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# Photocatalytic elimination of aqueous 2-methyl-4chlorophenoxyacetic acid in the presence of commercial and nitrogen-doped $TiO_2$

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Abstract An attempt to synthesize an active photocatalyst for 2-methyl-4-chlorophenoxyacetic acid removal has been accomplished. Black light (main emission wavelength at 365 nm) photocatalytic experiments with bare and N-doped titania have been carried out, and the results compared to those obtained in the presence of titania Degussa P-25. Doping percentage and calcination temperature influences have been investigated in photocatalytic runs using pure and commercial 2-methyl-4-chlorophenoxvacetic acid. In no case, the results obtained with synthesized titania improved the activity of P-25. Some kinetic tests allowed for the proposal of a pseudoempirical reaction mechanism capable of acceptably simulating the process in the presence of P-25. From the proposed mechanism, the roles played by hydroxyl, peroxyl and organic radicals have been suggested.

**Keywords** Black light · Herbicides · Photocatalysis · Reaction mechanism · Titania

# Introduction

2-Methyl-4-chlorophenoxyacetic acid (MCPA) is an herbicide belonging to the phenoxy or phenoxyacetic acid family. MCPA is used as a post-emergence herbicide for the selective control of broadleaf weeds. Phenoxy herbicides act by simulating the action of natural hormones, producing uncoordinated plant growth. MCPA disrupts both seedling emergence and vegetative vigour, and can be used to control both dicots and monocots. In USA, approximately 4.6 million pounds of MCPA active ingredient is annually applied (EPA 2013).

Surface water contamination by MCPA may directly result from spray drift or indirectly from runoff and/or leaching. Extreme contamination is generated from spills, deliberate dumping of tank residues, or equipment-washing operations. Groundwater contamination may occur through improper handling procedures or through normal use in areas with shallow aquifers. Contamination of water with MCPA is common due to its extensive application, high water solubility, and low affinity for most soils. Thus, MCPA is frequently found in rivers and wastewater treatment plants effluents (Kuster et al. 2008a, b). Phenoxyacid herbicides are only moderately toxic compared to other family herbicides; however, they can affect the nervous system irreversibly after adsorption through the skin. Additionally, their prolonged inhalation can cause dizzines, burning in the chest, and coughing (Crespin et al. 2001).

Development of inexpensive and suitable technologies to remove trace contaminants in waters is in continuous growth. Hence, since solar radiation is an incessant source of energy in Mediterranean countries, water treatments developed under the idea of using solar radiation constitute an interesting research field from the economic point of view (Muñoz et al. 2005). Also, the use of low-cost black light lamps (if compared to UV-C lamps) can be considered as a parallel alternative in those regions where solar radiation is limited by weather conditions.

In this context, illumination of photocatalysts with photons of energy equal to or greater than their band gap leads to the formation of electron/hole pairs with free electrons moving to the empty conduction band ( $e_{CB}$ ), leaving behind an electron vacancy or "hole" in the



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valence band  $(h_{VB}^+)$ . Under appropriate conditions, these charged species can react with adsorbed electron donors or electron acceptors to generate a free radical mechanism.

Having in mind all the previous statements, in this work, an attempt has been conducted to manufacture a TiO<sub>2</sub>based photocatalysts to efficiently remove MCPA from water while showing acceptable settling properties. Due to the influence of the presence of substances other than the parent compound in photocatalytic process, runs have been conducted in the presence of MCPA of high purity degree and also by using marketable MCPA (60 %) commonly used in agriculture. Additionally, some tests have also been conducted to clarify the species involved in the photocatalytic degradation of MCPA. From the previous results, a pseudoempirical mechanism has been proposed and tested. All the experiments have been carried out at the University of Extremadura (Badajoz, Spain) during the second half of 2012 and first half of 2013.

#### Materials and methods

#### Photoreactor and procedure

A 1L capacity perfectly mixed borosilicate glass photoreactor was used in all the experiments (see Fig. 1). The reactor was placed in the middle of a 31 cm external diameter pipe (54 cm height). The internal wall of the pipe was covered by aluminium foil to increase the photons reflection towards the reaction media. Four black light



lamps (41 cm length) were evenly distributed and attached to the pipe. The lamps (LAMP15TBL HQPOWER<sup>TM</sup> manufactured by Velleman<sup>®</sup>) had a nominal power of 15 W mainly emitting within the range 350–400 nm, the maximum being located at 365 nm. Actinometry experiments in the presence of ferrioxalate led to values of 1.77, 3.26, 5.13 and  $6.86 \times 10^{-5}$  Einstein min<sup>-1</sup> L<sup>-1</sup> when 4, 3, 2 and 1 lamps were used. Additionally, when the aluminium foil covering the internal walls of the installation was substituted by a black surface, the intensity (4 lamps switched on) decreased to  $3.60 \times 10^{-5}$  Einstein min<sup>-1</sup> L<sup>-1</sup>.

