Photocatalytic degradation of oxalic and dichloroacetic acid on TiO$_2$ coated metal substrates

Irina Ivanova[a], Jenny Schneider[a], Henning Gutzmann[b], Jan-Olliver Kliemann[b],
Frank Gärtner[b], Thomas Klassen[b], Detlef Bahnemann[a], Cecilia B. Mendive[a,c,*]

[a] *Institut fuer Technische Chemie, Leibniz Universitaet Hannover, Callinstr. 3, D-30167 Hannover, Germany*
[b] *Helmut Schmidt University Hamburg, Holstenhofweg 85, D-22043 Hamburg, Germany*
[c] *Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Dean Funes 3350, 7600 Mar del Plata, Argentina*

ARTICLE INFO

ABSTRACT

The photocatalytic activity of TiO$_2$ immobilized on three different metal substrates (stainless steel, copper and titanium) has been investigated using dichloroacetic (DCA) and oxalic acid (OA) as model compounds. The TiO$_2$ immobilization was realized by a novel process of Cold Spraying. The photocatalytic degradation experiments were performed in two cycles on every TiO$_2$-coated metal substrate following two methodologies: (a) the same acid, i.e., OA or DCA, was degraded in the first and in the second cycle, and (b) one acid was used in the first cycle and the other acid in the second.

OA was found to be more efficiently photocatalytically degraded than DCA; moreover, OA helps for the regeneration of the surface when employed after DCA. The use of copper as a substrate material was found to be photochemically active releasing basic species to the aqueous solution. Stainless steel and titanium are therefore less interfering choices to carry out mechanistic studies or, eventually, for environmental applications. The photonic efficiencies of the TiO$_2$ particles immobilized on the three different metallic supports were compared to those found for TiO$_2$ in an aqueous suspension. From the viewpoint of the amount of the employed photocatalyst, the TiO$_2$-coated metal substrates are significantly more efficient for the degradation of OA than a highly efficient TiO$_2$ suspension (Evonik P25), which content of nanoparticulate photocatalyst was enormously higher. Furthermore, OA and DCA can be completely mineralized at the supported catalyst.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Heterogeneous photocatalysis has attained great interest in recent years due to its promising approach for environmental remediation, and other applications [1–6]. Due to the rapid industrial development the importance for efficient and eco-friendly decomposition and mineralization of the organic contaminants in wastewater and air has grown exponentially [7]. Ultimately, many researchers centered on advanced oxidation processes (AOPs), which allow the complete oxidation of organic compounds to harmless products such as carbon dioxide and water [8–10].

TiO$_2$-based photocatalysis has been shown to be one of the most important advanced oxidation processes especially as promising technology for air and water purification treatment [11–13]. TiO$_2$

is a wide band semiconductor (band gap 3.2 eV for anatase) [12–14], chemically and photochemically stable, non toxic, inexpensive, largely available, has strong oxidizing power and high photocatalytic activity [15,16]. The photocatalytic process involves, as primary and initial step, the generation of an electron–hole pair in the TiO$_2$ semiconductor particle by the irradiation with light of wavelength equal or greater energy than the band gap [17]. These charge carriers can recombine or participate in red-ox reactions at the particle–solution interface [18]. Valance band holes and conduction band electrons become, therefore, in strongly oxidizing and reducing species, respectively [19]. Consequently, the semiconductor particles act as electron donors and electron acceptors for molecules in the surrounding medium. For instance, the reaction of the photogenerated holes with water molecules and hydroxyl ions adsorbed on the surface of TiO$_2$ leads to the formation of hydroxyl radicals (·OH), capable of mineralizing a wide range of organic pollutants at ambient temperature and pressure [20–23].

TiO$_2$-based photocatalysts are very versatile and can be utilized either suspended in aqueous solutions or immobilized on a supporting solid substrate [18]. Most studies have reported that

---

suspension reactors are more efficient due to the high surface area available for red-ox reactions [18] However, the use of an aqueous suspension of fine powdered TiO_2 requires a post-treatment removal of the TiO_2 particles, which can be a time consuming and a costly process [24]. Recently an interesting method has been suggested which promises more feasible separation of suspended photocatalyst powders [25].

Since 1993 the idea of an immobilized photocatalyst on an inert support has gained much attention due to the possibility of reducing costs in phase separation processes [22,26]. In addition, the amount of photocatalysts employed in such immobilization design is considerably low as compared to the approach of using aqueous suspensions. And the fact that a lower amount of photocatalyst is necessary is of economical interest. The immobilization of TiO_2 has been achieved on a variety of supports, such as glass, silica gel, metal, ceramics, polymer, thin films, activated carbon and others [27,28].

In the present work the three different metal substrate types, stainless steel, copper and titanium have been coated with nanoparticulate TiO_2 using the Cold Spraying technique. Cold Spraying is a relatively new thermal spray process, which allows producing coatings without significant heating of the feedstock powder [29,30]. Therefore it is possible to avoid the phase transformation from anatase to rutile in Cold Spraying and thus preserve the photocatalytic active anatase phase [31]. In contrast to conventional thermal spray techniques, the gas temperatures are low enough and the exposure time to the hot gas stream is short enough to avoid melting of the particles [29]. As Cold Spraying has become in the last years an established industrial spray process, the production of large scale active surfaces on metallic supports is a promising challenge to carry out. Furthermore, this process allows the utilization of metal supports with relatively low weight for example aluminum. Hence the overall weight of a system thus will not exceed that of those photocatalysts fixed on glass supports.

