Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 129 (2007) 127–135

www.elsevier.com/locate/cattod

Photocatalytic removal of Pb(II) over TiO_2 and Pt–TiO_2 powders

Leonardo Murruni [a], Gabriela Leyva [b,c], Marta I. Litter [a,c,*]

[a] Unidad de Actividad Química, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, San Martín, 1650 Buenos Aires, Argentina
[b] Unidad de Actividad Física, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, San Martín, 1650 Buenos Aires, Argentina
[c] Universidad de General San Martín, Av. 25 de Mayo y Martín de Irigoyen, San Martín, 1650 Buenos Aires, Argentina

Abstract

Results on Pb(II) photocatalytic removal using TiO_2 and Pt-loaded TiO_2 under different conditions shed light on the mechanisms of previous reports on this complex system. Efficiencies are dependent on the reaction conditions and on the type of photocatalyst. Low efficiency is obtained when only pure TiO_2 is used. The reaction is enhanced: (1) using platinized TiO_2, (2) bubbling ozone, and (3) by addition of 2-propanol. Different mechanisms, via reductive and oxidative pathways, can be proposed for each experimental condition. The nature of the lead deposits depends on the reaction conditions, and supports the proposed mechanisms.

Keywords: Heterogeneous photocatalysis; Lead; Titanium dioxide; Platinized titanium dioxide; Ozonation

1. Introduction

Lead(II) is a toxic metal ion frequently found in wastewater coming from industrial effluents. Maximum contaminant level (MCL, i.e., the highest permissible level of a contaminant in drinking water) has been established by USEPA in 15 $\mu g\ L^{-1}$, while the maximum contaminant level goal (MCLG, i.e., the level of a contaminant in drinking water below which there is not known or expected health risk) has been set by USEPA at zero, indicating the extreme potential toxicity of lead [1]. Lead pollution is mainly anthropogenic and originates in municipal sewages, mining, chemical manufacture and other sources. The element can be found as a component of insecticides, batteries, water pipes, etc. It has been extensively used as a gasoline additive. Although this application has been fortunately forbidden or reduced in most countries, some dangerous wastes could be still present which should be treated. Lead is also present in natural form in groundwater [2].

Generally, removal of lead from water is performed by precipitation as carbonate or hydroxide with or without coagulation. Chelation with ethylendiaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) or other agents is another usual treatment followed by recovery by precipitation, electrolysis or chemical oxidation [3]. All these treatments are expensive, and some other ways of lead elimination from wastewater have to be developed.

Heterogeneous photocatalysis with TiO_2 and UV light (HP) is an emergent technology able to destroy or transform a variety of pollutants by oxidative or reductive mechanisms [4]. The process provides a rapid procedure for removal of toxic organics and even microbiological pollution. Comparatively, photocatalytic transformation of metal ions, including recovery of valuable metals, has been less studied. In this sense, HP can be envisaged as a potential method for eliminating Pb(II) from aqueous solutions, although the process has received scarce attention. In an early paper, lead oxide deposition from solutions containing lead ions was reported to occur onto illuminated areas of TiO_2 and other SC electrodes under anodic polarization [5]. Previous reports indicate that Pb(II) removal is poor over bare TiO_2, but the efficiency can be improved using platinized samples or hole scavengers [6–10]. However, no reports exist in last times on the subject and, as the details and mechanisms involved in the photocatalytic process are not still completely understood, efforts for their elucidation seem valuable.

In this work, we compare the efficiency of the photocatalytic removal of Pb(II) from aqueous solutions under different conditions, proposing the corresponding mechanisms.

---

* Corresponding author. Tel.: +54 11 6772 7016; fax: +54 11 6772 7886.
E-mail address: litter@cnea.gov.ar (M.I. Litter).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.06.058

2. Experimental

2.1. Chemicals

TiO_2 (Degussa P-25) was provided by Degussa AG Germany and used as received. 0.5 wt.% Pt–TiO_2 was prepared in the laboratory according to a published procedure [11]. Lead(II) was added as $Pb(NO_3)_2$ (Merck). 2-Propanol was Merck. Ozone was produced from dry air using an Ozonogen® unit (Ass. Model 015, USA). All other reagents were at least of reagent grade and used without further purification.

Milli-Q water was used for preparation of solutions and suspensions.

2.2. Degradation experiments

Irradiations were performed in a recirculating system (1.5 L min^{-1} flow rate) consisting of an annular photoreactor (435 mm length, 30 mm internal diameter, 115 mL irradiated volume), a peristaltic pump and a thermostatted (298 K) 400 mL Pyrex glass cylindrical reservoir. A black light tubular UV lamp (Philips FL15 BLB, 15 W), emitting in the range $300 < \lambda$ (nm) < 450, was installed inside the annular reactor as the source of illumination. Actinometric measurements were performed by the ferrioxalate method [12]. A photon flow per unit volume (P_0) of 7.3 μEinstein s^{-1} L^{-1} was calculated.

Typically, an aqueous suspension (450 mL) containing the photocatalyst and the Pb(II) salt (0.5 mM), previously adjusted to pH 3 with diluted $HClO_4$, was continuously recirculated from the reservoir. One gram per liter of the catalyst was used in all cases, unless indicated. Prior to irradiation, suspensions were ultrasonicated for 1 min to homogenize the system, and kept in the dark with stirring for 30 min to ensure substrate–surface equilibrium. Pb^{2+} adsorption over TiO_2 particles was evaluated previously to the irradiation by measuring the concentration before and after the stirring in the dark, and the amount of Pb(II) adsorbed was discounted to evaluate only changes under light irradiation. Suspensions were magnetically stirred in the reservoir, and bubbled with O_2, O_3 or N_2, at a constant rate of 2 L min^{-1} throughout the experiment. Saturation of ozone in the aqueous suspension was assured by spectrophotometric measurements [13], while O_2 concentration was determined with a dissolved oxygen probe (HACH Sension156).

No lead elimination was observed in any conditions in the dark or under irradiation in the absence of photocatalyst, even under ozone bubbling or in the presence of 2-propanol.

Samples were periodically withdrawn from the reservoir and analyzed previous filtration through 0.45 μm cellulose acetate filters. All experiments have been performed at least by duplicate and results averaged. The experimental error was never higher than 10%.

2.3. Analytical determinations

Pb(II) concentration changes were measured by colorimetry with 4-(2-pyridylazo)-resorcinol (PAR reagent) at 520 nm [14]. In some cases, parallel determinations were made by total reflection X-Ray fluorescence (TRXRF), according to reference [15], using an X-ray fluorescence spectrometer composed of a Philips generator, a fine focus Mo X-ray tube and a TRXRF module; a CANBERRA Si(Li) detector with a Be window was employed.

Deposits on the photocatalysts after filtration of the suspension at the end of the runs were analyzed by SEM-EDS (Philips 515) and XRD (Philips PW-3710 diffractometer), in order to identify the products formed during the photocatalytic process.