Previously to the photodegradation experiments, the mixture water + photocatalysts was stirred for 60 min in the dark to achieve the MCPA adsorption equilibrium on the photocatalyst surface. With the exception of the run conducted at low oxygen concentration (nitrogen bubbling), oxygen was continuously bubbled into the water bulk by means of a diffuser placed at the reactor bottom. The gas flow rate was kept constant at 30 L h<sup>-1</sup> in all the experiments. Photocatalysts were maintained in suspension by magnetic stirring. Prior to the analysis, the solid was removed from samples by filtration through Millex-HA filters (Millipore, 0.45 µm).

# Materials

Commercially available MCPA (60 %) and pure MCPA from Aldrich (>99 %) were used in different experiments,

and the rest of chemicals were purchased from Sigma-Aldrich and used as received. Organic solvents were HPLC grade obtained from Panreac. For comparison purposes, a commercial TiO<sub>2</sub> Degussa P25 photocatalyst (70 % anatase and 30 % rutile) was used with an average particle size of 30 nm and BET surface area of 50 m<sup>2</sup> g<sup>-1</sup>. Water purified by a Milli-Q water system (Millipore) was used in the preparation of solutions and suspensions.

Different manufactured photocatalysts abbreviated as  $TiO_2$  (U or E 1:x\_T °C) were used. In this nomenclature, the first letter indicates the nitrogen source (urea -U- or ethylenediamine -E-), 1:x is the ratio of N atoms to Ti atoms in the synthesis process and T °C is the calcination temperature in Celsius. The photocatalysts were synthesized following the methodology described by Senthilnathan and Philip (2010). Basically, the steps were the mixing of titanium isopropoxide in ethyl alcohol and addition of predetermined amounts of the nitrogen source to meet the N:Ti ratio. When required, NH<sub>4</sub>F was added to get a ratio Ti:F 5:1 [nitrogen from NH<sub>4</sub>F is not accounted for in the general formula TiO<sub>2</sub> (U or E 1: $x_T$  °C)]. HCl was added to the previous mixture to get a clear liquid. Precipitation was accomplished after autoclaving at 80 °C for 12 h. The suspension was centrifuged and the solid dried at 100 °C. Calcination was carried out for 4 h.

#### Analysis

MCPA was analysed by high-performance liquid chromatography (Agilent 1100). The column used was a Kromasil 100 5C18. The mobile phase acetonitrile (40)/water (60) was acidified with 0.1 % of phosphoric acid and pumped at a flow rate of 1 mL min<sup>-1</sup>. Detection was conducted at 230 nm. Reaction intermediates were tentatively identified by direct comparison of retention times and pure standards in the HPLC analysis. Some intermediates were also confirmed by LC–MS.

In order to assess the degree of mineralization, total organic carbon (TOC) was determined by a Shimazdu TOC 5000A analyser by directly injecting the aqueous solution.

The pH of the reaction media was measured by means of a Radiometer Copenhagen pH-meter (HPM82).

#### Catalyst characterization

XPS spectrum was obtained by means of a XPS K-alpha Thermo Scientific apparatus with a K $\alpha$  monochromatic source of Al (1,486.68 eV). Peak energies corresponding to Ti2p, N1 s were calibrated based on the response of the C1 s peak at 284.8 eV.

TEM analysis was carried out by a TEM Tecnai G2 20 Twin–FEI Company apparatus (filament LaB6, voltage hasta 200 kV, magnification up to  $1.05 \times 10^6$ ) while



**Fig. 2** Photocatalysis of pure MCPA (0.025 mM) in the presence of different photocatalysts (0.5 g L<sup>-1</sup>). *filled circle* Degussa P-25; *times symbol* TiO<sub>2</sub> (U 0:1.0\_550); *filled square* TiO<sub>2</sub> (U 1:0.4\_550); *filled triangle* TiO<sub>2</sub> (U 1:0.8\_550); *filled inverted triangle* TiO<sub>2</sub> (U 1:1.2\_550); *filled diamond* TiO<sub>2</sub> (U 1:1.6\_550). *Open symbols* stand for TOC conversion

SEM was conducted in a Quanta 3D FEG//FEI Company device.

#### **Results and discussion**

Experiments carried out with pure MCPA: influence of  $TiO_2$  doping

The positive effect of titania doping with different anions has previously been reported (Veréb et al. 2013). This positive effect is normally associated with a decrease in the energy band gap of the photocatalyst; however, some controversy has been raised in relation to this positive influence. Moreover, in some cases, titania doping can lead to an increase in the undesirable recombination rate of holes and electrons. In order to assess the effect of nitrogen doping, some experiments were carried out with pure MCPA in the presence of N-doped titania. For comparison purposes, control runs were also completed by using bare titania and the well-known Degussa P-25. Figure 2 shows the results obtained.