The advantages of using metals as substrates respond to the facts that (a) few authors have investigated the impact phenomena and layer formation process for spraying brittle ceramic materials on ductile metal surfaces, (b) Cold Spraying has proven to have minimum thermal influences, thus structures and properties of the powder feedstock can be retained, and (c) by Cold Spraying, comparatively thin layers of ceramics can build up on metal substrates, which are sufficient for a number of multiple applications.

Thus, since this technique can be easily applied on ductile materials such as metals, it appeared to be an excellent choice to produce innovative photocatalytic surfaces which properties reveal interesting features. The photocatalytic activity of the three different metal substrates coated with nanoparticles of TiO_2 has been investigated using dichloroacetic (DCA) and oxalic acid (OA) as model compounds. The resulting photocatalytic activities are compared to that of the commonly used TiO_2 suspension prepared with the highly active photocatalytic commercial powder P25 from Evonik.

2. Experimental procedures

All chemicals were of analytical grade and used as received without further purification. All solutions were prepared with deionized water from a Sartorius Arium 611 apparatus (resistance = 18.2 MΩ cm^{-1}).

2.1. Coating preparation

Cold Spraying was performed with the HSU CGT Kinetiks 8000 prototype by using nitrogen as process gas with standard nozzle of type 24 WC-Co and powder feeder PF4000 from CGT, Ampfing, Germany. The powder feed rate was kept constant at 0.22 g/s, and

the traverse speed of the spray gun was also maintained constant at 320 mm/s. The process parameters for Cold Spraying the TiO_2 coatings were set to a gas temperature of 800 °C and a gas pressure of 4 MPa. Substrates were fixed at a stand-off distance of 60 mm. The cold sprayed TiO_2 coatings have been obtained after one spray pass.

The sprayed material was TiO_2 TS40 from Hombikat, Sachtleben Chemie GmbH, Germany. TiO_2 TS40 consists of anatase with 15–20 nm average particle size and a surface area of ca. 50 m^2/g (according to the Brunauer–Emmett–Teller (BET) method). The amount of deposited TiO_2 on each metal substrate was around 20 g/m^2. The thickness of the films prepared by Cold Spraying was not uniform varying between 5 and 6 μm, with a maximum at around 10 μm [29].

2.2. Photocatalytic tests

The photocatalytic degradation tests of both, DCA and OA, were carried out in a glass reactor, equipped with a cooling jacket, and under vigorous stirring (Fig. 1). The glass reactor was connected to a semi-micro pH-electrode combined with an Ag/AgCl reference electrode (Thermo-Orion Ross 8115). A pH static technique was employed for the kinetic measurements. The details of which have previously been described in detail elsewhere [32]. The automatic dosing unit was a Basic Titrino 794 from Metrohm. The irradiation unit consisted of a Xe arc lamp CSX 450 W (Phillips) and a lamp house LAX 1450 with a power supply SVX 1450 from Müller Elektronik-Optik. A 10 cm IR blocking filter was placed between the reactor glass window and the lamp to protect the reaction solution from overheat associated to the irradiation. The temperature was kept constant at 25 °C during the entire experiment by means of a thermostatic bath from Julabo Company. An oxygen purge was used for all experiments.

The TiO_2 coated metal substrates were immersed into the reactor containing DCA or OA solutions. All solutions were prepared in 10 mM KNO$_3$ to maintain the ionic strength close to a constant value. The initial concentrations of DCA and OA were 1 mM and 2 mM, respectively. The pH of the solution was adjusted to 3.0 for DCA and 3.7 for OA. This pH values have been carefully selected to enable the comparison with previously published data concerning the photocatalytic degradation of these model compounds [33,34]. Due to the pH static technique employed in this work, the amount of base or acid added to the system to keep the pH constant was computed to assess the respective amounts of DCA or OA photocatalytically degraded. All the dry metal substrates were previously UV(A) irradiated for 3 days on a horizontal bench at ambient conditions to mineralize residual organic matter adsorbed at the surface [35].

The photocatalytic degradation experiments were performed on cold sprayed metal substrates consisting of TiO_2-coated stainless steel, copper, or titanium substrates, in two consecutive cycles for the mineralization of OA and DCA following two methodologies: (a) the same acid, i.e., OA or DCA, was degraded in the first and in the second cycle, and (b) one acid was used in the first cycle and the other acid in the second. Thus, each metal substrate was employed twice in the two consecutive cycles. After the first photocatalytic test using either OA or DCA, the metal substrate was thoroughly washed with deionized water, dried under a soft air current, and UV(A) irradiated for 24 h on the horizontal bench at ambient conditions.