3. Results

3.1. Pb^{2+} adsorption on TiO_2

To evaluate adsorption, Pb^{2+} concentration before and after stirring in the dark was measured. After 30 min and over 1 g L^{-1} TiO_2 or Pt–TiO_2, adsorption was low, ranging 3–6%; over 3 g L^{-1} TiO_2, a higher value (15%) was obtained. No further changes in the adsorbed amount were observed when the stirring was prolonged until 300 min.

In line with our results, Chen and Ray [9] report 12% of adsorption of Pb(II) (0.6 mM) over 2 g L^{-1} of P-25 at natural pH. Lawless et al. [7] did not found adsorption of Pb^{2+} (0.5 mM) over 1 g L^{-1} of P-25 at pH 1.4, but at that pH approach of positive ions to the positive surface of TiO_2 may be inhibited.

The adsorption in the dark was discounted in all cases to fix the value of the initial Pb(II) concentration before illumination.

3.2. Photocatalytic experiments

Fig. 1 shows the results of photocatalytic experiments of Pb(II) (0.5 mM) at pH 3 performed using pure and platinized TiO_2. The fraction of Pb(II) in solution, $[Pb(II)]/[Pb(II)]_0$, is plotted against the irradiation time, $[Pb(II)]_0$ being the initial Pb(II) concentration after discounting the amount adsorbed in the dark. Our results are in agreement with previous works with TiO_2 (rutile, anatase or Degussa P-25) or platinized TiO_2 suspensions

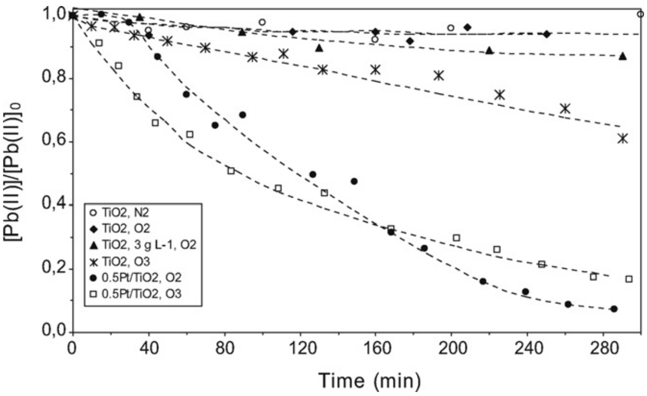


Fig. 1. Time profiles of normalized Pb(II) concentration. Conditions: $[Pb^{2+}]_0 =$ 0.5 mM, pH 3, [catalyst] = 1 g L^{-1} (unless indicated), $[O_3] = 0.5 \times 10^{-2}$ mM, $[O_2] = 0.2$ mM, $P_0 = 7.3$ μEinstein s^{-1} L^{-1}.

under UV illumination [6–9]. With pure TiO_2 (under oxygen or nitrogen), negligible elimination of Pb(II) from the suspension took place. In similar conditions, Lawless et al. [7] reported no removal at pH 1.4, while Chen and Ray [9] obtained only 8.6% working under nitrogen. We obtained a slightly higher removal when a higher mass of photocatalyst was used (3 g L^{-1}), amounting around 15% after 290 min of irradiation. As Pb^{2+} removal proceeded, the suspension pH decreased, and periodical additions of NaOH were necessary to keep the value at 3, confirming the occurrence of a photocatalytic response; however, due to the low conversion, no evidences of deposits (by color changes or by analysis, see later) could be observed on the photocatalyst surface at the end of the experiment. This contrasts with the results of Tanaka et al. [6], who reported PbO formation; however, they used a more powerful irradiation setup, and no removal yield is informed in their paper.

Reaction performed with platinized TiO_2 under nitrogen also gave negligible Pb(II) removal (not shown). Removal was remarkably higher (ca. 93% at 290 min) when the reaction was performed under oxygen; in this case, an induction period of 30 min is observed, which can be attributed to a slow photoadsorption of Pb^{2+} ions on the irradiated platinized semiconductor surface, as mentioned in [7] or to a photoinduced physical change in the metal phase as reported for another system [20]. A dark brownish color was observed as a deposit on the photocatalyst after the run, identified as PbO_2 (see later).

Bubbling of ozone improved Pb(II) removal in both pure and platinized TiO_2 suspensions in comparison with the same reaction under oxygen. As said in Section 2, no lead(II) removal took place with ozone in the absence of the photocatalyst, even under UV irradiation. With pure TiO_2, removal was ca. 35% after 290 min of irradiation. A better removal (83% at 290 min) was attained with Pt–TiO_2 and, although the final value was somewhat lower than in the absence of ozone, no induction period was observed. The inhibition of the photocatalytic removal at the final stages can be attributed to the formation of some oxidized product of Pt on the photocatalyst such as PtO or PtO_2, which could reduce the promoting ability of Pt, which will be discussed in sections 4.2 and 4.3. In both runs, with pure and Pt–TiO_2, $PbO_{1.37}$ and PbO_2 were identified as deposits on the catalyst (see later).

By addition of 2-propanol to the system with pure TiO_2 in the absence of O_2, it was possible to remove lead(II) with a significant yield (Fig. 2). Curves of runs with TiO_2 under nitrogen and with Pt–TiO_2 under oxygen are also included in Fig. 2 for comparison. The results indicate that the alcohol plays a synergetic role in the reaction. The extent of removal depended on the concentration of the alcohol, and a reasonable enhancement of the rate was obtained only with high 2-propanol concentrations (0.5 or 1 M). The best case (1 M) presented a yield similar to that of the run with Pt–TiO_2 under oxygen, which was the best experiment in Fig. 1; however, a shorter induction period appeared in the presence of the alcohol. Oxygen inhibits rather strongly the reaction in the presence of 1 M 2-propanol, but no induction period was observed in this case.

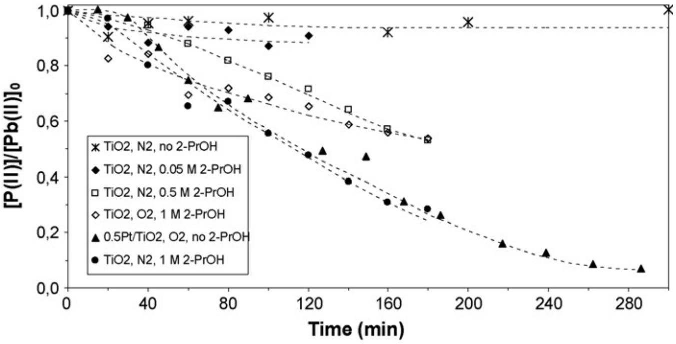


Fig. 2. Time profiles of normalized Pb(II) concentration in the presence of different amounts of 2-propanol during TiO_2 photocatalytic runs. Curve corresponding to Pt–TiO_2 under oxygen is also shown. Conditions: $[Pb^{2+}]_0 = 0.5$ mM, pH 3, [catalyst] = 1 g L^{-1}, $[O_2] = 0.2$ mM, $P_0 = 7.3$ μEinstein s^{-1} L^{-1}.

