Advanced photocatalytic oxidation processes for micropollutant elimination from municipal and industrial water

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Abstract

The objective of this study was to develop and validate an innovative technology to ensure efficient elimination of different types of micropollutants and toxic compounds in waste water. The process is a tertiary treatment process, which can be easily integrated into municipal and industrial waste water treatment plants. It is based on oxidation by ozone and subsequent photocatalytic treatment. After development and validation of this system at laboratory scale, the solution was tested at pilot scale.

The first part of this work was to develop a TiO_2-based film on glass substrate, characterize its physico-chemical properties and optimize its composition at laboratory scale to be photoactive on the degradation of model water containing several pollutants. The model water consisted of a mixture of 22 major micropollutants including pesticides, plasticizers, brominated compounds, and pharmaceuticals. The best photocatalyst for the degradation of the selected micropollutants was a TiO_2 coating doped with 2 wt.% of Ag and where 10 wt.% P25 was added. Then, in order to scale up the process, its deposition on steel substrates was tested with dip and spray coating at laboratory scale. Calcination parameters were optimized to limit steel corrosion while keeping similar photoactive properties regarding the degradation of the model polluted water. The optimized solution was deposited by spray coating in a pilot scale reactor in order to assess its efficiency in a pilot water treatment plant.

Keywords: Sol-gel process, TiO_2-based film, photocatalysis, waste water treatment, pilot reactor

1. Introduction

Controlling pollutant concentrations in our rivers and lakes is a topic of steadily increasing importance. Severe pollution can have grave consequences for human health and the environment [1]. For humans and animals, negative effects include breathing problems, cardiovascular problems, cancer, neurobehavioral disorders, and endocrine effects. It can also cause serious damage to flora. In Europe, people have become increasingly aware of the problem; this is why measures to reduce water pollution are being employed more frequently.

Wastewater treatment plants are able to remove a large majority of the pollution in our wastewaters. However, some trace organic compounds cannot be degraded by the conventional three-stage waste water treatment process [2]. These micropollutants mostly result from domestic and industrial use of pharmaceutical preparations, cosmetic and hygiene products, and pesticides.

Because of the negative effects mentioned earlier, the European Union updated its Water Framework Directive (WFD) in 2018 [3]. Beside the list of priority substances (2013/39/EU) [4] the WDF includes a watch list of substances that need to be examined (EU 2018/840) [5]. After evaluation of the European monitoring programs also environmental quality standards (EQS) for these substances could become mandatory in the future.

It is important to direct our research efforts to the development of an advanced treatment step for micropollutant removal. This is often also called a tertiary waste water treatment step. One of the conceivable solutions is titania-based photocatalysis [6–9]. Titania (TiO_2) is a semiconductor with a band gap energy of 3.2 eV for its anatase phase [10]. When a photon of sufficiently high energy meets the surface of titania, an electron ($e-$) can be ejected from the valence band into the conduction band. At the same time, this creates a hole ($h+$), which is the absence of an electron in the valence band. The holes can act as powerful oxidizing agents, whereas the ejected electrons have strong reducing potential.

To increase TiO_2 photoactivity, several possibilities have been envisaged and studied [11–13]: metallic doping to increase photoefficiency, various types of doping to increase TiO_2's activity in the visible spectrum of light, or combination with other semiconductors to achieve synergistic effects. In this study, silver nanoparticles were used to increase the photocatalytic efficiency by trapping electrons [14–16]. In addition, commercial Evonik P25 [17] was used as an additive. Many papers confirm P25's efficiency for the degradation of a large range of compounds under UV light [18–22].

To increase the efficiency of water treatment, photocatalysis was coupled with another advanced oxidation process, ozonation. Ozone (O_3) was produced using electrical energy. When ozone is dissolved in water, it becomes unstable [23]. The subsequent decomposition of ozone can take different paths. In general, it leads to a mixture of superoxide radicals ($O_2^{-}\cdot$), peroxides ($HO_2\cdot$ and H_2O_2), and hydroxyl radicals ($OH\cdot$). Since these species are all strong oxidizing agents, their presence in the water can cause beside the slow direct reaction with ozone, organic pollutants to be oxidized and finally transformed into carbon dioxide and water.

This work focuses on a general approach to degrade environmentally harmful trace substances in waste water. After the development and validation of this system (ozonation + photocatalysis) at laboratory scale, the solution was also tested at pilot scale. The first part of this work focused on the development of a TiO_2-based film on a glass substrate, the characterization of its physico-chemical properties, and the optimization of its composition to degrade water containing up to 22 different micropollutants. In order to scale up the process, its deposition on steel substrates was tested using dip and spray coating at laboratory scale. Calcination parameters were optimized to limit steel corrosion while maintaining similar photoactive properties. The optimized solution was deposited by spray coating in a pilot scale reactor in order to assess its efficiency in these conditions.