The photocatalytic test employing a TiO_2 suspension has been performed in the same reactor and experimental set-up as shown in Fig. 1. The photocatalyst was TiO_2 P25 from Evonik. TiO_2 P25 consists of anatase and rutile in a proportion of approximately 80 and 20% respectively, with 25–50 nm average particle size and a surface area of ca. 50 m^2/g (according to the Brunauer–Emmett–Teller
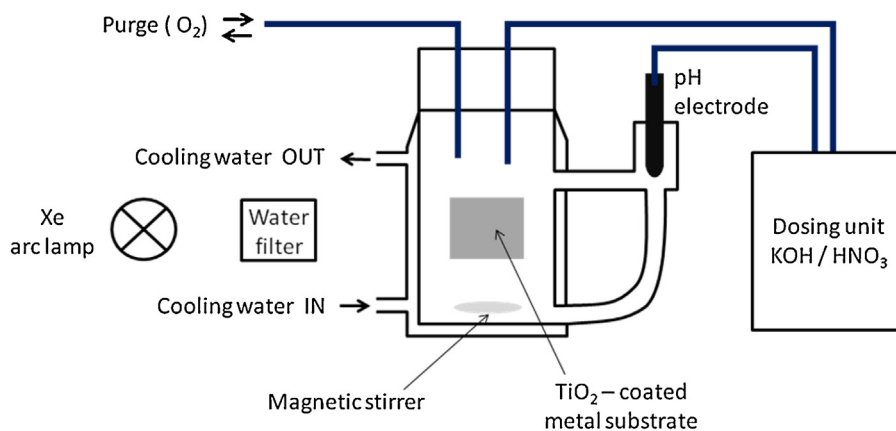
Fig. 1. Scheme of the experimental set-up used for the photocatalytic degradation experiments. A glass reactor with a double jacket for thermal control.

method). The reactor was filled with 230 ml of a suspension 2.5 g TiO_2/l in 10 mM KNO_3 and 2 mM OA. The suspension was allowed to reach adsorption equilibrium in the dark for 24 h under vigorous stirring. The pH was adjusted to 3.7 and the suspension was stirred for further 40 min to ensure equilibrium previous to the photocatalytic reaction.

In the case of the TiO_2 coated metal substrates an aliquot of 1 ml was withdrawn every 30 min to monitor the DCA or OA concentration, as well as those of other anions such as chloride. The quantification was performed by means of high performance ionic chromatography (HPIC). In the case of the suspension an aliquot of 1 ml was withdrawn every 10 min.

The chromatograph was a DIONEX ICS-1000 with a conductivity detector and an electro-regenerator-suppressor. The column was an Ion Pac AS9-HC 2×250 mm and the guard column was an Ion Pac AG9-HC 2×50 mm from DIONEX. The eluent was an alkaline solution of 8×10^{-3} mol/l Na_2CO_3 and 1.5×10^{-3} mol/l $NaHCO_3$. The temperature of the detector conductivity cell was kept constant at 35 °C.

The photocatalytic activity of three different cold sprayed TiO_2-coated metal substrates, e.g., stainless steel, copper and titanium, has been investigated using DCA and OA as model compounds. They were compared to the photocatalytic activity of a TiO_2 suspension prepared with the commonly used highly active photocatalytic commercial powder P25 from Evonik [36].

In aqueous solution OA ($H_2C_2O_4$) and DCA ($HC_2HCl_2O_2$) deprotonate giving rise to three and two species, respectively. Table 1 lists the nomenclature used in the present work for the five species. For instance, in the case of OA at pH 3.7 the test solution contains species B and C while in the case of DCA at pH 3 species E.

The photocatalytic degradation of OA was studied at pH 3.7. The three species A, B and C degrade upon photocatalysis according to Eqs. (1)–(3), respectively.
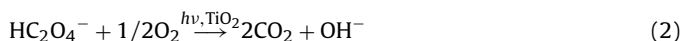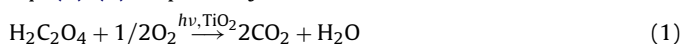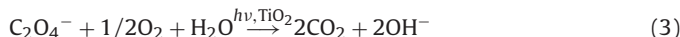
$$H_2C_2O_4 + 1/2O_2 \overset{h\nu,TiO_2}{\longrightarrow} 2CO_2 + H_2O \tag{1}$$

$$HC_2O_4^- + 1/2O_2 \overset{h\nu,TiO_2}{\longrightarrow} 2CO_2 + OH^- \tag{2}$$
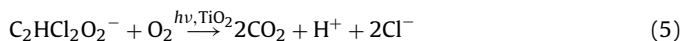
Table 1
Nomenclature for the different species present in the photocatalytic systems. The pKa constants at 25 °C and low ionic strength are 1.25 and 4.27 for OA, and 1.29 for DCA [35].

Species	Nomenclature
$H_2C_2O_4$	A
$HC_2O_4^-$	B
$C_2O_4^{2-}$	C
$HC_2HCl_2O_2$	D
$C_2HCl_2O_2^-$	E

$$C_2O_4^- + 1/2O_2 + H_2O \overset{h\nu,TiO_2}{\longrightarrow} 2CO_2 + 2OH^- \tag{3}$$

The generation of OH^- ions makes possible the monitoring of the photocatalytic degradation of species B and C using a pH static technique. The number of moles of H^+ (addition of HNO_3) necessary to neutralize all OH^- produced is computed and stoichiometrically assigned to the number of moles of species B or C degraded. The concentration of all species present in the system at any time is therefore calculated as the difference between their corresponding initial and degraded concentrations.

The photocatalytic degradation of DCA was studied at pH 3.0. Both species D and E degrade upon photocatalysis according to Eqs. (4) and (5), respectively.

$$HC_2HCl_2O_2 + O_2 \overset{h\nu,TiO_2}{\longrightarrow} 2CO_2 + 2H^+ + 2Cl^- \tag{4}$$

$$C_2HCl_2O_2^- + O_2 \overset{h\nu,TiO_2}{\longrightarrow} 2CO_2 + H^+ + 2Cl^- \tag{5}$$

Due to the very low concentration of species D in the system at the working pH, only species E was taken into account, and analogously to OA, the DCA concentration present at any time was calculated by neutralizing the H^+ generated upon the course of the photocatalytic reaction (addition of KOH).