No lead deposits on the photocatalyst were obtained in any of these experiments. However, yellow-greenish deposits were observed on the lamp surface after runs under N_2, identified as PbO, whereas the deposits were dark gray after the run under O_2, identified as hydrated PbO as the main component, mixed probably with Pb and PbO (see later). To confirm lead removal, determinations by TRXRF were made, which coincided with the amount determined by PAR spectrophotometry.

3.3. Changes in pH in the photocatalytic systems

Periodic NaOH additions were needed to maintain pH at the initial value of 3 in photocatalytic runs with appreciable Pb removal. As we will see later, reactions (16), (27) and (42) can explain at least part of the observed pH decrease, although changes may be due, of course, to other reactions derived from the whole processes.

3.4. Analysis of products

In order to identify some photoproducts, SEM/EDS and XRD analyses were performed. Fig. 3 shows two selected EDS spectra of deposits recovered after photocatalytic runs, showing unequivocally the presence of Pb.

XRD patterns of deposits formed on TiO_2 after different photocatalytic runs are shown in Fig. 4. In the cases of runs performed with pure TiO_2 (either 1 or 3 g L^{-1}) in the presence of O_2, only peaks of anatase and rutile could be observed, same peaks present in the initial Degussa sample (Fig. 4A). Patterns of deposits formed in runs with pure TiO_2 under O_3 and with Pt–TiO_2 under O_2 or O_3 exhibited clear PbO_2 peaks, in agreement with their brownish colors. Other peaks assigned to an unstoichiometric lead oxide, $PbO_{1.37}$, were also observed in the diffractograms corresponding to runs under ozone (Fig. 4B and C).

Experiments with 2-propanol (under nitrogen and oxygen) did not give deposits on the photocatalyst, but colored spots were observed on the lamp surface. Platinum spots were observed similarly by Kraeutler and Bard on the cell wall where the light impinged, during the photocatalytic deposition of Pt on TiO_2 powders [16]. According to XRD patterns, the yellow-greenish deposit formed in the run under N_2 was PbO (Fig. 5A), whereas the dark gray deposit formed under O_2 exhibited peaks

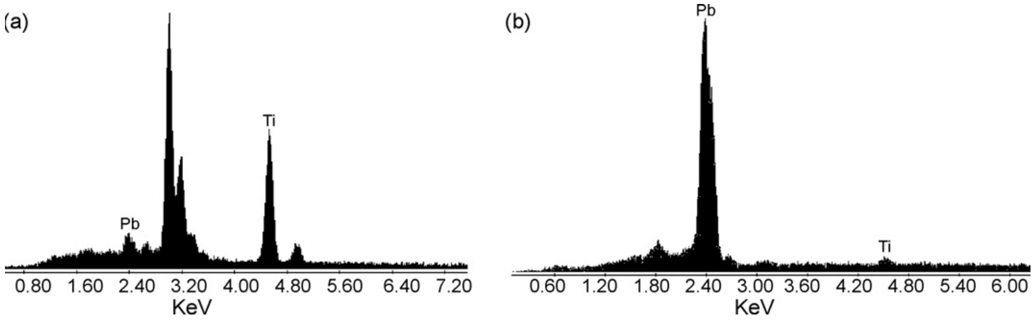


Fig. 3. EDS spectra of photocatalyst particles after selected photocatalytic runs: (a) deposits on Pt/TiO_2 particles after run under oxygen and (b) deposits on the lamp surface after run on TiO_2 in the presence of 2-propanol under oxygen.

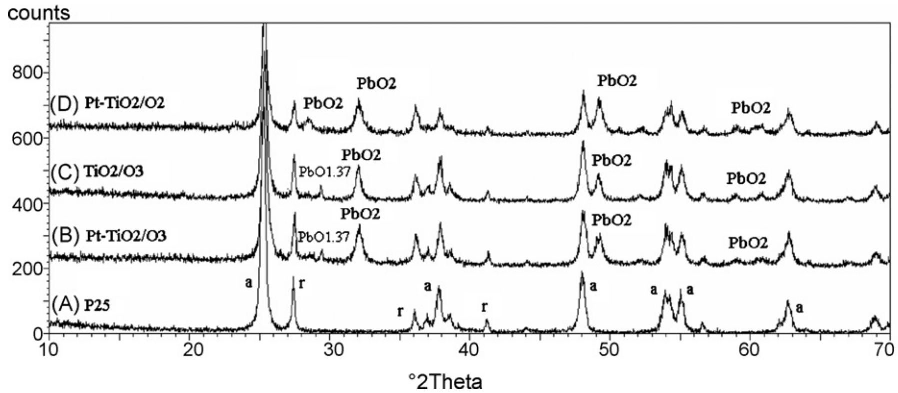


Fig. 4. XRD patterns: (A) pure P-25 before photocatalysis, (B) Pt–TiO_2 after photocatalysis under O_3, (C) TiO_2 after photocatalysis under O_3, and (D) Pt–TiO_2 after photocatalysis under O_2. r: rutile, a: anatase.

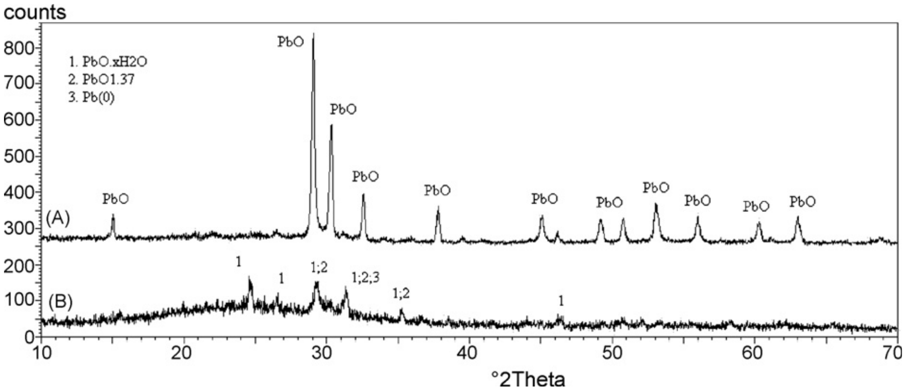


Fig. 5. XRD patterns of solid residues deposited on the lamp surface: (A) photocatalytic run with P-25 under nitrogen in the presence of 1 M 2-propanol and (B) same but under oxygen.

corresponding to hydrated plumbous oxides, $PbO\cdot xH_2O$ (with $x = 1/3$ or 4, a unique assignation being not possible). Metallic Pb and PbO can also be present because their peaks matched those of $PbO\cdot xH_2O$. No PbO_2 peaks were observed in these cases.

$Pb(CO_3)_2$ was not detected in any of the diffractograms.