From Fig. 2, it can be observed that in no case, the manufactured photocatalyst did show a better activity than the commercial P-25. Thus, in the presence of 0.5 g L<sup>-1</sup> of P-25, MCPA was degraded in just 15 min compared to 60–90 min when doped titania was used. Similar trends were experienced when analysing the mineralization degree in terms of TOC conversion. The photocatalyst Degussa P-25 was capable of removing approximately the 50 % of the initial TOC in 180 min, and slightly lower values around 40 % of mineralization were obtained when N–TiO<sub>2</sub> was used. The reason for these differences in reactivity may rely, amongst others, in the different particle





Fig. 3 XPS, TEM and SEM of catalyst TiO<sub>2</sub> (U 1:0.4\_550)

size observed for the two types of catalysts. Hence, particle size of synthesized photocatalysts was higher than P-25 grain size suggesting that some external diffusion limitations may occur in the adsorption process previous to the photocatalytic reaction.

The influence of the ratio N:Ti adopted in the synthesis process is also depicted in Fig. 2. In this study, bare titania showed a lower activity than N-doped titania, indicating the beneficial effect of the doping stage. Additionally, the photocatalyst manufactured with the lowest urea dose (lowest N:Ti ratio) showed a better performance in terms of MCPA removal. No appreciable variances between the rest of experiments were experienced. When monitoring TOC conversion, no significant differences were experienced regardless of the N:Ti ratio used. The role played by N in doped titania is controversial. Hence, even if N-doped  $TiO_2$ materials may absorb visible light, some authors claimed that they are frequently inactive in photooxidation reactions under visible light irradiation (Dozzi and Selli 2013). Similarly to the results found in this work, under visible light irradiation, the quantum yield of isopropanol decreased with increasing the dopant N content, a fact that was attributed to the parallel increased formation of oxygen vacancies, acting as recombination centres for photoproduced electron-hole couples (Irie et al. 2003). Fu et al. (2006) claimed that many examples of visible light photodecomposition of organics on N-doped TiO<sub>2</sub> actually proceeded via electron-mediated reactions involving  $O_2$ .<sup>-</sup> and not through holes generated at N dopant sites.

In spite of the fact of a poorer performance of the  $TiO_2$  (U 1:0.4\_550) photocatalyst, its settling properties were significantly better than Degussa P-25. Hence, contrarily to Degussa P-25, almost 90–100 % of the manufactured photocatalyst could be recovered from solution by the action of gravity with no need of centrifugation. However, this behaviour can just be attributed to the higher particle size.

The TiO<sub>2</sub> (U 1:0.4\_550) catalysts were characterized by TEM, SEM and XPS. Figure 3 shows the results obtained. TEM image (up right) depicts the normal anatase bipyramidal shape with a large percentage of {101} facets although some truncated octahedral shapes largely dominated with {101} and {001} facets are also envisaged. SEM analysis shows a broad range of particle sizes. It has to be highlighted the rugosity of particle surfaces (bottom right).

The N 1 s peak showed a bonding energy of 400.2 eV m, typical of interstitial positions in the environment O–Ti–N (Chen and Burda 2004). Formation of N–Ti–N structures is ruled out due to the lower binding





**Fig. 4** Photocatalysis of commercial MCPA (0.025 mM) in the presence of different photocatalysts (0.5 g L<sup>-1</sup>). *filled circle* Degussa P-25; *filled square* TiO<sub>2</sub> (U 1:0.4\_200); *filled triangle* TiO<sub>2</sub> (U 1:0.4\_300); *filled inverted triangle* TiO<sub>2</sub> (U 1:0.4\_400); *filled diamond* TiO<sub>2</sub> (U 1:0.4\_500); *empty circle* TiO<sub>2</sub> (U 1:0.4\_600); *empty square* TiO<sub>2</sub> (U 1:0.4\_700)

energy (397.2 eV) of TiN (Saha and Tomkins 1992). The substitution of oxygen atoms by N atoms involves the decrease in the electronic density around N if compared to TiN crystals. Accordingly, the binding energy of N 1 s in O–Ti–N is higher than in N–Ti–N. Ti 2p peak appears at 458.8 eV, also indicating the presence of structures O–Ti–N (Senthilnathan and Philip 2010). Nitrogen shifts the binding energy of Ti 2p in pure anatase (459.1 eV). The presence of nitrogen atoms provokes the increase in the titanium atoms electronic density. The Shirley method led to a N:Ti ratio of roughly 1 %.

Experiments carried out with commercial MCPA: influence of calcination temperature

Following the results obtained previously, it was decided to assess the influence of the photocatalyst calcination temperature. Hence, the ratio N:Ti of 1:0.4 was thereafter used to photodegrade an aqueous solution of the commercial MCPA.

Calcination temperature plays a crucial role in the activity of synthesized titania. Accordingly, temperature governs the elimination rate of organics used in the synthesis process and the distribution of the rutile and anatase phases. At macroscopic scale, the transformation of anatase to rutile reaches a measurable speed for bulk TiO<sub>2</sub> at T > 600 °C.

Figure 4 shows the results obtained. As seen in this figure, once again none of the photocatalysts manufactured at different calcination temperatures could enhance the results obtained with P-25. Low temperatures (i.e. 200 °C) seem to be insufficient to remove the organic template used in the synthesis process while high temperatures (i.e.



