0 mg L⁻¹) of ibuprofen, mefenamic acid and MCPA sodium monohydrate prepared in ultrapure water was carried out under artificial irradiation simulating solar light. Figure 7 illustrates the degradation behaviour for each compound during the photolysis experiment. The results exhibited a relatively fast degradation rate for MCPA sodium monohydrate compared with other tested compounds in the same experiment. MCPA sodium

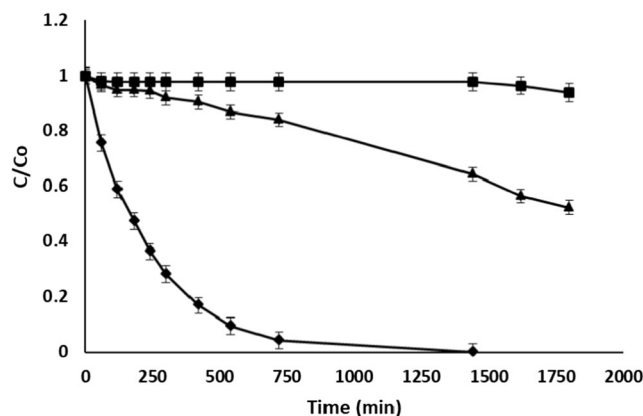


Fig. 7 Degradation of ibuprofen (■), mefenamic acid (▲) and MCPA sodium monohydrate (◆) during photolysis experiment. Values reported are the means of three replicates; error bars represent the standard error of estimate

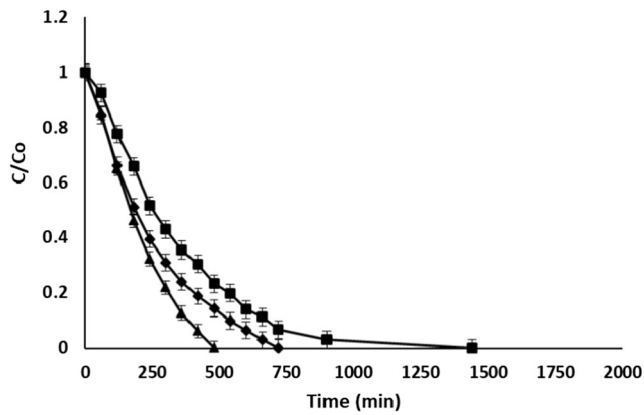


Fig. 8 Degradation of ibuprofen (■), mefenamic acid (▲) and MCPA sodium monohydrate (◆) during photocatalysis experiment using the sol-gel-coated borosilicate tubes. Values reported are the means of three replicates; error bars represent the standard error of estimate

monohydrate concentration decreased by about 53% from its initial value after 3 h and approximately 96% after 12 h. These results seem to agree with a previous study that indicated as direct photolysis the main phototransformation pathway for MCPA in ecosystems (Chiron et al. 2007). Although direct photolysis achieved fast degradation for MCPA, another study

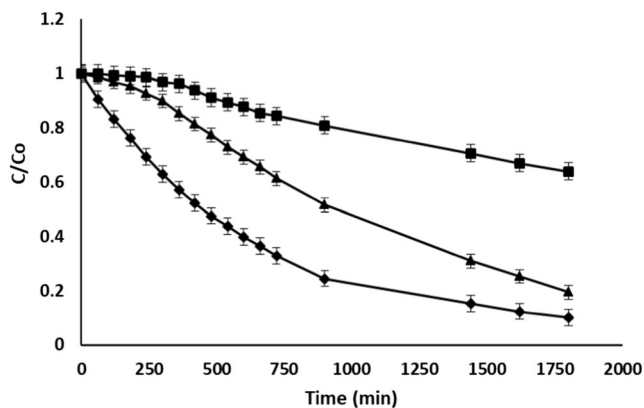
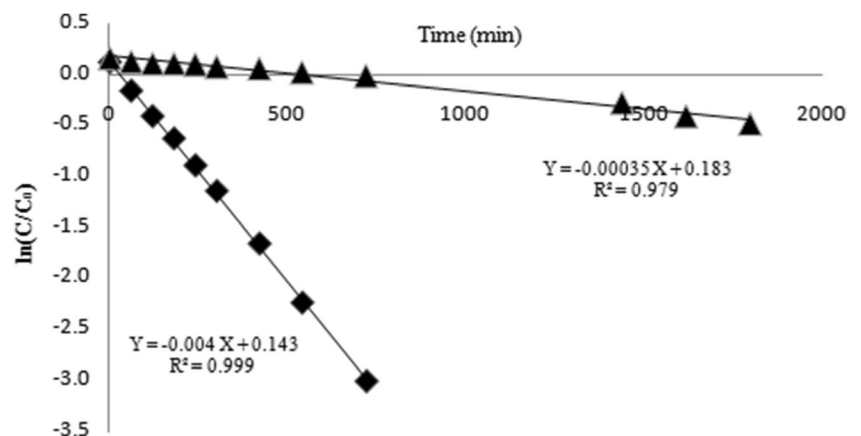