4. Discussion

4.1. Initial photocatalytic pathways

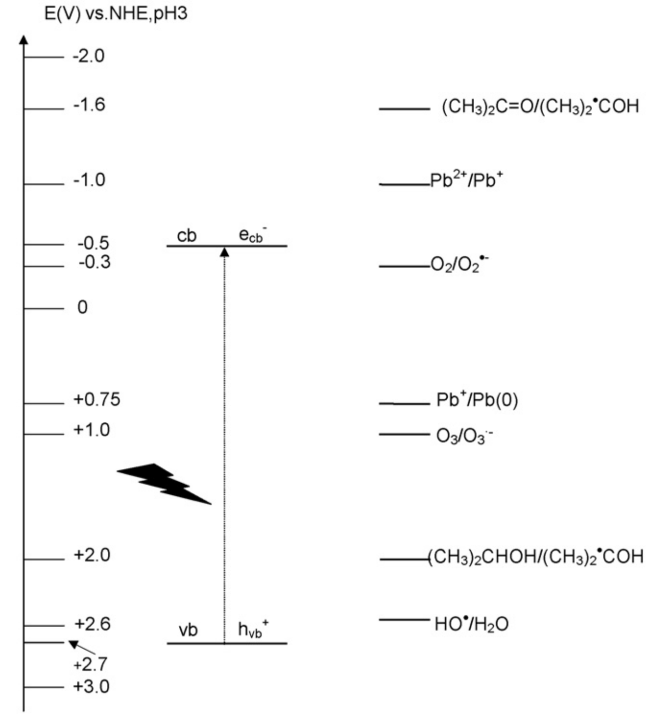
According to the very well established mechanism of heterogeneous photocatalysis, excitation of TiO_2 with light of energy higher than that of the band gap creates electrons in the conduction band (e_{cb}^-), leaving holes in the valence band (h_{vb}^+):

$$TiO_2(\text{or } Pt/TiO_2) + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \quad (1)$$

TiO_2 (Degussa P-25) conduction band electrons at pH 3 are mild reductants[1]; the band edge is located at −0.5 V at pH 3 [17] (see Scheme 1). Electrons are quickly trapped on the TiO_2

---

[1] Although not strictly right (quasi-Fermi levels under irradiation would be more correct), we will use flat band potentials to calculate the ability of electrons and holes to reduce or oxidize species in the photocatalytic system. Redox potentials presented in this work are those reported for aqueous homogeneous solutions vs. NHE at pH 3; species absorbed on TiO_2 may present different values.



Scheme 1. Energy levels of conduction and valence band edges of Degussa P-25 and various redox couples involved in the photocatalytic system studied in this work. Values vs. NHE at pH 3. Redox potentials of couples Pb(IV)/Pb(III) and Pb(III)/Pb(II) are not reported.

surface or in deep traps; trapped electrons have been estimated to lie in the range of 25–50 meV below the conduction band edge of P-25, presenting then a lower reduction ability than that of e_{cb}^- [18]. Electrons are able to reduce acceptors of less negative redox potential present in the interface or near to it.

$$e_{cb}^- + (TiO_2)_n Ti(IV)OH \rightarrow (TiO_2)_n Ti(III)OH \text{ (shallow trap)} \quad (2)$$

$$e_{cb}^- + (TiO_2)_n Ti(IV) \rightarrow (TiO_2)_n Ti(III) \text{(deep trap)} \quad (3)$$

$$e_{tr}^- + A \rightarrow (TiO_2)_n Ti(IV)OH + A^{\bullet -} \quad (4)$$

$(TiO_2)_n$ represents the bulk material.

Valence band holes are strong oxidants (+2.7 V) that forms hydroxyl radicals ($HO^\bullet$) from water or surface hydroxyls. $HO^\bullet$ radicals or holes may attack oxidizable species D.

$$h_{vb}^+ + (TiO_2)_n Ti(IV)OH \text{ or } (H_2O)_{ads} \rightarrow (TiO_2)_n Ti(IV)OH^{\bullet +} (\text{or } HO^\bullet_{surf} + H^+) \quad (5)$$

$$h_{vb}^+ (\text{or } (TiO_2)_n Ti(IV)OH^{\bullet +} \text{ or } HO^\bullet_{surf}) + D \rightarrow D^{\bullet +} \quad (6)$$

In what follows, simply e^-, h^+ and $HO^\bullet$ will be written.

In particular, oxygen adsorbed to TiO_2 can be reduced by e^- generating $O_2^{\bullet -}$; although $E^0(O_2/O_2^{\bullet -}) = -0.3$ V in homogeneous solutions, the redox potential of O_2 adsorbed onto TiO_2 is probably less negative; moreover, at pH 3, superoxide is in equilibrium with $HO_2^\bullet$, whose redox potential ($E^0(O_2/HO_2^\bullet)$) at that pH is −0.23 V. Thus, electron transfer from TiO_2 to O_2 is thermodynamically possible, although it is rather slow [18]. As the following set of equations indicates, the cathodic pathway can generate an additional minor amount of hydroxyl radicals, but it is important to point out that three electrons are needed for the generation of only one $HO^\bullet$ [19]:

$$3O_{2(ads)} + 3e^- (+H^+) \rightarrow 3O_2^{\bullet -} (HO_2^\bullet) \quad (7)$$

$$2O_2^{\bullet -} + 2H_2O \rightarrow 2HO_2^\bullet + 2OH^- \quad (8)$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2 \quad (9)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow HO^- + HO^\bullet + O_2 \quad (10)$$

In anoxic conditions, protons are the strongest electron acceptors, being reduced to hydrogen atoms:

$$H^+ + e^- \rightarrow H^\bullet \quad (11)$$

Reaction (11) is generally better using a cocatalyst as Pt, which decreases the overpotential for proton reduction, generating hydrogen atoms on the Pt surface [20]. Finally, hydrogen atoms give rise to hydrogen:

$$2H^\bullet \rightarrow H_2 \quad (12)$$

In all cases, electrons and holes recombine quickly, leading to a very low photocatalytic efficiency, and several means of avoiding this recombination have been attempted. In particular, for reductive reactions, addition of hole scavengers has been the most used way of inhibiting recombination.

4.2. *Reductive mechanism of lead(II) removal*

Electrons can also reduce metal ions of convenient redox potentials. The possibility of lead(II) reduction was considered more than two decades ago by Kobayashi et al. [21] who, working with TiO_2 single crystals immersed in UV irradiated $Pd(NO_3)_2 + Pb(NO_3)_2$ solutions, observed simultaneous photodeposition of lead dioxide (brown deposits of PbO_2 on illuminated areas) and $Pd(0)/Pd_3Pb$ (grayish white deposits on back dark surfaces). Lawless et al. [7] also considered the possibility of metallic lead formation in their study of Pb(II) photocatalysis. In fact, metallic lead was observed as a black deposit, identified by XRD, when a system composed of two consecutive layers of calcium oxalate on paper with TiO_2 on top was irradiated under UV light in a Pb^{2+} containing solution [22].