**Fig. 5** Photocatalysis of commercial MCPA (0.025 mM) in the presence of different photocatalysts (0.5 g L<sup>-1</sup>). *filled circle* TiO<sub>2</sub> (U 1:0.2\_300); *filled square* TiO<sub>2</sub> (U 1:0.3\_300); *filled triangle* TiO<sub>2</sub> (U 1:0.4\_300); *filled inverted triangle* TiO<sub>2</sub> (U 1:0.5\_300). *Inset figure: filled circle* TiO<sub>2</sub> (U 1:0.4\_300) + NH<sub>4</sub>F; *filled square* TiO<sub>2</sub> (U 1:0.4\_500) + NH<sub>4</sub>F; *filled triangle* TiO<sub>2</sub> (E 1:0.4\_500) + NH<sub>4</sub>F; *filled triangle* TiO<sub>2</sub> (E 1:0.4\_700); *filled triangle* TiO<sub>2</sub> (E 1:0.4\_300)

700 °C) seem to favour the formation of the less active rutile phase in contraposition to the anatase phase. In any case, according to the literature, the presence of both phases (anatase and rutile) shows a better photocatalytic activity than the use of single anatase (Sun and Xu 2010). Also, the sintering process into larger particles may be favoured at high temperatures decreasing the photocatalyst activity.

Experiments carried out with commercial MCPA: influence of the ratio N:Ti in the synthesis process

Based on previous results, a new attempt to synthetase a photocatalyst with similar activity than P-25 was completed. Accordingly, a series of photocatalytic experiments was carried out with different catalysts calcinated at 300 °C (lowest temperature with maximum activity) and using different N:Ti ratios in the synthesis process. Figure 5 illustrates the results obtained. From this figure, it is inferred that an excess of urea in the synthesis process leads to the deactivation of the photocatalyst. It seems that an excessive doping of the titania crystals increases the sites of electron hole recombination, reducing therefore the beneficial effects of band gap narrowing. It can be hypothesized that there exists an optimum in nitrogen doping, assuming a balance between the positive narrowing of the band gap and the negative effect of increasing electron hole recombination.

Stabilization of the 001 faces of anatase was also tried by adding  $NH_4F$  (Gong and Selloni 2005) in the synthesis process; however, no positive results were



obtained (see Fig. 5 inset). Similarly, based on the work of Senthilnathan and Philip (2010), the nature of the nitrogen source was changed from urea to ethylenediamine leading to disappointing results if compared to the performance of the P-25 photocatalyst (see Fig. 5 inset).

#### Preliminary kinetic tests

In an attempt to assess the species involved in the photocatalysis of MCPA, some experiments with pure MCPA and Degussa P-25 were completed in the presence of different specific scavengers of the common reactive species in photocatalytic processes.

#### Influence of free hydroxyl radicals scavengers

Tert-butyl alcohol (TBA) was chosen as a molecule capable of scavenging free radicals in solution with a low tendency to be absorbed onto titania particles (Klauson et al. 2008). The rate constant of free hydroxyl radicals and TBA is in the proximity of  $6 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>. Accordingly, an experiment in the presence of 0.25 M in TBA was conducted. The results are plotted in Fig. 6. From this figure, it can be inferred that free hydroxyl radicals in solution play an important role; however, even in the case of using an extremely high TBA concentration, MCPA removal was not totally prevented. As the reaction time increased, some MCPA conversion was experienced. Hence, it is hypothesized that MCPA can be degraded by other routes different from free HO· attack, leading to the formation of reactive intermediates (i.e. organic radicals or peroxyradicals, quinones, etc.), which can act as promoters of the chain reaction. In this way, Zertal et al. (2001) report the significant role played by quinonic derivatives in MCPA photodegradation. These authors claim the occurrence of an auto-photocatalytic mechanism according to:



Similarly to TBA, the influence of 2-propanol was also tested in photocatalytic experiments. This alcohol can react with free and adsorbed HO· radicals and also with generated holes. As observed in Fig. 6, the curve of MCPA degradation was altered in the presence of 0.25 M of 2-propanol. In this case, however, the influence was less pronounced than in the case of TBA. The rate constant between 2-propanol and HO radicals is  $2 \times 10^9$  $M^{-1}s^{-1}$ . These results are somehow contradictory. According to the rate constants between hydroxyl radicals and the two alcohols used, 2-propanol should deactivate MCPA degradation to a higher extent than TBA. Hence, 2-propanol could not quench the reaction to the same extent than TBA due to the formation of peroxy radicals (see reactions 3-5), suggesting the participation of the pair  $O_2$ ·-/HO<sub>2</sub>· in MCPA degradation (Bielski et al. 1985).