2. Materials and methods

2.1 Photocatalyst synthesis

6 sols were produced. Each sol was associated with two numbers corresponding to their Ag and P25 wt%, respectively: Ag2, Ag1/10P25, Ag2/10P25, Ag4/10P25, Ag2/5P25, and Ag2/20P25. For example, Ag1/10P25 contains 1 wt.% Ag and 10 wt.% P25.

In the case of samples containing no P25, the material synthesis is adapted from [14–16]: (i) A mass, m_{AgAc}, of silver acetate (Merck, purity ≥99%, called AgAc) was dissolved in 32 mL *2*-methoxyethanol (Acros Organics, purity ≥99.5%, called MetOH). This solution was then agitated at 180 rpm for the rest of the synthesis. (ii) After 30 min, a volume, V_{EDAS}, of *N*-[*3*-(trimethoxysilyl)propyl]ethylenediamine (Sigma-Aldrich, purity 97%, called EDAS) was added to the solution. (iii) After another 30 min, a volume $V_{H2O,1}$ of ultrapure water (18.2 MΩ·cm^{-1}) was mixed with 32 mL MetOH and added to the solution. (iv) After another 30 min, a volume V_{TTIP} of titanium tetraisopropoxide (Sigma-Aldrich, purity ≥97%, called TTIP), was dissolved in 96 mL MetOH, and added to the solution. Then, the solution was put under a nitrogen atmosphere. (v) After another 45 min, a volume $V_{H2O,2}$ of ultrapure water was mixed with 32 mL MetOH and added to the solution. After another 45 min, the sol was ready for further use.

In the case of samples containing P25, a preliminary step was added to the synthesis: the volume V_{TTIP} of TTIP was dissolved in 96 mL MetOH. A mass of P25, m_{P25}, was added to this solution, which was then heated to 80 °C. 12 h later, the protocol mentioned in the previous paragraph was carried out with the following differences: Before arriving at step (iv), the P25 solution was sonicated by ultrasound (Branson 2510 ultrasonicator) for 15 min. During step (iv), the sonicated solution was added to the main solution instead of the MetOH-TTIP solution mentioned in the previous paragraph.

The weights and volumes of the reagents varied depending on the material's final contents of Ag and P25. They are shown in Table S1. The calculations leading to these values are detailed in the Supplementary Materials.

2.2. Photocatalyst coating

For film formation, glass microscope slides (AF32ECO, Schott AG, Mainz, Germany) and stainless steel slides (316L steel, Mecanic Systems, Braine-l'Alleud, Belgium), of dimensions 2.5 cm × 7.5 cm × 0.7 mm, were used as substrates for dip coating. The glass and steel slides were thoroughly cleaned before coating. The speed of withdrawal of the slide from the solution during the dip coating operation was 60 mm/min, as optimized by Malengreaux *et al.* [24] for this type of TiO_2 organic synthesis.

To obtain crystalline TiO_2, the coating must be calcined. For glass samples, the calcination was performed at 500 °C for 1 h with a heating ramp of 10 °C/min. Two dip coating operations were conducted for each slide and both were followed by a calcination step.

Each of the 6 sols was used to produce 5 coated glass slides, leading to 30 coated glass slides in total. These represent the first series of samples called series 1.

2.3. Calcination study for steel substrate

To reduce corrosion effects on the steel, calcination below 500 °C would be favorable. In order to optimize the calcination temperature for steel, different times and calcination temperatures were tested and reported in Table 1: 3 temperatures (500 °C, 390 °C, 280 °C) and 3 times (1 h, 6 h, 12 h) were chosen. Anticipating the results, it was observed that (i) calcination at 280 °C for 12 h failed to produce any type of crystallinity in the samples, and (ii) calcination at 500 °C for 1 h corroded steel at an unacceptable level. Thus, shorter times of calcination at 280 °C and longer times of calcination at 500 °C were excluded from this study.

These conditions were applied to both glass and steel samples using the Ag2 sol. For each substrate and each set of parameters, 5 slides were coated, leading to 70 coated substrates overall (35 glass substrates and 35 steel substrates). These represent the second series of samples, called series 2. 5 samples belonged to series 1 and series 2 simultaneously.

The nomenclature for all samples is as follows: the film samples contain the name of the sol used for deposition followed by “G” or “S” depending on the substrate (glass or steel) and the temperature and time of calcination. For example, Ag2/10P25-G-500/1 sample was coated with Ag2/10P25 sol on a glass substrate, and calcined at 500 °C for 1 h.

2.4. Sample characterization

The actual amount of dopant in TiO_2 was evaluated by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) on a Varian Liberty Series II device (Agilent Technologies, Palo Alto, USA)

[25]. The samples underwent alkaline fusion, corresponding to the *modus operandi* described in J.G. Mahy et al. [24].