In recent papers, we proposed that metal ions submitted to TiO_2 photocatalytic reduction follow a general mechanism through consecutive one-electron reductive steps until the formation of a final stable species, provided the thermodynamic requirements are fulfilled. We proved the validity of this assumption for the cases of Cr(VI) and Hg(II) [23–26]. It is possible to suggest a similar pathway for Pb(II) reduction to metallic lead:

$$Pb^{2+} + e^- \rightarrow Pb^+ \quad (13)$$

$$Pb^+ + e^- \rightarrow Pb(0) \quad (14)$$

The anodic reaction would be the oxidation of water by holes, beginning with reaction (5) and ending in protons and oxygen:

$$H_2O + h^+ \rightarrow \rightarrow \rightarrow 1/2O_2 + 2H^+ \quad (15)$$

The global reaction can be written:

$$2Pb^{2+} + 2H_2O \rightarrow 2Pb(0) + 4H^+ + O_2 \quad (16)$$

According to thermodynamic requirements, direct metal reduction by electrons formed in TiO_2 photocatalytic systems is only possible if the redox potentials of the involved species are less negative than the e^- redox level. Although formation of Pb ions in the unusual monovalent oxidation state has been proposed in flash photolysis and radiolysis experiments [27–31], the reported one-electron redox potential of the couple Pb^{2+}/Pb^+ is very negative (−1.0 V [27]), making unfavorable monoelectronic reduction by TiO_2 conduction band or trapped electrons (see Scheme 1). Taking into account that redox potentials of divalent metal ions to the monovalent state are generally very negative, Thurnauer et al. [32] proposed that reduction to the metallic form can occur only through accumulation of electrons that can be then simultaneously injected. In fact, under laser illumination, they succeeded in reducing Pb^{2+} to Pb(0) by modification of the surface of TiO_2 nanoparticles with adsorbents or ligands able to change the redox properties of the semiconductor [32–34]. Two-electron processes have been also proposed for photocatalytic reduction of halogenated compounds in TiO_2 suspensions [20,35,36], especially at high light intensities, but their occurrence is still somewhat obscure. Multielectronic processes could be rather unlikely in small P-25 particles under our own conditions, considering the low frequency of photon absorption [20,37,38]. Therefore, the high energetic one-electron process leading to Pb^+ can take place only when platinum islands are present on the TiO_2 surface, because Pt can increase the redox potential of electrons to more negative values [39]. In fact, the improved photoelectrochemical performance of semiconductor-metal composite films has been attributed to a shift in the quasi-Fermi level of the composite to more negative potentials [20], around 0.4 V for the case of Pt on TiO_2 [40,41]. It is possible to propose that electrons are trapped by Pt, reducing divalent Pb to the monovalent state.

$$Pt + e^- \rightarrow Pt(e^-) \quad (17)$$

$$Pb^{2+} + Pt(e^-) \rightarrow Pb^+ \quad (18)$$

Once a small amount of Pb^+ is formed, easy reduction ($E^0(Pb^+/Pb(0)) = +0.75$ V) or disproportionation (reaction (20), $k = 1.7 \times 10^8\ M^{-1}\ s^{-1}$) can occur [27]:

$$Pb^+ + Pt(e^-) \rightarrow Pb(0) \quad (19)$$

$$2Pb^+ \rightarrow Pb^{2+} + Pb(0) \quad (20)$$

In the absence of any hole scavenger, the reductive pathway of Pb(II) elimination by an one-electron transfer process would be difficult because, in addition of a rapid recombination of electrons and holes, reaction (15) is sluggish and back-electron transfer processes can be operative, leading again to Pb(II):

$$h^+/HO^\bullet + Pb(0)/Pb(I) \rightarrow Pb(I)/Pb(II) \quad (21)$$

Oxygen will inhibit the reductive process by competition with Pb(II) for electrons, giving superoxide. This will occur especially if the catalyst is platinized, because Pt reduces the overpotential for oxygen reduction (see later); in fact, reaction (15) forms oxygen, being an additional source of competition, even in nitrogenated suspensions. We could anticipate that, if taking place, the reductive mechanism in the absence of a hole scavenger will contribute at a low extent to lead removal. This is reinforced by the fact that reaction with Pt–TiO_2 under nitrogen yields also negligible Pb(II) removal; if the reductive pathway were important, it would be enhanced in the absence of oxygen.

XRD results also confirm the assumption that the reductive mechanism plays a minor role, because Pb(0) was not detected in any case. However, its formation cannot be ruled out because it can be produced at a low extent or without the adequate crystallinity. Metallic lead can also suffer various ways of transformation. Under anaerobic conditions, it can be reoxidized by protons and, under oxygen, it can be quickly returned to Pb^{2+} in the highly oxidizing acid atmosphere [27,29]:

$$Pb + 2H^+ \rightarrow Pb^{2+} + H_2 \quad (22)$$

$$Pb + O_2 + H_3O^+ \rightarrow Pb^{2+} + 3OH^- \quad (23)$$

XRD analyses (Fig. 4) revealed PbO_2 (in a mixture with $PbO_{1.37}$ when O_3 was bubbled), which can be formed by the oxidative mechanisms described in next sections.

4.3. Oxidative mechanism for lead(II) removal

An oxidative pathway through two consecutive one-electron charge transfer steps can be also proposed. Pb(II) can be oxidized by holes or hydroxyl radicals passing through the trivalent to the tetravalent state:

$$h^+/HO^\bullet + Pb(II) \rightarrow Pb(III) \quad (24)$$

$$h^+/HO^\bullet + Pb(III) \rightarrow Pb(IV) \quad (25)$$

The one-electron redox potentials for the Pb(III)/Pb(II) and Pb(IV)/Pb(III) couples are not reported in the literature, but it is not unreasonable to assume that Pb(II) and Pb(III) species can be easily oxidized by holes or $HO^\bullet$ in monoelectronic steps (the redox potential values of the oxidizing species are +2.7 V [17] and +2.6 V [42], respectively).

Formation of Pb(III) has been reported in flash photolysis [28,30,43] and radiolysis studies [44,45]. Pb(III) is unstable, forming Pb(IV) by simple oxidation by O_2 [30] or by disproportionation [45]:

$$2Pb(III) \rightarrow Pb(II) + Pb(IV) \quad (26)$$

The conjugate cathodic and global reactions for lead(II) oxidative removal are (7) and (27), respectively. The distinctive feature of this route is PbO_2 formation as the final product:

$$2Pb^{2+} + 2H_2O + O_2 \rightarrow 2PbO_2 + 4H^+ \quad (27)$$

In an oxidative pathway, the role of oxygen is that of an electron acceptor (Eq. (7)), acting as a promoter of charge separation, thereby inhibiting recombination of electrons and holes; this would be the rate-limiting step. The high overpotential of reaction (7) explains the low yield of Pb(II) removal over pure TiO_2. Platinum decreases this overpotential and increases the yield; this argument has already been given by us to explain the beneficial effect of Pt on TiO_2 samples for EDTA photocatalytic oxidation [11,46]. This assumption would be in agreement with results of Tanaka et al. [6], who found a decrease of the concentration of dissolved oxygen during Pb(II) removal over Pt–TiO_2, and with those of Torres and Cervera-March [8], who found a dependence of the removal rate with oxygen concentration.