Photonic efficiencies ζ have been calculated for all investigated samples as well as for the TiO_2 suspension using Eqs. (6) and (7).

$$\zeta = \frac{\text{degradation rate} \quad [\text{mol/s}]}{\text{photon flux} \quad [\text{mol} h\nu/\text{s}]} = \frac{V \cdot \Delta c}{I_0 \cdot A \cdot \Delta t} \tag{6}$$

$$I_0 = \frac{I \cdot \lambda}{N_A \cdot h \cdot c} \tag{7}$$

where V is the volume of the glass reactor, $\Delta c/\Delta t$ the degradation rate, A the illuminated area (8.04 cm^2), I_0 the photon flux, I is the light intensity, λ is 365 nm, N_A is Avogadro's constant, h is Planck's constant and c is the velocity of light.

Additionally to the pH static technique, an independent measurement of the OA and DCA present in the system was done by means of high performance ionic chromatography (HPIC). Aliquots of 1 ml were withdrawn from the solutions in contact to the photocatalytic samples every 30 min. In the case of DCA the concentration of chloride ions was as well quantified by this analytical technique.

3. Results and discussion

Fig. 2 shows the photocatalytic degradation of OA and DCA at the three different cold sprayed TiO_2-coated metal substrates.

Table 2 summarizes the calculated photonic efficiencies for all species at different cycles.

The photonic efficiency of all TiO_2-coated metal substrates in contact to the same acid tends to be lower in a second
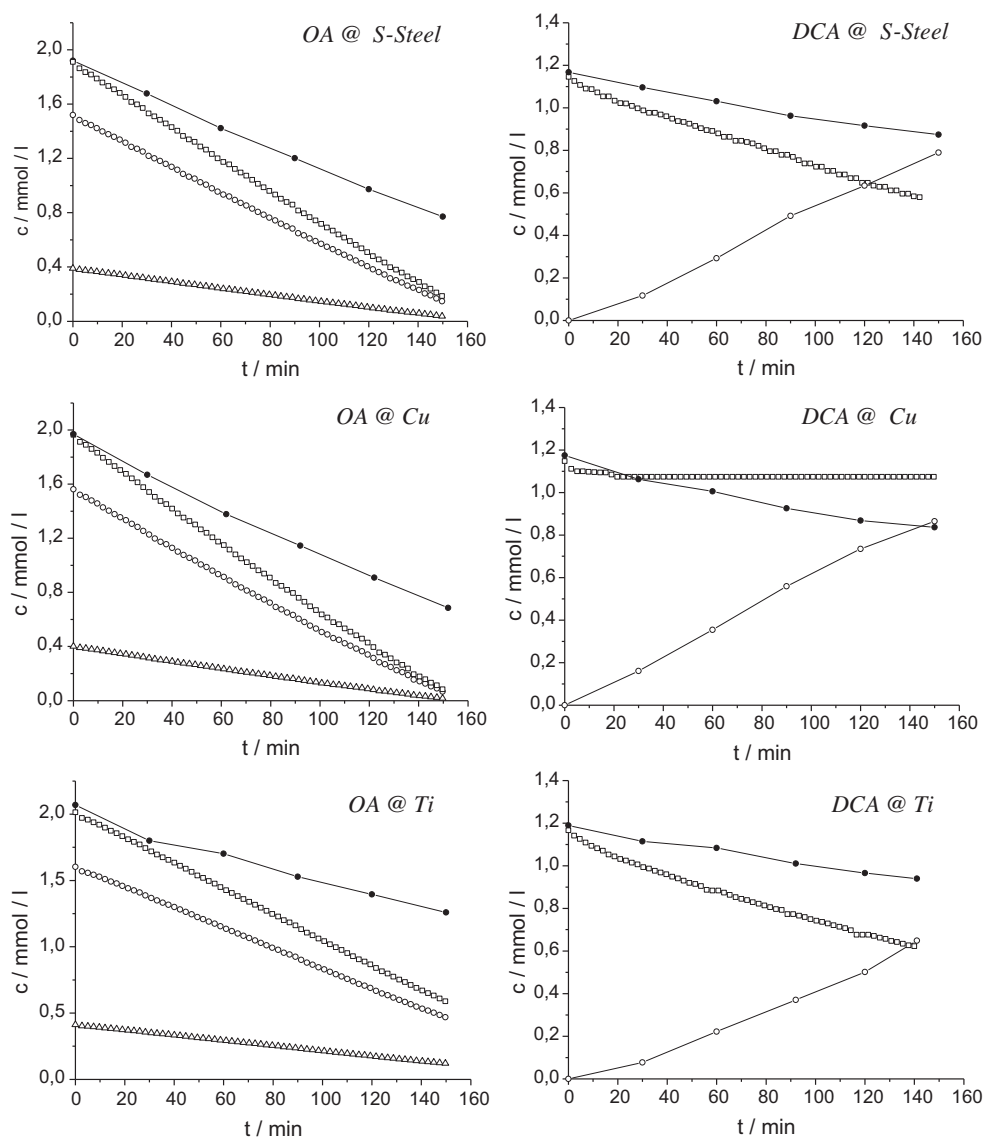
Fig. 2. The photocatalytic degradation of OA (on the left) and DCA (on the right) at different TiO$_2$-coated substrates, from top to bottom: stainless steel, copper and titanium (first cycle). The initial oxalic acid concentration was 2 mM in 10 mM KNO$_3$ at pH 3.7. Oxalic acid concentration measured by means of a pH-static technique: (□) species (B + C), (○) species B and (△) species C. (●) Oxalic acid concentration in the solution measured by HPIC. The initial DCA concentration was 1 mM in 10 mM KNO$_3$ at pH 3.0. (□) DCA concentration measured by means of a pH-static technique. (●) DCA and (○) chloride concentrations in the solution measured by HPIC.