An estimation of the films' thickness and roughness was done by profilometry (Veeco Dektak 8 Stylus Profiler, Bruker). Each sample was measured 2 times, and the measurements were repeated on 5 different samples for each type of synthesis. For each measurement, the baseline was set at the level of the uncoated zone. Then, three quantities were measured: (i) film thickness (mean trough height, T_v): the average height below which there is a continuous film; (ii) film thickness (average, T_p): the average height, taking into account all troughs and peaks; (iii) absolute roughness of the film (Eq. 1).

$$R_a = \frac{1}{n}\sum_{i=1}^{n}|h_i - \mu| \qquad (1)$$

where R_a is the absolute roughness (nm), h_i is the height of point i (nm), μ is the average film thickness (nm), and n is the number of points (-).

The crystallinity was characterized on both substrates by grazing incidence X-ray diffraction (GIXRD) in a Bruker D8 diffractometer (Bruker, Billerica, MA, USA) using Cu radiation and operating at 40 kV and 40 mA. The incidence beam angle was 0.5°. The Scherrer formula (Eq. 2) was used to determine the size of the TiO_2 crystallites, d_{XRD} [26]:

$$d_{XRD} = 0.9\frac{\lambda}{(B\cos(\theta))} \qquad (2)$$

where d_{XRD} is the crystallite size (nm), B the peak full-width at half maximum after correction of the instrumental broadening (rad), λ the wavelength (nm), and θ the Bragg angle (rad).

Titania layers were also investigated using a JEOL JSM-840 (JEOL, Peabody, MA, USA) scanning electronic microscope (SEM) at an acceleration voltage of 20 kV. An elemental analysis by energy-dispersive X-ray spectroscopy (EDX) was also performed.

2.5. Micropollutant degradation test

In order to compare the performance of the different coatings synthesized in this work, their degradation efficiency was tested on a model water containing ten micropollutants with an initial concentration of

10 µg/L. The 10 compounds were lindane, atrazine, 2,2′,4,4′,6-penta-bromodiphenyl ether, tributylphospate, di(2-ethylhexyl)phthalate, metoprolol, carbamazepine, diclofenac, sulfamethoxazole, and 1H-benzotriazole.

The testing protocol was the following:

(i) 420 mL of a solution containing all 10 pollutants was poured into a stirred glass bottle. The first sample of 60 mL was immediately taken to measure the initial concentrations of the 10 pollutants.

(ii) The glass bottle was wrapped in aluminum foil in order to protect the solution from light. An Aqua Medic Ozone 200 device was used for the ozonation, which produces 200 mg O_3/h. The solution was ozonated for 30 min (with a concentration of 15 mg/L in the solution measured with the Ozone MColortest Disk comparator test from VWR). The second sample of 60 mL was then taken.

(iii) The solution was transferred into a crystallizing bowl with four coated slides. The bowl was covered by a quartz plate, which was transparent to UVC radiation. It was stirred by an orbital shaker (Grant Bio POS 300) throughout the rest of the experiment. The system was placed inside a thermostatic box at 15 °C in the dark for 30 min. After that, the third sample of 60 mL was taken.

(iv) The UVC lamp (λ=254 nm, 20 W/m^2 at the photocatalyst surface) was turned on. After different times (1 h, 2 h, 4 h, 6 h), a sample of 60 mL was taken (from the total of 240 mL at the end of (iii)) and one of the four slides was removed, in order to keep the concentration of photocatalyst constant in the solution until the end of the photocatalytic test.

Table 2 summarizes the procedure described in the previous paragraphs.

In addition, one experiment was conducted without any slides, but with an otherwise identical protocol. Measurement of the degradation of the 10 pollutants by ozone and UVC alone was made possible by this “blank experiment”.

Finally, another experiment was carried out in the presence of the slides but without light. This was done in order to evaluate the adsorption of the micropollutants onto the slides (dark experiment).

Each sample was analyzed using GC/MS-MS and LC/MS-MS. Detailed information about the chromatography is given in Supplementary Materials.

2.6. Extended micropollutant degradation test

In the case of the optimized coating, the degradation activity was tested on another model water containing more pollutants. The list was extended to 22 compounds: the 10 compounds listed in Section 2.5 plus desethylatrazine, *2,6*-dichlorobenzamide, bromacile, simazine, chlortoluron, isoproturon, dichlorodiphenyltrichloroethane (DDT), acetyl-4-sulfamethoxazole, iohexole, iopromide, clarithromycin, and terbutryn.

The protocol for the test was the same as described in Section 2.5.

2.7. Leaching in water medium and toxicity test

As the coatings are designed for a water purification application, leaching of TiO_2 and Ag needs to be very low.