$C_3H_7OH + HO \rightarrow C_3H_6OH + H_2O \tag{2}$	3`	)
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$$C_3H_6OH \cdot + O_2 \to C_3H_6OOOH \tag{4}$$

$$C_3H_6OOOH \rightarrow C_3H_6O + HO_2 \tag{5}$$

Additionally, the radicals  $C_3H_6OH$  and  $C_3H_6OOOH$  might also attack the MCPA molecule initiating an alternative route of MCPA degradation. In this sense, the reaction between  $C_3H_6OH$  and 2-propanol has been given a value of 53 M<sup>-1</sup>s<sup>-1</sup> (Burchill and Ginns 1970).

$$HO \neq O \\ \downarrow O \\ \downarrow$$





**Fig. 6** Photocatalysis of pure MCPA in the presence of Degussa P-25 (0.5 g L<sup>-1</sup>). Influence of scavengers: *filled circle* No scavenger; *filled square* 0.25 M TBA; *filled triangle* 0.25 M 2-propanol; *filled inverted triangle*  $3 \times 10^{-4}$  M KI; *filled diamond*  $1 \times 10^{-3}$  M Oxalate; *empty circle*  $1 \times 10^{-3}$  M p-benzoquinone; *empty square*  $2.5 \times 10^{-5}$  M Tiron, *empty triangle* N<sub>2</sub> bubbling

#### Influence of electron donors (hole reacting substances)

The effect of  $3 \times 10^{-4}$  M of KI was investigated in the photodegradation of MCPA. As inferred from Fig. 6, potassium iodide significantly reduced the conversion rate of MCPA if compared to the control run. It has to be highlighted that the amount of KI used was sensibly lower than the concentration of TBA, leading to comparable results. Iodide can react with holes; however, it can also be oxidized by free HO· radicals (rate constant  $1.3 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>), so the negative effect experienced cannot be associated with a unique scavenging effect.

Oxalate has been claimed to mainly react with photogenerated holes (Waldner et al. 2007). However, oxalate ions can also scavenge hydroxyl radicals with a lower rate constant ( $7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) than KI. Accordingly, an experiment was carried out in the presence of  $10^{-3}$  M in oxalate. The curve obtained suggests that MCPA is partially photodegraded by holes. The influence experienced is less pronounced than in the case of KI. According to these results, it can be hypothesized that HO· radicals play a more important role than holes in MCPA photocatalytic degradation.

Alternatively, hydroperoxyl radicals generated in oxalate photodegradation (Eqs. 7–8) might also contribute to MCPA conversion.

$$C_2O_4^- + h + \rightarrow CO_2^- + CO_2 \tag{6}$$

$$\mathrm{CO}_2^- + \mathrm{O}_2 \to \mathrm{O}_2^- + \mathrm{CO}_2 \tag{7}$$

The possible reactivity of  $CO_2^{--}$  with MCPA could also be considered. Hence, the reaction between the radical COOHCOO- and oxalate has been given a value of  $2 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$  (Ershov et al. 2008).

# Influence of ${}^{1}O_{2}$ reacting substances

The addition of 0.01 M of NaN<sub>3</sub> to the reaction media completely deactivated the MCPA photodegradation process. NaN<sub>3</sub> is known to steadily react with singlet oxygen (Xu et al. 2008); however, this compound can also react with hydroxyl radicals and holes. The azide ion reacts with HO· with a high rate constant value of  $8 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> (Shinohara et al. 1962). Accordingly, from the results obtained, no fundamental conclusions can be derived.

#### Influence of quinonic substances

To ascertain the occurrence of reactions similar to those presented in Eqs. 1–2, an additional reaction was carried out in the presence of 0.001 M in p-benzoquinone. The results indicate the deactivating nature of this species, capable of reacting with HO· radicals, peroxyl and hydroperoxyl radicals. According to the MCPA profile obtained, it seems that reactions of the type 1–2 do not occur.

# Influence of $HO_2/O_2^-$ scavengers

The potential role played by the pair  $HO_2/O_2^-$  has been postulated in previous sections. To assess the participation of these species, one experiment in the presence of a substance capable of scavenging the  $HO_2/O_2^-$  radicals has been conducted. Hence, when MCPA photocatalysis was carried out in the presence of  $2.5 \times 10^{-5}$  M in 1,3-benzenedisulfonic acid, 4,5-dihydroxy-, disodium salt (Tiron), the process experienced an induction period of roughly 60 min. Thereafter, MCPA disappeared with a rate similar to the control run. Likely, after 60 min, Tiron has been removed from the media and afterwards MCPA is photodegraded. Unfortunately, this substance can also react with HO· radicals so the participation of the pair  $HO_2/O_2^$ cannot be confirmed but only suggested.

# Influence of oxygen concentration

One more experiment was carried out by firstly purging the system with nitrogen and bubbling this gas throughout the experiment. Amazingly, it can be seen that oxygen had no influence at all. This fact was mechanistically confirmed in next section

# The proposed mechanism

From the previous results and identification of some intermediates by direct comparison of retention time and standards, the following considerations can be assumed to tentatively propose a pseudoempirical model mechanism (see Fig. 7).