photocatalytic degradation cycle. It must be noted that after the first cycle all metal substrates showed a dark grayish color where the UV(A) light beam impacted. This may be indicative of a loss of photocatalytic material affecting the capability of the surface for degrading OA and DCA.

The photonic efficiencies for both, OA and DCA, calculated from the concentrations measured by means of the pH static technique are higher than those from the concentrations measured by ionic chromatography. This is consistent with the fact that both techniques sense different set of species present in the systems. While the pH static technique is able to monitor all changes arising either from dissolved or from adsorbed species, the chromatographic method only accounts for those present in the liquid bulk solution, i.e. dissolved species.

Table 2 reveals some interesting points regarding the photonic efficiency for DCA in a second photocatalytic degradation cycle. It appears to be dependent on which acid had been employed in the first cycle. For instance, for the case of TiO$_2$-coated stainless steel substrates it is 1.23% or 1.48% if DCA or OA is used first,

respectively. Analogously, for TiO$_2$-coated titanium substrates, it is found to be 0.98% or 1.61%. Furthermore, if DCA is used in a second cycle on TiO$_2$-coated stainless steel after OA (1.48%), the photonic efficiency is rather similar to the one obtained using DCA in the first cycle (1.50%). This may indicate that, despite OA adsorbs strongly, its photocatalytic degradation products do not remain at the surface thus no active sites are thereafter blocked for further degradation of DCA. Another explanation for the decreased photocatalytic activity would be a partial release of TiO$_2$ from the metal substrate to the solution which, however, such a phenomenon is unlikely since TiO$_2$ layers prepared by drying a suspension on a substrate at room temperature, i.e., the adherence of the particles to the surface is much lower than that of the TiO$_2$ particles on these metallic substrates, are stable for longer periods of time even when they are exposed to a continuous flow of an aqueous solution [37]. Whereas the photocatalytic degradation of DCA either yields adsorbed products, such as chloride ions, which block active sites, or promotes the buildup of a polymeric adsorption structure which remains so strongly adsorbed that cannot be removed in the subsequent

Table 2
Photonic efficiencies (in %) calculated using OA or DCA concentrations measured by pH static techniques, or by high performance ionic chromatograph; and using chloride concentrations for the photocatalytic degradation of OA and DCA at the different TiO$_2$-coated substrates after one or two cycles.

Substrate	Cycle	Photonic efficiency, ζ (%)				
		OA		DCA		
		pH-static	HPIC	pH-static	HPIC	(Cl$^-$)
S-Steel	1	3.22	2.28	–	–	–
	2	2.40	2.02	–	–	–
	1	–	–	1.50	0.66	1.49
	2	–	–	1.23	0.65	1.38
	1	3.26	2.35	–	–	–
	2	–	–	1.48	0.62	1.78
	1	–	–	1.50	0.79	1.41
	2	2.40	1.82	–	–	–
Copper	1	3.70	2.62	–	–	–
	2	3.12	2.28	–	–	–
	1	3.61	2.81	–	–	–
	2	–	–	0	0.99	2.09
	1	–	–	0	1.03	1.71
	2	3.19	1.94	–	–	–
Titanium	1	2.56	1.62	–	–	–
	2	2.03	1.68	–	–	–
	1	–	–	1.42	0.68	1.24
	2	–	–	0.98	0.49	0.99
	1	2.56	1.68	–	–	–
	2	–	–	1.61	0.54	1.45
	1	–	–	1.43	0.68	1.24
	2	2.35	1.44	–	–	–

Fig. 3. The consumption of HNO$_3$ 0.42 M by a TiO$_2$-coated copper substrate immersed in water (OA and DCA free solution) at pH 3.70 under UV(A) irradiation.

cleaning process for the preparation of the second photocatalytic cycle. Similar observations have been reported previously for anions such as Cl$^-$, SO$_4^{2-}$, and PO$_4^{3-}$, respectively [33]. Such a situation can be more evinced in the case of TiO$_2$-coated titanium substrates where the photonic efficiency for DCA after the photocatalytic degradation of OA is higher than that obtained when using DCA in the first cycle, i.e., 1.61% and 1.42–1.43%, respectively.

Contrary to the case of DCA, the photocatalytic degradation of OA in a second cycle does not appear to depend on the acid previously used. For instance, the photonic efficiencies for OA in the case of TiO$_2$-coated stainless steel substrates after the photocatalytic degradation of either OA or DCA are, in both cases, 2.40%. A possible explanation can be that due to the strong inner sphere adsorption of OA, any species remaining at the active sites upon the photocatalytic degradation of DCA can be easily replaced. Furthermore, the species produced upon photocatalytic reaction of OA can easily desorb leaving the active sites free for further adsorption and subsequent reaction. Experimental evidence for similar adsorption replacements were reported by Weisz and co-authors [38]. Thus, OA is suggested to play an important role in the regeneration of the photocatalytic surface.