The tested coatings are Ag2/20P25-G-500/1, Ag4/10P25-G-500/1, Ag2/10P25-G-500/1, and Ag2/10P25 spray coated (sample found line 6 from Table 9, see Section 2.8.1.). The pilot reactor was also tested (coating from Section 2.8.2.). These coatings have the highest fractions of P25 and silver, making them potentially the most unsafe with regard to leaching.

The testing protocol is the following: For each aforementioned composition, a slide was put into a Petri dish and approximately 30 mL of polluted water was added. Then, quartz plates were put onto the two Petri dishes, which were introduced into the thermostatic cabinet, under the same conditions as described earlier. The Petri dishes were agitated by the orbital shaker and the UVC lamp was turned on. After 96 h, the Petri dishes were taken out of the cabinet and the liquid was analyzed by ICP-AES.

The toxicity of each coating was also assessed. The samples on which the test was carried out were obtained exactly as described in Section 2.5. The toxicity of the model water described in Section 2.6 was also assessed. The toxicity of the water was characterized on the microcrustacea *Daphnia magna* according to the ISO 6341 standard [27]. During this experiment, *Daphnia magna* microcrustaceans were incubated for 24 h with different concentrations of model water. After 24 h of contact, the number of dead microcrustaceans was counted. This number was plotted against the concentration of the toxic water. From this, the concentration EC50 at which half of the microcrustaceans died was found. The toxicity of the water is defined as TU = 100/EC50. The water was considered toxic if $1 < TU < 10$, and very toxic if $TU > 10$.

2.8. Scaling up

To validate the results obtained at laboratory scale, degradation of the same batch of pollutants was carried out in a semi-continuous system. The main challenge to overcome was the coating method. Dip coating requires a quantity of sol scaled to the volume of the reactor, rendering it unfit for industrial applications. Spray coating was instead chosen and optimized.

2.8.1. Spray coating at laboratory scale

Stainless steel 316 slides were washed by scrubbing with paper soaked in RBS T105, rinsed with distilled water, then ethanol, and finally dried with a flux of compressed air. Some slides were used as such; the rest were dipped in a 2 mol/L solution of HNO_3 for 5 s, then dried with a flux of compressed air.

Each slide was manually spray-coated using an airbrush (Harder & Steenbeck). The nozzle was held about 5 cm above the slide and 3-bar compressed air was used to distribute the sol onto the slide as homogeneously as possible. A covering of tape prevented sol deposition at the edge of every slide. In every case, Ag2/10P25 was sprayed. The flow rate and the total quantity sprayed were studied as presented in Table 9 in Section 3.5. Afterwards, the slides were calcined at 390 °C for 12 h. All slides were subsequently analyzed by SEM, by X-ray diffraction, and underwent the tape test and the water flow test. In the tape test, some tape was applied onto the calcined layer, then sharply pulled off. In the water flow test, a water tap was used to produce a 32.5 mL/s water flow 10 cm above the upper part of the slide for 5 s duration. The slide was held at a 45° angle relative to the flow. Then, the slide was dried in an oven at 100 °C. In either test, if the aspect of the layer visibly changed, it was considered a failure and the operating parameters were rejected.

2.8.2. Spray coating at pilot scale

A pilot-scale cylindrical reactor (see Figure 1) made of stainless steel was spray-coated on its inside surface according to the results presented in Table 9. A nozzle was mounted on a motor-powered bar moving vertically along the central axis of the reactor from the top. At first, a nitric acid solution (weight concentration 50%) was abundantly sprayed inside the reactor, which was then dried at 120 °C. 7 mL of a freshly prepared Ag2/10P25 sol was then sprayed, the reactor was dried at 120 °C, and calcined at 390 °C for 12 h.

As the reactor was closed and the spray direction was horizontal, no loss of sol occurred. This allows us to calculate the average thickness of the layer, which was equal to 104 nm after calcination and corresponds to the thickness of the equivalent layer at laboratory scale.

2.8.3. Degradation test in pilot scale installation

The degradation tests were carried out in the pilot reactor described in Section 2.8.2, in the center of which a UVC lamp of 71 W power and monochromatic wavelength of 254 nm was placed (intensity of 110 W/m^2 at the walls of the reactor). Two ozone generators and a tank were connected to the reactor according to Figure 2. 200 L of model water containing around 10 µg/L of each pollutant (see the list in Section 2.5) was circulated at a flow rate of 500 L/h for 1.5 h. During the first 30 minutes, the ozone generators were on, but not the UVC lamp. After this time, samples were taken and analyzed, and the lamp was turned on. After a further 30 min and 1 h, samples were taken and analyzed again. This experiment was called “standard pilot test”.