Fig. 9 Degradation of ibuprofen (■), mefenamic acid (▲) and MCPA sodium monohydrate (◆) during photocatalysis experiment using the PECVD-coated borosilicate tubes. Values reported are the means of three replicates; error bars represent the standard error of estimate

Fig. 10 Plotting of $\ln(C/C_0)$ versus time for photolysis of mefenamic acid (▲) and MCPA sodium (◆)



indicated the formation of intermediates more toxic than the parent compound during the photolysis reaction (Vione et al. 2010). The concentration of ibuprofen was decreased by about 6% from the initial value after 24 h; this result does not show significant degradation for ibuprofen through direct photolysis reaction. The negligible ibuprofen degradation obtained by direct photolysis was expected, due to its high chemical stability and low molar adsorption coefficient above 300 nm (Renge et al. 2012). The degradation rate of mefenamic acid in the situation was higher than ibuprofen as its concentration decreased by about 42% from its initial value after 24 h, but evidently, the degradation of mefenamic acid was slower compared with MCPA. Previous studies showed that mefenamic acid scarcely reacts under UV radiation and has a low photo-reactivity (Gimeno et al. 2010). In addition, since our previous photolysis experiment on mefenamic acid as unique component in the solution gave a faster degradation rate (Khalaf et al. 2013a), we can speculate that some antagonistic effects with other target compounds in the mix solution arose during the photolysis reaction causing a slow degradation rate of mefenamic acid.

The overall results indicated that the direct photolysis cannot be considered as an efficient system towards degradation of all tested compounds. Therefore, the photocatalytic degradation becomes necessary. For this reason, the photocatalytic degradation over TiO_2 supported on borosilicate tubes was investigated.

Photocatalysis using TiO_2 supported on borosilicate tubes

In order to evaluate the photocatalytic activity of titanium dioxide (TiO_2) supported on stationary substrates, two kinds of coated tubes have been examined in separated experiments. As mentioned previously, titanium dioxide (TiO_2) has been coated over these tubes through two different methodologies: (i) sol-gel technique and (ii) chemical vapour deposition (PECVD) process.

Table 1 Kinetic parameters for photolysis and catalytic photodegradation of ibuprofen, mefenamic acid and MCPA sodium

Compound	Direct photolysis			Photocatalysis					
				Sol-gel-coated borosilicate tube			PECVD-coated borosilicate tube		
	k (min ⁻¹)	R ²	t _{1/2} (min)	k (min ⁻¹)	R ²	t _{1/2} (min)	k (min ⁻¹)	R ²	t _{1/2} (min)
Ibuprofen	–	–	–	0.0030	0.976	231	0.00027	0.990	2567
Mefenamic acid	0.00035	0.979	1980	0.0060	0.968	116	0.00092	0.984	753
MCPA sodium	0.0040	0.999	173	0.0040	0.960	173	0.0010	0.987	545