The lower photonic efficiencies for either DCA or OA in a second cycle, as compared to those corresponding to the first cycle can be attributed to a very small loss of TiO$_2$, as pointed above, thereby affecting the sample's capability of photocatalytic degradation.

The pH static technique was not possible to apply to monitor the DCA photocatalytic degradation on the TiO$_2$-coated copper substrates. During this reaction almost no base (KOH) was consumed for the neutralization of the generated H$^+$ ions (see Fig. 2 DCA@Cu). The TiO$_2$-coated copper substrates are not photochemically inert. Basic species are produced under UV(A) irradiation, and can be neutralized by addition of acid (Fig. 3). These basic species are likely to be involved in capturing the H$^+$ produced upon the DCA photocatalytic degradation, thus disabling the pH static technique for the quantification of the corresponding concentrations. However the photocatalytic degradation of DCA could be estimated from the
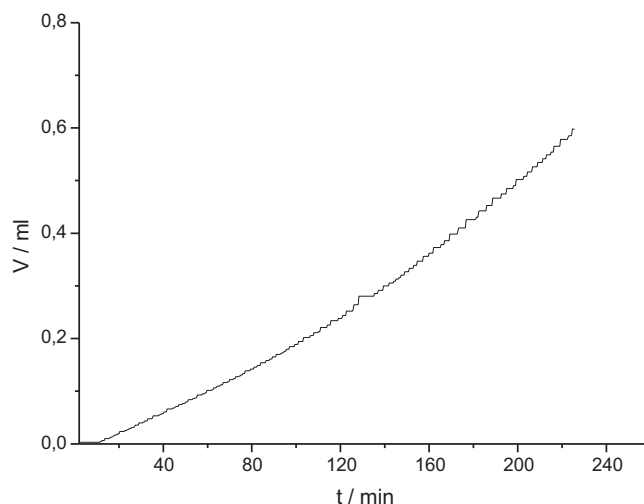
concentrations measured by high performance ionic chromatography. Similar values for the photonic efficiency of DCA when it was used in a first cycle or in a second cycle after OA were found, i.e., 1.03 and 0.99%, respectively. Despite the fact that these type of metal substrates, i.e., TiO$_2$-coated copper substrates, do show a non-negligible photocatalytic activity, its use for environmental applications imply the production of the basic species (the unrevealing of their nature demands an investigation beyond the scope of this work), that may interfere in the system and play a key role for the exact interpretation of the results. The use of stainless steel or titanium as a support material is therefore a better choice than copper. It must be remarked that not only in the case of copper, thorough the clear evidence of the production of these basic species, but in the cases of stainless steel and titanium there also exist a participation of both metal substrates in the photocatalytic reaction. Although their contribution is not as evident as in the case of copper, they are expected to very likely play a role. Electrochemical and photoelectrochemical measurements are currently being carried out to explore such interactions.

From Fig. 2 a rough calculation was made and it was found that the photocatalytic degradation of 1 mole of DCA yields approximately 2 moles of chloride ions. This is in agreement with Eq. (5) and it supports the assumption that at the working pH the concentration of the protoned species D is sufficiently low to be neglected. Such observations were as well reported by Bahnemann and co-authors [39]. It must be noted that at the low working pH (3.0) the TiO$_2$ surface is positively charged and electrostatic adsorption of anions such as chloride can be favored, blocking therefore active sites for the photocatalytic degradation of other species in the system.

The photonic efficiencies for DCA calculated from DCA and chloride concentrations follow a similar trend and reflect a consistent photocatalytic degradation mechanism (Eq. (5)).

As pointed out above, the photonic efficiencies calculated from the data obtained by the pH static technique are higher than those calculated by ionic chromatography. The pH static technique accounts for all species present in the system which are photocatalytically degraded, i.e., adsorbed and dissolved species. Although the difference is not large (Table 2), it can be perfectly assessed experimentally, and should not be neglected or underestimated. These measurements support the fact that narrowing the study of a photocatalytic reaction species to the solely monitoring of dissolved species, even employing highly sensitive techniques such as chromatographic methods, will surely yield to a wrong or
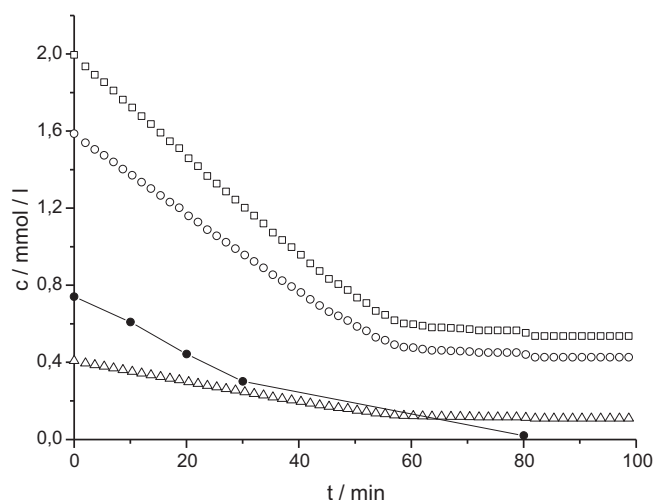
Fig. 4. The photocatalytic degradation of OA by a TiO$_2$ suspension (Evonik P25) with a photocatalyst concentration of 2.5 g/l. The initial OA concentration was 2 mM in 10 mM KNO$_3$ at pH 3.7. Oxalic acid concentration measured by means of a pH-static technique: ($\square$) species (B + C), ($\bigcirc$) species B and ($\triangle$) species C. ($\bullet$) Oxalic acid concentration in the solution measured by HPIC.

incomplete result. For the case of both model compounds employed in this work, OA and DCA, the pH static technique is the method of choice for a thorough study of the systems.