The test was repeated three times by varying the operating conditions in the following ways. (i) identical conditions as in the previous paragraph, but no coating inside the reactor (blank pilot test). (ii) identical conditions as in the previous paragraph, but without turning on the UVC lamp (dark pilot test).

After the photocatalytic experiments, water samples were also analyzed by inductively coupled plasma (ICP-AES) to determine the amount Ag, Si, or Ti leached during the test.

3. Results and discussion

3.1. Coating thickness at laboratory scale

For series 1 and 2, the thicknesses (T_v and T_p) and roughness (R_a) measured by profilometry are reported in Tables 3 and 4.

Figure 3 illustrates the calculation of these values for Ag2/20P25-G-500/1, as an example. The presence of the coating is clearly observed with the step at around 1700 µm.

In series 1 (Table 3), all three calculated values (T_v, T_p, and R_a) increase with the amount of P25. Firstly, the increase of thickness at the base of the film (T_v) could be linked to an increase of the viscosity of the sol due to aging. When coating the slide with the second layer, 24 h have passed and the sol has aged. This is coherent with the thickness formula calculated for dip coating [28]. Secondly, the increasing average film thickness (T_p) indicates that the amount of TiO_2 sol deposited on the substrate increases with the amount of P25. Thirdly, the increase in roughness, which leads to higher values of the surface area, can be attributed to P25 itself. The numerous peaks and troughs are due to P25 agglomerates, which are bigger in size than the coating. The presence of these aggregates was confirmed thanks to the camera mounted on the profilometer. They only appear in the presence of P25: otherwise, the profilometry profiles are almost flat, and the roughness decreases dramatically, as shown in Table 3.

Concerning the films with different silver loadings (Table 3), it is observed that the film thickness increases slightly when the loading of silver increases from 1% to 2%, although this increase lies in the uncertainty range. Between 2% and 4% of silver, no differences are observed for the film thickness nor for their roughness.

In series 2 for glass substrates (Table 4), the film thicknesses evolve from 80 to 100 nm except for sample Ag2-G-500/6, which is inexplicably thicker and slightly rougher. In the absence of commercial P25 nanoparticles in the TiO_2 sol, the films are very smooth. Overall, the glass-supported film thicknesses vary very little between the various calcination parameters.

In a previous study [24], it was shown that the ideal film thickness is around 80 nm. Increasing film thickness above 80 nm barely increases the performance of the photocatalyst because only a small fraction of light is able to reach the deepest regions of the photocatalyst. However, reaching thickness values higher than 80 nm costs additional material, and is in consequence economically less interesting. The values for series 2 are close to that optimum, but those of series 1 are slightly higher.

The profilometry measurements on steel slides (series 2 in Table 4) are more complex than those on glass. This is due to the surface roughness of steel that is very different from that of glass. While glass is relatively smooth and flat, stainless steel has an intrinsic surface roughness, microcracks, and curvature. This makes profilometry unsuitable for the determination of film thicknesses on steel slides.

The thickness measurement on steel slides was only possible on Ag2-S-390/12 sample, giving a thickness (T_p) around 90 nm which is in agreement with measurements on the glass substrate.

SEM images of the cross-section of broken glass slides and of powders were taken.

Figure 4 shows SEM images of the cross-sections of glass slides with different magnifications. Figure 4A shows the cross-section of a coating without P25 (Ag2-G-500/1 sample) at a magnification of 2500×. In this case the surface is smooth, in accordance with what was found by profilometry. In the presence of P25, agglomerates form at the surface of the films. For Ag2/5P25-G-500/1, some agglomerates can be seen in Figure 4B. When the amount of P25 increases (Ag2/20P25-G-500/1 sample, Figure 4C), the agglomerates become bigger and more numerous. During the profilometry measurements, the agglomerates were detected as surface roughness (Table 3). Additional SEM images (Figures S4a and S5a) of the surfaces of Ag2/10P25-G-500/1 and Ag2/10P25-S-390/6 samples are presented in the Supplementary Materials, confirming the presence of agglomerates at the surface.

An EDX analysis was also performed on these two samples to confirm their compositions. Ti, Si, and Ag were well observed (Figures S4b and S5b); the other elements came from the substrate.

In Figure 4D, the section of a glass slide with the coating Ag1/10P25-G-500/1 is shown at a magnification of 20000×. At this magnification, the film can be seen as a slim, light layer on the glass slide. For this example, a thickness of approximately 80 nm was measured, which is in good accordance with the profilometry measurements (Table 3).

3.2. Crystallinity of TiO_2-based laboratory films

Figure 5 shows the XRD patterns of the samples in series 1.