scheme



The adsorption of contaminants onto the TiO<sub>2</sub> surface is normally a crucial stage in photocatalytic processes; however, in this study, adsorption of MCPA has not been detected to an appreciable extent in dark experiments (or, alternatively, adsorption is under the detection limit used in the analytical procedure). Some authors have reported the partial adsorption of MCPA onto Degussa P25. Hence, Zertal et al. (2004) claim 20 % of MCPA ( $5.6 \times 10^{-4}$  M initial concentration) removal in dark experiments in the presence of 1 g  $L^{-1}$  of P-25. Considering a concentration of adsorption sites in the proximity of  $4 \times 10^{-5}$  M (Feitz et al. 1999) and the initial concentration of MCPA used in this study  $(2.5 \times 10^{-5} \text{ M})$ , by using 0.5 g L<sup>-1</sup> of TiO<sub>2</sub>  $(6.25 \times 10^{-3} \text{ M})$ , only  $2.5 \times 10^{-7} \text{ M}$  in MCPA could have been adsorbed, below the detection limit of the analytical procedure. In any case, an adsorption stage has been added to the model:

$$> \mathrm{Ti}^{\mathrm{IV}} - \mathrm{OH} + \mathrm{MCPA} \xrightarrow{K_{\mathrm{MCPA}}^{\mathrm{K}}} > \mathrm{Ti}^{\mathrm{IV}} - \mathrm{OH} \equiv \mathrm{MCPA}$$
$$\rightarrow \log K^{\mathrm{eq}} > 4$$
(8)

The value of the equilibrium constant is normally high and does not affect the kinetics of the process (Gimeno et al. 2007). This is particularly applicable to molecules mainly degraded in the water bulk (as in this case).

Noncompetitive oxygen adsorption was also considered. It is assumed that reduction sites  $(>TiO_2^{RED})$  are different from oxidation sites  $(>Ti^{IV} - OH)$  (Minero 1995). The adsorption of  $O_2$  (log  $K_{O_2}^{eq} = 4$ ) has been taken from the work of Feitz and Waite (2003). The number of oxygen molecules adsorbed (TiO<sub>2</sub><sup>RED</sup>  $\equiv$  O<sub>2</sub>) at any time is constant, provided that oxygen is continuously fed.

$$> \operatorname{TiO}_{2}^{\operatorname{RED}} + \operatorname{O}_{2} \xrightarrow{K_{O_{2}}^{\operatorname{eq}}} \operatorname{TiO}_{2}^{\operatorname{RED}} \equiv \operatorname{O}_{2}$$
 (9)

The simultaneous presence of radiation and TiO<sub>2</sub> involves a series of well-assumed reactions in photochemistry. For instance, the initiation stage is the formation of holes and electrons:

$$> \mathrm{TiO}_{2} + h\nu({}^{3}\mathrm{E}_{\mathrm{G}}) \xrightarrow{k_{\mathrm{e}_{\mathrm{CB}}^{-}, h_{\mathrm{VB}}^{+}}} e_{\mathrm{CB}}^{-} + h_{\mathrm{VB}}^{+}$$
(10)

Generation of holes and electrons mainly depends on the lamps characteristics and catalyst nature and concentration. Theoretical calculations about the rate of holes/electrons generation and recombination can be conducted by computing the local volumetric rate of photon absorption (LVRPA); however, this is out of the scope of this study and the formation rate of holes and electrons has been considered to be proportional to TiO<sub>2</sub> concentration and optimized according to experimental data:

$$\frac{\mathrm{d}C_{\mathrm{e}_{\mathrm{CB}}^{-}}}{\mathrm{d}t} = \frac{\mathrm{d}C_{\mathrm{h}_{\mathrm{VB}}^{+}}}{\mathrm{d}t} = k_{\mathrm{e}_{\mathrm{CB}}^{-},\mathrm{h}_{\mathrm{VB}}^{+}}C_{\mathrm{TiO}_{2}} \tag{11}$$



The parameter  $k'_{e_{CB}, h_{VB}^+}$  is not a true constant and depends on the radiation intensity and catalyst loading (Gimeno et al. 2007).

Trapping of electrons by adsorbed oxygen has been considered with a rate constant of  $7.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (Bahnemann 1999):

$$\mathbf{e}_{\mathrm{CB}}^{-} + > \mathrm{TiO}_{2}^{\mathrm{RED}} \equiv \mathbf{O}_{2} \xrightarrow{k_{\mathbf{e}_{\mathrm{CB}}^{-},\mathrm{TiO}_{2}\equiv\mathbf{O}}} \mathrm{TiO}_{2} \equiv \mathbf{O}_{2}^{-} \cdot \tag{12}$$

The adsorbed peroxy radical can be desorbed according to the equilibrium with  $\log(K_{\text{TiO}_2 \equiv O_2^{-.}}^{\text{eq}}) = 4$  (Feitz and Waite 2003).

$$> \mathrm{TiO}_2 \equiv \mathrm{O}_2^- \cdot \stackrel{K_{\mathrm{TiO}_2=\mathrm{O}_2^-}^{\mathrm{eq}}}{\longleftrightarrow} > \mathrm{TiO}_2^{\mathrm{RED}} + \mathrm{O}_2^- \cdot \tag{13}$$