Additionally, based on the results of Table 2, the metal substrates perform more efficiently degrading OA than DCA. OA appears as a better choice for a comparative study of samples with high photocatalytic activity.

Fig. 4 shows the photocatalytic degradation of OA by a TiO$_2$ suspension (Evonik P25) and performed in the same conditions as in the case of the TiO$_2$-coated metal substrates. Table 3 lists the corresponding photonic efficiencies from the pH static and chromatographic techniques.

The photocatalytic degradation of OA at the TiO$_2$ suspended particles shows a linear decrease in the concentration within the initial 50 min. After this period of time the concentration of species B and C reach a plateau and remain constant. It is therefore suggested that an amount of OA cannot be photocatalytically degraded, remaining approximately 0.5 mmol/l in the system (estimated from Fig. 4). The data obtained by means of ionic chromatography show that after a reaction time of 80 min the OA concentration is close to zero (see Fig. 4). Such a complimentary information thus supports that a big portion of the total initial amount of OA is adsorbed at the particles, in agreement with adsorption isotherms measured for the same system (results not shown), and that the photocatalytic reaction very likely mostly involves adsorbed OA species [40].

Comparison of Fig. 4 to Fig. 2 evinces the important role of the adsorbed species since the exposed surface area is considerably higher in the system with suspended particles (25–28 m^2) than in the one where they are immobilized on the metal substrates (1.2–1.9 m^2). While the photonic efficiency of the TiO$_2$ suspension is higher than that of the TiO$_2$-coated substrates, i.e. 7.17% and values around 3%, respectively, the later ones ensure the complete photocatalytic degradation of the model compound (no plateau is

observed neither for OA nor DCA on different TiO$_2$-coated metal substrates, see Fig. 2).

The system P25 and DCA has been thoroughly studied in our laboratory previously [33]. Typically, photonic efficiencies $\zeta = 4\ (\pm 1)\%$ are observed here. Comparison with the values given in Table 2 shows that the Cold Spraying technique employed here leads to the formation of rather active samples ($\zeta = 1.4\%$).

An additional advantage of the TiO$_2$-coated substrates is the considerably lower amounts of TiO$_2$ present in the system (20 g/m^2) as compared to the approx. 500 mg of TiO$_2$ (2.5 g/l) employed in the suspension to photocatalytically degrade the same OA concentration. The immobilization of the TiO$_2$ particles on metal substrates not only represents a convenient way for photocatalytic applications, i.e., easier removal of the photocatalytic material from a liquid phase that has been treated, and highly portability of devices based on such preparations, but an interesting new challenge to unravel fundamental questions about the mechanisms of cooperation between the nanoparticulate photocatalyst and the metallic support which whom interacts intimately. A thorough characterization of such photoelectrochemical properties is the focus of a forthcoming work to shine light on this not yet understood mechanism.

4. Conclusions

The photocatalytic degradation of the two model compounds, i.e. OA and DCA, on TiO$_2$-coated metal substrates revealed that OA can be more efficiently photocatalytically degraded than DCA, and that OA helps for the regeneration of the surface when employed after a first cycle with DCA. The use of copper as a substrate material was found to be photochemically active producing basic species which are released to the aqueous system. Stainless steel and titanium appear to be more suitable substrates materials for photocatalytic environmental applications.

The photonic efficiencies of the immobilized TiO$_2$ particles on the three different metal substrates compared to those found for a highly active TiO$_2$ (Evonik P25) aqueous suspension showed that the Cold Spraying technique allows a very good electronic interaction between the photocatalyst and the metal substrate for an efficient photocatalytic degradation of simple organic acids such as OA and DCA.

Table 3
Photonic efficiencies (in %) calculated using OA concentrations measured by the pH static technique and high performance ionic chromatography for the photocatalytic degradation of OA by a P25 TiO$_2$ suspension.

TiO$_2$ suspension	Photonic efficiency, ζ (%)	
	pH-static	HPIC
Evonik P25	7.17	4.15

References

[1] M. Grätzel, Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983.
[2] N. Serpone, E. Pelizzetti (Eds.), Photocatalysis, Wiley, New York, 1989.
[3] H. Shu, J. Xie, H. Xu, H. Li, Z. Gu, G. Sun, Y. Xu, Journal of Alloys and Compounds 496 (2010) 633–637.
[4] C. Tizaoui, K. Mezughi, R. Bickley, Desalination 273 (2011) 197–204.
[5] N. Banić, B. Abramović, J. Krstić, D. Šojić, D. Lončarević, Z. Cherkezova-Zheleva, V. Guzsvány, Applied Catalysis B: Environmental 107 (2011) 363–371.
[6] E.M. Saggioro, A.S. Oliveira, T. Pavesi, C.G. Maia, L.F.V. Ferreira, J.C. Moreira, Molecules (Basel, Switzerland) 16 (2011) 10370–10386.
[7] C. Fernández, M.P. Callao, M.S. Larrechi, Journal of Hazardous Materials 190 (2011) 986–992.
[8] B. Tryba, A.W. Morawski, M. Inagaki, Applied Catalysis B: Environmental 41 (2003) 427–433.
[9] J. Grzechulska, A.W. Morawski, Applied Catalysis B: Environmental 46 (2003) 415–419.