In Figure 5, the effect of a varying silver fraction is evaluated. The highest crystallinity is obtained for 1% of silver. As the amount of silver increases from 1% to 4%, the peaks become broader and decrease in height. This is an indicator of decreasing crystallinity [15]. During the synthesis of the TiO_2 sol, silver is incorporated inside the TiO_2 lattice thanks to the complexation between silver ions and $(OCH_3)_3$-Si-$(CH_2)_3$-NH-$(CH_2)_2$-NH_2 (EDAS). This shows that the amount of silica present in samples increases with the Ag loading. In previous studies [15], it was shown that the presence of silica inside the TiO_2 lattice hindered the crystallization of amorphous TiO_2 into anatase. Anatase is the only TiO_2 phase detectable by this method for all samples. The presence of silver and/or other crystalline phases of TiO_2, such as rutile, are not observed on films. The method is not precise enough to allow their visualization [15]. In particular, rutile is expected to correspond to a maximum of 4 wt.% in the case of samples loaded with 20 wt.% P25, equaling the maximum loading of silver.

In Figure 5, no visible difference in the diffractograms of the films can be observed when comparing samples containing 5 to 20% of P25.

Figure 6 shows the influence of the calcination parameters (time and temperature) on the crystallinity of layers deposited on glass substrates. Both films calcined on glass at 500 °C are well crystallized: the film calcined for 6 h is more crystalline than that calcined for 1 h (Figure 5). Once again, the only TiO_2 crystalline phase visible in this diffractogram is anatase. The effect of reducing the calcination temperature from 500 °C to 390 °C is shown in Figure 6, showing that the duration of the calcination is an important factor. The diffractograms of films calcined for 6 h and 12 h are nearly identical and present the characteristic peaks of TiO_2-anatase. However, the sample calcined at 390 °C for 1 h seems to be amorphous, as no peaks are observed in Figure 6.

As expected, the films calcined at 280 °C are completely amorphous, whatever the duration of calcination.

In Figure 7, the diffractograms for steel slides from series 2 are shown. Only the two characteristic peaks of the chromium-iron alloy are observed for all samples calcined at 280 °C and 390 °C. The main peak of TiO_2-anatase at 25.3° is only observed for Ag2-S-390/12 sample. The crystallization of TiO_2 is thought to be hindered by the migration of components present in the steel support [15].

Finally, in Figure 7, the same conclusions relative to the beneficial effect of an increase of the calcination temperature and duration can be drawn. The main characteristic peaks of anatase are observed. Nevertheless, the degree of TiO_2-anatase crystallization is lower on steel than it is on glass. To limit steel corrosion, calcination at 390 °C for 12 h seems to be ideal.

The TiO_2 crystallite sizes for all the samples are calculated by using the Scherrer equation (Eq. 2) and are presented in Tables 3 and 4. As extrapolated from the XRD patterns (Figure 4), the size of TiO_2 crystallites decreases when the Ag loading increases. The amount of silica present in samples increases with the Ag loading (Table 4), because EDAS is used to complex silver. The presence of silica inside the TiO_2 lattice hinders the crystallization of amorphous TiO_2 into anatase [15]. This is why the size of TiO_2 crystallites decreases from 30 nm for Ag1/10P25-G-500/1 to 10 nm for Ag4/10P25-G-500/1. Concerning the loading of P25 inside samples, it seems that the loading of P25 does not significantly influence the crystallization of amorphous TiO_2, as observed in Figure 5. When the loading of P25 increases from 5% to 20%, the size of TiO_2 crystallites decreases only from 25 nm to 20 nm, which is not significant because of the precision of the Scherrer method.

Table 4 shows that the size of crystallites in layers calcined at 390 °C on glass is not influenced by the duration of the calcination step: the size of TiO_2 crystallites stays equal to 25 nm after either 6 h or 12 h. At 500 °C, the size of TiO_2 crystallites increases with the length of the calcination step: after 1 h of calcination the size of TiO_2 crystallites is equal to 25 nm, and after 6 h it increases to 30 nm.

3.3. Degradation activity at laboratory scale

As explained in Section 2.5, the degradation can be attributed to 3 different phenomena: ozonation, photolysis by UVC light, and photocatalysis. The importance of each process needs to be compared to validate the usefulness of photocatalysis and the use of UVC light.

Due to the large amount of degradation results, some Tables are provided in the Supplementary Materials.

3.3.1. Degradation test on the first model water

3.3.1.1. Series 1 samples

All coatings from series 1 were tested for the degradation of the model water in order to find the best formulation for pollutant degradation (results can be found in Table 5 and in Supplementary Materials, Tables S4 to S8). The limit of detection is 0.4 µg/L for the GC-MS/MS method (first half of the micropollutants in Table 5) and 0.025 µg/L for the LC-MS/MS method (second half of the micropollutants in Table 5). The error then is around 5% for GC-MS/MS and 1% for the LC/MS-MS method.