 $O_2^{-}$  is in equilibrium with the hydroperoxyl radical log  $(K_{HO_2^{-}}^{eq}) = 4.8$ :

$$\mathbf{H}^{+} + \mathbf{O}_{2}^{-} \cdot \underbrace{\longleftrightarrow}_{\mathbf{HO}_{2}^{-}}^{\mathbf{K}_{\mathbf{HO}_{2}^{-}}} \mathbf{HO}_{2}^{-} \cdot \tag{14}$$

Radical-radical recombination can lead to hydrogen peroxide formation,  $k_{\text{HO}_2^-, \text{O}_2^-} = 9.7 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$  and  $\log(K_{\text{HO}_2}^{\text{eq}}) = 11.7$ :

$$\mathrm{HO}_{2} \cdot + \mathrm{O}_{2}^{-} \cdot \xrightarrow{k_{\mathrm{HO}_{2}}, \mathrm{O}_{2}^{-}} \mathrm{HO}_{2}^{-} + \mathrm{O}_{2}$$
(15)

$$\mathrm{HO}_{2}^{-} + \mathrm{H}^{+} \underset{\longrightarrow}{\overset{K^{\mathrm{eq}}_{\mathrm{H}_{2}\mathrm{O}_{2}}}{\longrightarrow}} \mathrm{H}_{2}\mathrm{O}_{2} \tag{16}$$

Hole–electron recombination  $(k_{\text{recomb}} = 4.6 \times 10^{23} \text{ M}^{-1} \text{s}^{-1})$  can proceed lowering the efficiency of the photocatalytic process:

$$e_{CB}^{-} + h_{VB}^{+} \xrightarrow{\kappa_{recomb}} Heat/light$$
 (17)

Holes can react with adsorbed water or hydroxide groups to generate hydroxyl radicals (Almquist and Biswas 2001).

$$h_{VB}^+ \xrightarrow{k_{HO\circ}} > HO$$
 (18)

In Eq. 18,  $k_{\rm HO^{\circ}}$  is a lumped rate constant involving the invariability of the concentration of adsorbed water/OH<sup>-</sup> molecules. Davis and Huang (1993) used a value of  $2.0 \times 10^{12} \text{ M}^{-1} \text{s}^{-1}$  for this constant. When hydrogen peroxide is generated, trapping of  $e_{\rm CB}^-$  by this species might occur (Gimeno et al. 2007):

$$> \text{TiO}_{2}^{\text{RED}} + \text{H}_{2}\text{O}_{2} \stackrel{K_{\text{H}_{2}\text{O}_{2}}^{\text{eq}}}{\longrightarrow} > \text{TiO}_{2}^{\text{RED}} \equiv \text{H}_{2}\text{O}_{2}$$
(19)

$$\mathrm{TiO}_{2}^{\mathrm{RED}} \equiv \mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{e}_{\mathrm{CB}}^{-} \xrightarrow{k_{\mathrm{TiO}_{2} \equiv \mathrm{H}_{2}\mathrm{O}_{2}, \mathrm{e}_{\mathrm{CB}}^{-}}} > \mathrm{HO} \circ + \mathrm{OH}^{-} \qquad (20)$$

where  $K_{\text{H}_2\text{O}_2}^{\text{eq}}$  has been given a value similar to  $K_{\text{O}_2}^{\text{eq}}$  and  $k_{\text{TiO}_2 \equiv \text{H}_2\text{O}_2, \text{e}_{\text{CB}}^-} = 1.1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$  has been assumed to be similar to the reaction of aqueous electrons and hydrogen peroxide (Buxton et al. 1988). The scavenging effect of H<sub>2</sub>O<sub>2</sub> is represented by:

$$H_2O_2 + HO \stackrel{k_{H_2O_2,HO}}{\longrightarrow} HO_2 \cdot + H_2O$$
(21)

$$\operatorname{TiO}_{2}^{\operatorname{RED}} \equiv \operatorname{H}_{2}\operatorname{O}_{2} + \stackrel{\operatorname{h}_{\operatorname{VB}}}{>} \operatorname{HO} \left\{ \stackrel{k_{\operatorname{Scav}}}{\longrightarrow} \left\{ \begin{array}{c} \operatorname{TiO}_{2}^{\operatorname{RED}} + \operatorname{HO}_{2} \cdot + \operatorname{H}^{\top} \\ \operatorname{TiO}_{2}^{\operatorname{RED}} + \operatorname{HO}_{2} \cdot + \operatorname{H}_{2}\operatorname{O}_{2} \end{array} \right\} \right\}$$

$$(22)$$

The negative effect of TBA (this alcohol does not absorb onto titania) in MCPA degradation suggests that the removal process of the parent compound mainly takes place in solution. Accordingly, once the initiating stages proceed, MCPA degradation can progress through the following steps:

A small fraction of MCPA adsorbed onto  $TiO_2$  can react with adsorbed HO· radicals or/alternatively directly oxidized by holes (Zertal et al. 2004):

$$>Ti^{IV}-OH \equiv MCPA + hole \xrightarrow{k_{oxidation}} CO_2 + CI \xrightarrow{CH_3} O \xrightarrow{CH_2} (23)$$
(R1•)