Photocatalysis using sol-gel coating of borosilicate tube

Photocatalytic efficiency of the sol-gel-coated borosilicate tube was evaluated by monitoring the disappearance of the tested compounds (ibuprofen, mefenamic acid and MCPA sodium monohydrate) determined in the irradiated mix solution at different intervals as described previously. The photocatalytic degradation results of the three tested compounds over sol-gel tube are summarised in Fig. 8. The degradation of all tested compounds was much faster than degradation obtained through direct photolysis experiments. This result could be easily justified due to the presence of the semiconductor titanium dioxide on the surfaces of the borosilicate tube and its ability to produce highly reactive hydroxyl radicals ($\cdot\text{OH}$) after the absorption of irradiated light. These hydroxyl radicals can facilitate and accelerate the degradation process. From the results exhibited in Fig. 8, mefenamic acid decreased by about 54% from its initial concentration after 3 h, followed by MCPA sodium monohydrate, which decreased by about 49% during the same period, and then ibuprofen approximately by 34% in the same time. The critical step of organic compounds oxidised in the photocatalytic reactions with TiO_2 fixed on borosilicate tubes is initiated with hydroxyl radicals produced on the photocatalyst surface (Pruden and Ollis 1983; Pelizzetti et al. 1990; Lu et al. 1993). Therefore, the adsorbability of the pollutants onto the photocatalyst surface

is an important factor for evaluating the photocatalytic reaction efficiency and for understanding the variation in degradation rate between the target compounds.

Mefenamic acid degradation was faster than MCPA sodium and ibuprofen. Hence, we can conclude that the adsorbability of mefenamic acid onto borosilicate tube surface was higher, and therefore, it has had the major opportunity to be oxidised by hydroxyl radicals produced on the photocatalyst surface. The degree of adsorbability of organic compounds onto photocatalyst surface is governed by the nature and characteristics of these compounds such as solubility in water, since slightly soluble compounds in water will be more easily adsorbed than compounds with high solubility. Non-polar compounds will be more easily adsorbed than polar compounds since the latter have a greater affinity for water; also, compounds having a larger number of carbon atoms are generally associated with a lower polarity and hence a greater potential for being adsorbed (Allen et al. 1995).

Photocatalysis using PECVD photocatalytic coating on borosilicate tube

The photocatalytic activity of the titanium dioxide immobilised nanoparticles via the PECVD process was lower than the borosilicate tube treated with the sol-gel coating. Figure 9 illustrates the efficiency of the photocatalytic degradation reaction towards removal of tested compounds. The

Fig. 11 Plotting of $\ln(C/C_0)$ versus time for catalytic photodegradation of ibuprofen (●), mefenamic acid (▲) and MCPA sodium (◆) over TiO_2 immobilised by sol-gel process on borosilicate tubes

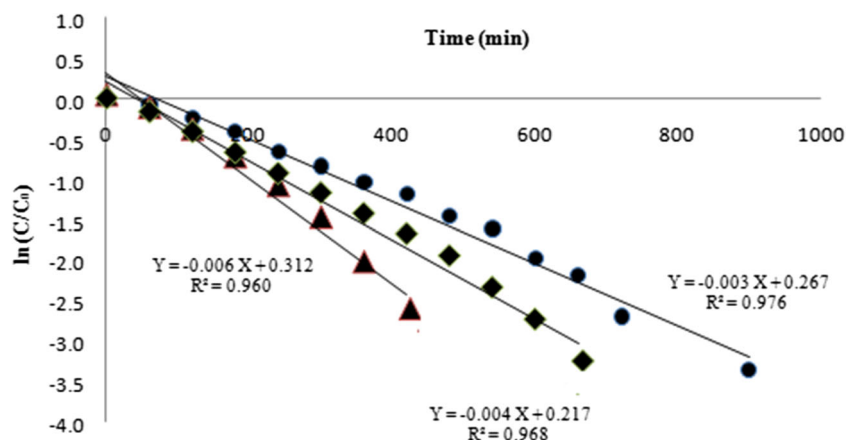
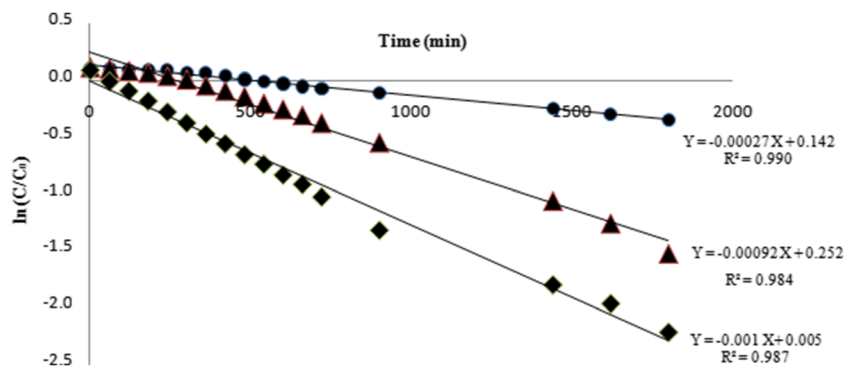