The average degradation of the pollutants after ozonation is represented in Table 5 for Ag2/10P25-G-500/1. Carbamazepine, diclofenac, and sulfamethoxazole are completely degraded after 30 min under O_3; metoprolol is partially degraded (50%) and the other seven compounds are not affected by the O_3 treatment.

For UVC photolysis, atrazine, brominated diphenyl ether, and 1H-benzotriazole are completely degraded without photocatalyst. Di(2-ethylhexyl)phthalate and metoprolol are slightly degraded (around 10%).

Finally, regarding the contribution of photocatalysis, the adsorption of the coating needs to be taken into account. The dark test reveals that the variations of pollutant concentrations due to adsorption are not significant, therefore adsorption can be neglected in the framework of the degradation tests.

The best photocatalysis efficiency can be attributed to Ag2/10P25-G-500/1 (Table 5), with 84% of global degradation (compared to other samples shown in Tables S5 to S9). The four most resistant pollutants (lindane, tributylphospate, di(2-ethylhexyl)phthalate, and metoprolol) are partially degraded.

This coating seems to present the optimized loading ratio for Ag and P25. Silver increases the recombination time of photogenerated e^- and h^+ pairs [15,29,30] and P25 increases the roughness of the coating [2], leading to an increase of the area of contact between the micropollutants and TiO_2.

3.3.1.2. Series 2 samples

The series 2 samples were tested to assess the influence of the substrate and/or the calcination parameters on the pollutant degradation. For this, Ag2-G-390/12, Ag2-S-390/12, and Ag2-S-500/1 were tested. In order to validate the previously selected parameters (calcination at 390 °C for 12 h), the corresponding samples must be tested for micropollutant degradation.

The three samples lead to nearly identical results (as shown in Supplementary Materials, Table S10 to S12). The same test was conducted on Ag2/10P25 with varying substrate and calcination parameters (samples Ag2/10P25-G-390/12, Ag2/10P25-S-390/12, and Ag2/10P25-G-500/1), as shown in Table 5, S13 and S14. The photocatalytic results (Table S13 to S14) lead to the same conclusion as with Ag2 samples: the calcination parameters and the substrate do not influence the pollutant degradation.

In conclusion, steel substrates are suitable for further pilot scale tests.

3.3.2. Degradation of the model water containing all 22 micropollutants

In order to validate the optimized coating at pilot scale, a second degradation test was carried out on the Ag2/10P25-G-500/1 sample. As described in Section 2.6, this test is similar to the first one but the model water contains additional pollutants so that it is more similar to real polluted industrial or domestic waste water. 22 pollutants in total were analyzed. The results of degradation are reported in Table 6, differentiating between the O_3, UVC, and photocatalysis contributions. The mean degradation of micropollutants is 89%.

The coating enhances the degradation of 5 resistant molecules: lindane, tributylphospate, metoprolol, 1H-benzotriazole, and 2,6-dichlorobenzamide. The chemical architectures of these molecules are very different, showing that the efficiency of the photocatalytic process on a specific molecule is difficult to predict. The combination of ozonation, photolysis, and photocatalysis seems to be a very efficient combined process for micropollutant degradation at laboratory scale, with each process able to decompose specific molecules.

For these reasons, the Ag2/10P25-G-500/1 coating was selected for the final experiment at pilot scale. The deposition method is also scaled up by using spray coating.

3.4. Leaching and toxicity of the dip coating at laboratory scale

Results of the leaching test are given in Table 7. They indicate that there is no significant leaching of the dip coatings. Although there are no limit values for silver and titanium in drinking water [3], having low leaching is advantageous since this increases the lifetime of the photocatalyst.

The toxicity experiment (Table 8) shows that the water toxicity decreases gradually with the different treatments. This shows that the molecules created during the degradation process are less toxic than the initial micropollutants.

3.5. Optimization of deposition by spray coating at laboratory scale

The characteristics of TiO_2 layers spray coated onto steel 316 slides are presented in Table 9. It appears that a very slow deposition speed is necessary to obtain a layer that is resistant to the mechanical stress caused by the tape. Furthermore, the nitric acid pretreatment is favorable to the layer's adherence, even if the corresponding non-treated layer is barely damaged by the tape. SEM analyses (Figure 8) show that the morphology of the spray-coated layers is a stack of plate-like crystallites.

Increasing the flow rate of the coating visibly increases the depth of the intercrystalline defects. The thickness is also massively increased by an increased flow rate, despite depositing the same quantity of sol. This means that the layer is much more porous when it is sprayed more quickly.

Increasing the total quantity sprayed increases the thickness. When 0.5 mL is sprayed, the layer is only one plate-like element thick. Increasing the thickness of the layer by spraying more sol is related to a lower adherence of the TiO_2 at the surface of the layer, as expected.