In the absence of O_2, removal may be poor because of the possibility of occurrence of back-electron transfer reactions:

$$e^- + Pb(IV)/Pb(III) \rightarrow Pb(III)/Pb(II) \tag{28}$$

Pb^{2+} could be alternatively oxidized by other reactive oxygen species. The oxidative mechanism is supported by the XRD detection of PbO_2 as the only product (Fig. 4D). The oxidative route seems to be the preferred pathway in the absence of electron donors in the photocatalytic system, and the deposition of PbO_2 agrees with findings of previous works in different reaction conditions [6,7,21]. An oxidative pathway was also proposed to explain the inhibition of nitrobenzene TiO_2-photocatalytic degradation when Pb^{2+} was added to the system, attributed to the competition of Pb^{2+} with nitrobenzene for the photogenerated holes [47].

4.4. Effect of ozone addition

In the combined TiO_2/O_3 process, different oxidation reactions can take place [48–50]. Ozone decomposition under UV light ($\lambda > 300$ nm) in the absence of TiO_2 proceeds through a chain reaction: initial ozone photolysis forms H_2O_2 and then $HO^\bullet$:

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \tag{29}$$

$$O_3 + H_2O_2 \rightarrow HO^\bullet + HO_2^\bullet + O_2 \tag{30}$$

$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^\bullet \tag{31}$$

$$O_3 + HO^\bullet \rightarrow O_2 + HO_2^\bullet \leftrightarrow O_2^{\bullet -} + H^+ \tag{32}$$

The hydroperoxyl radical ($HO_2^\bullet$), a weaker oxidant, is also generated, which by reaction with ozone generates more $HO^\bullet$ and H_2O_2:

$$O_3 + HO_2^\bullet \rightarrow 2O_2 + HO^\bullet \tag{33}$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2 \tag{34}$$

In fact, reaction (29) is not very fast ($k = 1.1 \times 10^{-4}$ $M^{-1}\,s^{-1}$) and, consequently, direct UV/ozonation probably does not contribute very much in acid or neutral media (although it is highly enhanced in alkaline media). However, ozone is a powerful electrophilic agent $E^0(O_3/O_3^{\bullet -}) = 1.0$ V [51] that adsorbs strongly on the TiO_2 surface; in the presence of the photocatalyst and illumination, it can generate $HO^\bullet$ radicals through the formation of an ozonide radical ($O_3^{\bullet -}$) in the adsorption layer [49,52]. Reaction (35) depicts the effect of charge separation and inhibition of recombination due to electron acceptance by O_3:

$$O_{3(ads)} + e_{cb}^- \rightarrow O_3^{\bullet -} \tag{35}$$

The generated $O_3^{\bullet -}$ reacts rapidly with H^+ to give $HO_3^\bullet$, and further reactions produce a higher number of $HO^\bullet$ radicals than in the presence of solely oxygen:

$$O_3^{\bullet -} + H^+ \rightarrow HO_3^\bullet \tag{36}$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2 \tag{37}$$

Actually, the mechanism may be more complicated because the process involves the combination of UV, O_3 and TiO_2.

As said before, electron transfer from TiO_2 to O_2 (reaction (7)) is slow, and the photocatalytic process requires three electrons for the generation of only one $HO^\bullet$ (reactions (7)–(10)). By the contrary, the $O_3^{\bullet -}$ reaction pathway requires only one electron, producing $HO^\bullet$ more effectively. Thus, the effect of ozone is to enhance the photocatalytic oxidative route. This argument was used to explain the faster photocatalytic degradative oxidation of organic compounds in UV/TiO_2/O_3 combined systems [53].

When O_3 is added to the photocatalytic system, XRD patterns reveal deposition of PbO_2 and $PbO_{1.37}$ on the photocatalyst (Fig. 4B and C). As $PbO_{1.37}$ was not observed in the absence of ozone, it can be assumed that this unstoichiometric oxide is formed by the action of the ozonide radical or other species formed in the above process:

$$Pb^{2+} \xrightarrow{O_3^{\bullet -}} PbO_{1.37} \tag{38}$$

4.5. Effect of 2-propanol addition

The enhancement of Pb(II) removal caused by 2-propanol in pure TiO_2 suspensions, either under nitrogen or under oxygen, can be explained by the efficiency of this alcohol as hole and $HO^\bullet$ scavenger. In this way, recombination and back-electron transfer processes as those of reaction (21) are greatly reduced.

2-Propanol is oxidized by holes or $HO^\bullet$ to $(CH_3)_2C^\bullet OH$ radicals ($E^0((CH_3)_2{}^\bullet COH/(CH_3)_2CHOH \cong +2.0$ V) [29,54]:

$$(CH_3)_2CHOH + h_{vb}^+(HO^\bullet) \rightarrow (CH_3)_2{}^\bullet COH + H^+(H_2O) \tag{39}$$

The photocatalytic cathodic pathway in anoxic conditions may be reduction of protons, ending in hydrogen production (Eqs. (11) and (12)). This reaction is enhanced on bare TiO_2 by sacrificial species as alcohols [55].

The 1-hydroxyalkyl radicals possess strong reducing ability ($E^0((CH_3)_2C = O/(CH_3)_2{}^\bullet COH = -1.6$ V [39,56]), and may be further oxidized through two alternative ways: (a) injecting electrons to the TiO_2 conduction band (reaction (40)), causing the current-doubling phenomenon; (b) promoting direct Pb^+ formation (reaction (41)).

$$(CH_3)_2C^\bullet OH \rightarrow (CH_3)_2C{=}O + e_{cb}^- + H^+ \tag{40}$$

$$(CH_3)_2C^\bullet OH + Pb^{2+} \rightarrow (CH_3)_2C{=}O + Pb^+ + H^+ \tag{41}$$

Although it is possible to think that TiO_2 particles charged by electrons could suffer a shift of the Fermi level toward more negative potentials, this shift was reported not to take place in the case of oxalate [57], indicating the rather low possibility of direct Pb^{2+} attack by e_{cb}^- via route (a).

In agreement, it has been demonstrated that several metal ions such as Au, Ag and Pt are reduced photocatalytically only in the presence of alcohols as scavengers, suggesting that e_{cb}^- did not take part in the photodeposition [39]. It has been pointed out, however, that direct reduction of metal ions by this type of reducing radicals is rather slow, but that once a metal nuclei is formed, they serve as cathodic site to facilitate further reduction [39].