Fig. 12 Plotting of $\ln(C/C_0)$ versus time for catalytic photodegradation of ibuprofen (●), mefenamic acid (▲) and MCPA sodium (◆) over TiO_2 immobilised by PECVD process on borosilicate tubes



degradation rate was approximately slow for all compounds, and the order of degradation versus time was as follows: MCPA sodium monohydrate, mefenamic acid and ibuprofen, respectively. The results obtained suggest that deposition of titanium dioxide using the nanoparticle deposition/PECVD technique is not efficient to produce active catalysing substrates. Likely, the PECVD silica coating functions as a barrier that isolates the titania nanoparticles from the reactants; thus, the photocatalytic reaction, which is basically a surface reaction, either does not take place or is substantially slowed down. Contrary to the nanoparticle/PECVD process, the sol-gel process allows the functionalization of the borosilicate tubes with a crystalline anatase TiO_2 surface, which shows a substantial photocatalytic activity.

Kinetics studies

The direct irradiation of a solution containing 10 mg L^{-1} of ibuprofen, mefenamic acid and MCPA sodium monohydrate was conducted over a period of 30 h using irradiation simulating solar light, with regular sampling at determined intervals. Analysis of solutions by HPLC-UV shows no degradation for ibuprofen and a steady decrease in the concentrations of both MCPA sodium and mefenamic acid versus the time of irradiation. The photolysis of MCPA sodium and mefenamic acid in water was modelled with a first-order kinetic as in Eq. 1

$$\ln C(t) = \ln C(0) - k t \tag{1}$$

The plot of $\ln(C/C_0)$ versus irradiation time for MCPA sodium and mefenamic acid (where C is the concentration of the compound at time t , C_0 is its initial concentration) provides a straight line (Fig. 10), which suggests the first-order kinetics of the simple photolysis reaction.

The reaction rate constant (k) was determined from the slope of the straight line and the reaction half time ($t_{1/2}$) as $\ln 2 \cdot k^{-1}$ (Table 1).

The kinetic studies of the photocatalytic degradation experiments performed by using sol-gel and PECVD coatings were monitored also by HPLC-UV. In both cases, a steady decrease

in the concentrations of all compounds was obtained, and by plotting $\ln(C/C_0)$ versus irradiation time, a straight line was obtained for both reactions (Figs. 11 and 12). For that, photocatalytic reactions could be depicted by first kinetic order. The reaction rate constant (k) and the reaction half time ($t_{1/2}$) were determined as above (Table 1).

Conclusions

Direct photolysis of recalcitrant organic compounds in water is not efficient for removal of some types of these compounds and insufficient to induce a complete mineralisation for other compounds. Titanium dioxide (TiO_2) supported on borosilicate tubes is able to function as catalyst for the photodegradation of organic compounds tested in this study. The activity of coated borosilicate tubes depends on the technique used for immobilisation of the catalyst; sol-gel technique was found to be a successful method for the preparation of an efficient catalyst immobilised on borosilicate substrates. Degradation of ibuprofen, mefenamic acid and MCPA sodium is consistent with first-order kinetics. The overall results of this study along with the photochemical reactor system employed could be used as a basis to optimise a large-scale application of the photodegradation method proposed since no significant deactivation or loss of the catalyst immobilised on the borosilicate tubes was noted during experiments.

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