The water flow test proved ineffective in damaging the calcined layers. XRD spectra after this operation (not represented here) are very similar to those before the test in all samples. Besides chromium oxide present in the steel slide, only TiO_2-anatase is detected.

The Ag2/10P25 spray coated sample (line 6 of Table 9) was also tested on the photocatalytic degradation of the first model polluted water (results presented in Table S15 in Supplementary Materials). Similar activity was obtained compared to the equivalent dip-coated Ag2/10P25 sample (whose results are presented in Table 5).

An additional leaching test was conducted on this spray coated sample (Table 7) showing no leaching of any of the three elements (Ag, Si, Ti).

3.6. Pilot spray coating

Due to the fact that the layer is deposited inside the reactor, characterizations of the coating are very difficult, and only macroscopic observations can be made. A uniform surface aspect is observed, and the TiO_2 layer appears to be homogenously coated on the surface. Water flow in the reactor does not alter the aspect of the layer.

3.7. Photocatalytic experiment at pilot scale

All the results of the experiment are listed in Table 10. As observed at laboratory scale, the dark test reveals that adsorption is not significant.

In Table 10, it is observed that 4 pollutants are directly degraded after 30 min of ozonation (bromacil, simazine, chlortoluron, and isoproturon). Some molecules are degraded by the UVC only (atrazine, desethylatrazine, and DDT) and five resistant molecules are degraded only when the photocatalyst is used. This pilot scale experiment corroborates the promising results obtained at the laboratory scale, at a scale much closer to potential industrial applications.

The global degradation, defined as the average degradation for the considered micropollutants, is 72%.

The results show that the spray coating method produces coatings of similar thickness and efficiency as the dip coating method, while being much cheaper, more flexible, and more easily scalable than dip coating.

The leaching test performed on water samples obtained at the end of the photocatalytic experiment (Table 7) revealed no leaching of any of the three elements (Ag, Si, Ti).

4. Conclusions

In this work, a global advanced oxidation process was developed to degrade environmentally harmful organic micropollutants in wastewater. This process combined the use of an ozonation step followed by a photocatalytic reactor equipped with a UVC lamp. After development and validation of such a system at laboratory scale, the solution was also tested at pilot scale (200 L).

In the first part of this work, the photocatalyst was developed at laboratory scale. TiO_2-based films were produced on two substrates, glass and steel, and with two additives: silver and Evonik P25. The aims were (i) to optimize the photocatalyst compositions on glass substrates in order to optimize the photoactivity at laboratory scale for the degradation of a model polluted water containing 10 pollutants, and (ii) to transfer the coating onto steel substrates while maintaining similar photoactivity. Pilot and industrial reactors are usually made of steel, necessitating this process.

All the coatings have been characterized and tested for photodegradation on the model polluted water.

From laboratory tests, it was found that similar 100 nm-thick anatase coatings could be deposited on both glass and steel, but that the calcination temperature had to decrease from 500 °C (glass) to 390 °C (steel) to prevent steel corrosion. The ideal photocatalyst had 2 wt.% Ag and 10 wt.% P25.

In the second part of the study, the process was extrapolated to pilot scale. Coatings were made by spray coating in order to obtain a more flexible deposition method, both at laboratory scale for optimization, and at pilot scale. Homogenous coatings were observed and a photocatalytic experiment was conducted with the pilot reactor treating 500 L/h of polluted water using only 7 mL of sol as the starting material for the coating. The results showed the usefulness of the coating compared to ozone and UV light alone. The promising results highlighted the successful transfer of the photocatalyst activity from the laboratory scale to a pilot scale, leaving the door open to a possible industrial application as a tertiary treatment in industrial and domestic waste water treatment plants.

Acknowledgements

S. D. L. thanks the Belgian National Funds for Scientific Research (F.R.S.-FNRS) for her Associate Researcher position. For their financial support, the authors are grateful to the Ministère de la Région Wallonne Direction Générale des Technologies, de la Recherche et de l'Energie (DGO6), in relation to the Plan Marshall, and with support from the "22nd CORNET Call" funds for the research project "AOPTi - Advanced photocatalytic oxidation processes for micropollutant elimination in municipal and industrial water". We also we would like to thank for financial support from the German Federal

Ministry of Economic Affairs and Energy within the agenda for the promotion of industrial cooperative research and development (IGF) in relation to the CORNET program based on a decision of the German Bundestag. The access was opened by member organisation environmental technology and organised by the AiF, Arbeitsgemeinschaft industrieller Forschungsvereinigungen, Cologne (IGF-Project No. 202 EN). The authors thank Aquatic Science S.A. for the use of the spray coating equipment. The authors also thank the CAREM platform of the University of Liège for SEM measurements.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflicts of interest.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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