[10] J.-M. Herrmann, C. Guillard, P. Pichat, Catalysis Today 17 (1993) 7–20.
[11] M. Lindner, D.W. Bahnemann, B. Hirthe, W.-D. Griebler, Journal of Solar Energy Engineering 119 (1997) 120.
[12] M. Schiavello, Photocatalysis and Environment: Trends and Applications, Kluwer, Dordrecht [U.A.], 1988.
[13] D.F.A.-E.H. Ollis, Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam [U.A.], 1993.
[14] C.O.F.C. Turchi, Journal of Catalysis 122 (1990) 178–192.
[15] Z. Wang, W. Cai, X. Hong, X. Zhao, F. Xu, C. Cai, Applied Catalysis B: Environmental 57 (2005) 223–231.
[16] C.M. Teh, A.R. Mohamed, Journal of Alloys and Compounds 509 (2011) 1648–1660.
[17] A. Mills, S. Le Hunte, Journal of Photochemistry and Photobiology A: Chemistry 108 (1997) 1–35.
[18] J.A. Byrne, B.R. Eggins, N.M.D. Brown, B. McKinney, M. Rouse, Applied Catalysis B: Environmental 17 (1998) 25–36.
[19] A.Y. Shan, T.I.M. Ghazi, S.A. Rashid, Applied Catalysis A: General 389 (2010) 1–8.
[20] R.L. Pozzo, J.L. Giombi, M.A. Baltanás, A.E. Cassano, Catalysis Today 62 (2000) 175–187.
[21] A. Alinsafi, F. Evenou, E.M. Abdulkarim, M.N. Pons, O. Zahraa, A. Benhammou, A. Yaacoubi, A. Nejmeddine, Dyes and Pigments 74 (2007) 439–445.
[22] M. Fabiyi, R. Skelton, Journal of Photochemistry and Photobiology A: Chemistry 132 (2000) 121–128.
[23] M.A. Aguado, M.A. Anderson, C.G. Hill, Journal of Molecular Catalysis 89 (1994) 165–178.
[24] D. Beydoun, R. Amal, G.K.-C. Low, S. McEvoy, Journal of Physical Chemistry B 104 (2000) 4387–4396.
[25] J. Blanco, S. Malato, F.J. de las Nieves, Method of sedimentation of colloidal semiconductor particles, 2001, EP-1-101-737-A1.
[26] D.S. Kim, Y.S. Park, Chemical Engineering Journal 116 (2006) 133–137.
[27] S. Parra, S. Elena Stanca, I. Guasaquillo, K. Ravindranathan Thampi, Applied Catalysis B: Environmental 51 (2004) 107–116.
[28] I. Turkevych, Y. Pihosh, M. Goto, A. Kasahara, M. Tosa, S. Kato, K. Takehana, T. Takamasu, G. Kido, N. Koguchi, Thin Solid Films 516 (2008) 2387–2391.
[29] J.-O. Kliemann, H. Gutzmann, F. Gärtner, H. Hübner, C. Borchers, T. Klassen, Journal of Thermal Spray Technology 20 (2010) 292–298.
[30] T. Schmidt, H. Assadi, F. Gärtner, H. Richter, T. Stoltenhoff, H. Kreye, T. Klassen, Journal of Thermal Spray Technology 18 (2009) 794–808.
[31] H. Assadi, F. Gärtner, T. Stoltenhoff, H. Kreye, Acta Materialia 51 (2003) 4379–4394.
[32] D. Bahnemann, D. Bockelmann, R. Goslich, Solar Energy Materials 24 (1991) 564–583.
[33] M. Lindner, D.W. Bahnemann, B. Hirthe, W.-D. Griebler, Journal of Solar Energy Engineering 119 (1997) 120–125.
[34] C.B. Mendive, M.A. Blesa, D. Bahnemann, Water Science and Technology 55 (2007) 139–145.
[35] R.M. Smith, A.E. Martell (Eds.), Critical Stability Constants, Plenum Press, New York, 1979.
[36] O.-O. Prieto-Mahaney, N. Murakami, R. Abe, B. Ohtani, Chemistry Letters 38 (2009) 238–239.
[37] C.B. Mendive, D. Hansmann, T. Bredow, D. Bahnemann, Journal of Physical Chemistry C 115 (2011) 19676–19685.
[38] M.A. Blesa, A.D. Weisz, P.J. Morando, J.A. Salfity, G.E. Magaz, A.E. Regazzoni, Coordination Chemistry Reviews 196 (2000) 31–63.
[39] M. Lindner, J. Theurich, D. Bahnemann, Water Science and Technology 35 (1997) 79–86.
[40] D. Monllor-Satoca, R. Gómez, M. González-Hidalgo, P. Salvador, Catalysis Today 129 (2007) 247–255.