Oxidative pathways to Pb(III) or Pb(IV) species by holes or $HO^\bullet$ attack, which would be the preferred route in the absence of $h^+/HO^\bullet$ scavengers (Section 4.3), seem to be not operative in the presence of 2-propanol because, in this case, the organic compound would compete with Pb species for the oxidant, leading to a decreased more than to an enhanced Pb(II) removal.

A similar indirect reductive pathway was given to explain why the thermodynamically forbidden Ni(II) photocatalytic reduction takes place in the presence of oxalate; it was proposed that the strong reducing $CO_2^{\bullet-}$ species first formed by e^- attack to oxalate gives rise to Ni(0) formation through a Ni(I) intermediate [4,57]. Breitenkamp et al. [27] suggest a similar mechanism to explain the enhancement of the yield of Pb(0) in the presence of 2-propanol in γ-radiolysis experiments; they even propose the formation of a complex intermediate, $PbC(CH_3)_2{}^+OH$. A same explanation was given by Kumar et al. [58] for the PbO_2 radiolytic reduction to Pb(0) in the presence of methanol at alkaline pH: the reaction was not possible in acidic media, and the effect was attributed to the highly negative redox potential attained by the radical of methanol at alkaline pH. Reaction (41) is rather slow as determined in radiolytic experiments ($k = 3.0 \times 10^4\ M^{-1}\ s^{-1}$) and the species rapidly decays by disproportionation (reaction (20)) [27,29], or easy reduction of Pb^+ by additional $(CH_3)_2C^\bullet OH$.

The global reaction is:

$$Pb^{2+} + (CH_3)_2CHOH \rightarrow Pb(0) + (CH_3)_2C{=}O + 2H^+ \quad (42)$$

The dependence of the rate on the 2-propanol concentration is due to its role in avoiding recombination as hole/$HO^\bullet$ scavenger. Additionally, as long as the reaction proceeds, 2-propanol is consumed by volatilization in the nitrogen stream and by simultaneous photocatalytic degradation. This explains the scarce Pb(II) elimination with the lowest 2-propanol concentration (0.05 M).

As it can be seen in Fig. 2, Pb(II) removal in the presence of 2-propanol is rather efficient even in oxygenated systems, but with a lower efficiency. However, this inhibition by oxygen reinforces the operation of a reductive mechanism because oxygen competes with Pb^{2+} for the 1-hydroxyalkyl radical:

$$(CH_3)_2C^\bullet OH + O_2 \rightarrow (CH_3)_2C{=}O + O_2^{\bullet-} + H^+ \quad (43)$$

The rate constant of reaction (43) in homogeneous solutions is $4.2 \times 10^9\ M^{-1}\ s^{-1}$ [35], indicating the high competence with reaction (41).

In the presence of 2-propanol under nitrogen or oxygen, no deposits of lead derivatives were detected on the TiO_2 surface after the photocatalytic reaction. Instead, spots on the lamp surface could be seen, whose XRD patterns revealed that they were composed solely of green–yellow PbO (Fig. 5A) or of a dark gray mixture of hydrated PbO ($PbO{\cdot}xH_2O$, with $x = 1/3$ or 4, Fig. 5B), metallic Pb and PbO. The oxides could be formed by oxidation of Pb initially formed by the photocatalytic reaction. The absence of PbO_2 reinforces the operation of a reducing mechanism.

2-Propanol seems to be more effective than other hole scavengers. Previous work demonstrates that with ethanol, whose radical has a lower reducing power than that of 2-propanol (−0.9 V at pH 3 [39,56]), extremely high concentrations (7 M) were needed to obtain reasonable photocatalytic Pb(II) elimination [10].

5. Conclusions

Our work sheds light on the mechanistic processes taking place in experiments of elimination of lead(II) from water by photocatalysis in TiO_2 and Pt–TiO_2 suspensions. The differences obtained in the different conditions and the products deposited on the catalyst or on the lamp surface reveal the complexity of the system. Lead(II) can be removed by reductive or oxidative photocatalytic mechanisms, and we propose that in every case, one-electron transfer processes take place. The reductive mechanism is a minor route, because direct reduction by conduction band electrons to Pb(I) is not favorable due to thermodynamic constraints; this has been proved by the scarce removal with pure TiO_2 or platinized TiO_2 in anoxic conditions or with pure TiO_2 in air. The efficiency of the reductive route can be increased using platinized TiO_2, because Pt acts as an electron acceptor, increasing the reduction power of electrons and making possible the one-electron transfer. However, we think that even in this case, the reductive route would be a minor one.

The reductive process is enhanced on pure TiO_2 when a strong hole/$HO^\bullet$ scavenger as 2-propanol is added. 2-Propanol leads to the formation of a strong reducing radical of enough redox potential to reduce directly Pb(II) by an one-electron transfer process. Inhibition by oxygen, which competes with Pb(II) for the 1-hydroxyalkyl radical, reinforces the proposed reductive pathway. In these conditions, we propose that an oxidative mechanism is not operative.

On the other hand, in Pt–TiO_2 suspensions or with ozone, oxidative routes leading to PbO_2 can take place. Platinum enhances the oxidative route lowering the overpotential for oxygen reduction, the rate-limiting step. Addition of ozone makes possible oxidation on pure TiO_2; the reaction does not take place in the absence of the semiconductor. Ozone helps the oxidative route by contributing to the formation of a higher concentration of $HO^\bullet$, enhancing the oxidative photocatalytic mechanism.

According to the complexity of the system, other alternative routes might be proposed. We think that the pathways here presented are the simplest and most probable. However, further research is needed for the complete elucidation.

From all the conditions tested in this work, use of 2-propanol demonstrates to be the most effective and economic method, as it avoids expensive platinization of the catalyst or use of ozone. Other hole scavengers should be tested, together with the optimization of the concentration of the additive. Mixtures of lead(II) and organic scavengers may be present in industrial wastes and this should be exploited to provide economical methods for removal of a so toxic pollutant as lead.

Acknowledgements

This work was performed as part of Agencia Nacional de la Promoción de la Ciencia y la Tecnología ANPCyT PICT03-13-13261 project. MIL is member of CONICET. LM thanks ANPCyT for a doctoral fellowship.

References

[1] http://epa.gov/safewater/mcl.html#8.
[2] M.S. Vohra, A.P. Davis, Wat. Res. 34 (2000) 952.
[3] L. Borrell-Damián, D.F. Ollis, J. Adv. Oxid. Technol. 4 (1999) 125.
[4] M.I. Litter, Appl. Catal. B: Environ. 23 (1999) 89.
[5] T. Inoue, A. Fujishima, K. Honda, Chem. Lett. (1978) 1197.
[6] K. Tanaka, K. Harada, S. Murata, Sol. Energy 36 (1986) 159.
[7] D. Lawless, A. Res, R. Harris, N. Serpone, Chem. Ind. (Milan) 72 (1990) 139.
[8] J. Torres, S. Cervera-March, Chem. Eng. Sci. 47 (1992) 3857.
[9] D. Chen, A.K. Ray, Chem. Eng. Sci. 56 (2001) 1561.
[10] O. Horváth, J. Hegyi, Progr. Colloid Polym. Sci. 117 (2001) 211.
[11] D. Hufschmidt, D. Bahnemann, J.J. Testa, C.A. Emilio, M.I. Litter, J. Photochem. Photobiol. A: Chem. 148 (2002) 225.
[12] C.G. Hatchard, C.A. Parker, Proc. R. Soc. A 235 (1956) 518.
[13] H. Shechter, Water Res. 7 (1973) 729.
[14] F.H. Pollard, P. Hanson, W.J. Geary, Anal. Chim. Acta 20 (1959) 26.
[15] G. Custo, M.I. Litter, D. Rodríguez, C. Vázquez, Spectrochim. Acta, Part B 61 (2006) 1119.
[16] B. Kraeutler, A.J. Bard, J. Am. Chem. Soc. 100 (1978) 4317.
[17] S.T. Martin, H. Herrmann, M.R. Hoffmann, J. Chem. Soc., Faraday Trans. 90 (1994) 3323.
[18] M.R. Hoffmann, S.T. Martin, W. Choi, D. Bahnemann, Chem. Rev. 95 (1995) 69.
[19] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, A. Itaya, Bull. Chem. Soc. Jpn. 58 (1985) 2015.
[20] D.W. Bahnemann, J. Mönig, R. Chapman, J. Phys. Chem. 91 (1987) 3782.
[21] T. Kobayashi, Y. Taniguchi, H. Yoneyama, H. Tamura, J. Phys. Chem. 87 (1983) 768.
[22] K. Tennakone, K.G.U. Wijayantha, J. Photochem. Photobiol. A: Chem. 113 (1998) 89.
[23] J.J. Testa, M.A. Grela, M.I. Litter, Langmuir 17 (2001) 3515.
[24] J.J. Testa, M.A. Grela, M.I. Litter, Environ. Sci. Technol. 38 (2004) 1589.
[25] S.G. Botta, D.J. Rodríguez, A.G. Leyva, M.I. Litter, Catal. Today 76 (2002) 247.
[26] E.M. de la Fournière, A.G. Leyva, E.A. Gautier, M.I. Litter, Chemosphere (2007), in press.
[27] M. Breitenkamp, A. Henglein, J. Lilie, Ber. Bunsen-Ges. Phys. Chem. 80 (1976) 973.
[28] B.G. Ershov, A.I. Aleksandrov, Radiat. Phys. Chem. 10 (1977) 327.
[29] M. Chaychian, M. Al-Sheikhly, J. Silverman, W.L. McLaughlin, Radiat. Phys. Chem. 53 (1998) 145.
[30] O. Horváth, J. Vörös, Inorg. Chem. Comm. 3 (2000) 191.
[31] M. Pospíšil, V. Čuba, V. Múčka, B. Drtinová, Radiat. Phys. Chem. 75 (2006) 403.
[32] M.C. Thurnauer, T. Rajh, D.M. Tiede, Acta Chem. Scand. 51 (1997) 610.
[33] T. Rajh, A.E. Ostafin, O.I. Micic, D.M. Tiede, M.C. Thurnauer, J. Phys. Chem. 100 (1996) 4538.
[34] T. Rajh, D.M. Tiede, M.C. Thurnauer, J. Non-Cryst. Solids 205-207 (1996) 815.
[35] W. Choi, M.R. Hoffmann, Environ. Sci. Technol. 29 (1995) 1646.
[36] S.T. Martin, H. Herrmann, W. Choi, M.R. Hoffmann, J. Chem. Soc. Faraday Trans. 90 (1994) 3315.
[37] M.A. Grela, A.J. Colussi, J. Phys. Chem. 100 (1996) 18214.
[38] B.R. Müller, S. Majoni, R. Memming, D. Meissner, J. Phys. Chem. B 101 (1997) 2501.
[39] R. Baba, R. Konda, A. Fujishima, K. Honda, Chem. Lett. (1986) 1307.
[40] V. Subramanian, E. Wolf, P.V. Kamat, J. Phys. Chem. B 105 (2001) 11439–11446.
[41] V. Subramanian, Ph.D. dissertation, University of Notre Dame, Indiana, USA, April 2004.
[42] W.H. Koppenol, Nature (London) 262 (5567) (1976) 420.
[43] A. Becht, A. Vogler, Inorg. Chem. 32 (1993) 2835.
[44] A.V. Gogolev, B.G. Ershov, J.E. Makarov, A.K. Pikaev, N.L. Sukhov, Radiat. Phys. Chem. 23 (1984) 743.
[45] S. Mosseri, A. Henglein, E. Janata, J. Phys. Chem. 94 (1990) 2122.
[46] U. Siemon, D. Bahnemann, J.J. Testa, D. Rodríguez, M.I. Litter, N. Bruno, J. Photochem. Photobiol. A: Chem. 148 (2002) 247.
[47] C. Maillard-Dupuy, C. Guillard, P. Pichat, New J. Chem. 18 (1994) 941.
[48] B. Kasprzyk-Hordern, M. Ziólek, J. Nawrocki, Appl. Catal. B: Environ. 46 (2003) 639.
[49] K. Tanaka, K. Abe, T. Hisanaga, J. Photochem. Photobiol. A: Chem. 101 (1996) 85.
[50] E. Brillas, J.C. Calpe, P.-L. Cabot, Appl. Catal. B: Environ. 46 (2003) 381.
[51] U.K. Kläning, K. Sehested, J. Holcman, J. Phys. Chem. 89 (1985) 760–763.
[52] M.D. Hernández-Alonso, J.M. Coronado, A.J. Maira, J. Soria, V. Loddo, V. Augugliaro, Appl. Catal. B: Environ. 39 (2002) 257.
[53] M.I. Litter, Introduction to Photochemical Advanced Oxidation Processes for Water Treatment, in: P. Boule, D.W. Bahnemann, P.K.J. Robertson (Eds.), The Handbook of Environmental Chemistry, Environmental Photochemistry Part II Part M, vol. 2, Springer-Verlag, Berlin Heidelberg, 2005, p. 325.
[54] T. Ohno, S. Izumi, K. Fujihara, Y. Masaki, M. Matsumura, J. Phys. Chem. B 104 (2000) 6801.
[55] A.L. Linsebigler, G. Lu, J.T. Yates, Chem. Rev. 95 (1995) 735.
[56] H.A. Schwarz, R.W. Dodson, J. Phys. Chem. 93 (1989) 409.
[57] F. Forouzan, T.C. Richards, A.J. Bard, J. Phys. Chem. 100 (1996) 18123.
[58] A. Kumar, A. Henglein, H. Weller, J. Phys. Chem. 93 (1989) 2262.