The main oxidation pathway seems to be the oxidation with free  $HO_{\cdot}$  in solution:

$$MCPA + HO \stackrel{\kappa_{\text{oxidation}}}{\longrightarrow} H_2O + R2$$
(25)

The value of  $k_{\text{oxidation}} = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Zona et al. 2012) has been assumed to be similar for reactions 23–25. Radical species R1· and R2· can trap dissolved oxygen leading to:

$$\mathbf{R1} \cdot + \mathbf{O}_2 \xrightarrow{k_{\mathbf{O}_2 \operatorname{addl}}} \mathbf{R1}\mathbf{O}_2 \tag{26}$$

$$R2 \cdot + O_2 \xrightarrow{k_{O_2 add2}} R2O_2 \tag{27}$$

Rate constants corresponding to oxygen addition to organic radicals are in the order of  $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Neta et al. 1990).

R2· can be reduced to generate 4-chloro-2-methylanisole:



Rate constant in Eq. 28 has been assumed to be of similar order than the reaction between hydrated electrons and anisole,  $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  (Buxton et al. 1988).

The organic peroxyradical  $R1O_2$ · decomposes into 4-chloro-2-methylphenylformate, releasing one hydroperoxyl radical:



First-order decomposition of organic peroxyl radicals varies in a wide range of values from some hundreds (or even lower figures) to values in the interval  $10^5-10^6 \text{ M}^{-1} \text{ s}^{-1}$  (Neta et al. 1990). An intermediate value of  $10^3 \text{ M}^{-1} \text{ s}^{-1}$  has been used in this work.

4-Chloro-2-methylphenylformate can be further oxidized by HO· radicals (or holes) to 4-chloro-2-methylphenol (main intermediate detected in the process). This stage has been given a generic rate constant of  $5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>.

As stated previously, the fact that TBA at high concentrations (0.25 M) cannot completely deactivate the MCPA degradation process suggests the existence of parallel routes of MCPA removal other than the direct attack of hydroxyl radicals. The autocatalytic behaviour observed has been attributed to reactions of organic peroxyradicals and MCPA:





**Fig. 8** Modelling the photocatalysis of pure MCPA in the presence of Degussa P-25 (0.5 g L<sup>-1</sup>). *Top figure: filled circle* MCPA evolution; *filled square* 4-chloro-2-methylphenol generation; *filled triangle* H<sub>2</sub>O<sub>2</sub> formation. *Bottom figure:* Experiment in the presence of: *filled circle* 0.25 M TBA; *filled square*  $3 \times 10^{-4}$  M KI; *filled triangle* 2.5 ×  $10^{-6}$  M O<sub>2</sub>; *filled inverted triangle* 0.25 M 2-propanol; *filled diamond* 0.01 M NaN<sub>3</sub>; *empty circle* 0.001 M Oxalate (*Dashed lines* = model calculations)

$$\begin{array}{l} \text{R1OO} \cdot (\text{or } \text{R2OO} \cdot) + \text{MCPA} \xrightarrow{\kappa_{\text{Peroxyl}}} (\text{R1} \cdot \text{or } \text{R2} \cdot) \\ + \text{R1OOH}(\text{or } \text{R2OOH}) \end{array}$$
(30)

No data are available for  $k_{\text{Peroxyl}}$ . Reactions of substituted alkylperoxyl radicals with several organic substrates were compiled by Neta et al. (1990). A generic value of  $10^5 \text{ M}^{-1} \text{ s}^{-1}$  has been assumed. Also, MCPA is assumed to react with hydroperoxyl radicals to generate hydrogen peroxide  $(k_{\text{Hydroperoxyl}} = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , assumed value). Pichat et al. (1995) state the role played by  $O_2^- \cdot /\text{HO}_2^-$  in photocatalytic processes.

$$HO_{2} + MCPA \xrightarrow{k_{Hydroperoxyl}} R1 \cdot + H_{2}O_{2}$$
(31)

Other routes of  $H_2O_2$  generation include the first-order decomposition of organic peroxides:

$$\begin{array}{l} \text{R1OOH}^{k_{\text{Hydroperodel}}} 4 \text{ - chloro - 2 - methylphenylformate} \\ + \text{H}_2\text{O}_2 \end{array}$$

$$(32)$$

$$R2OOH \xrightarrow{\kappa_{Hydroperode2}} 4 \text{ - chloro - 2 - methylphenol} + H_2O_2$$
(33)

Decomposition rates in Eqs. 32–33 have been optimized to fit experimental and calculated results.

4-Chloro-2-methylphenol can further be oxidized by means of hydroxyl ( $k_{\text{CMP-HO}}$ ) and/or perhydroxyl ( $k_{\text{CMP-HO}}$ ) radicals leading to methylhydroquinone. The later can also be oxidized to 1,2,4-trihydroxybenzene. Finally, 4-chloro-2-methylanisole can also be oxidized to 4-chloro-2-methylphenol by hydroxyl radicals.

The set of differential equation derived from the previous reactions applied to a discontinuous batch reactor was numerically solved by the fourth-order Runge–Kutta method. Figure 7 (top) shows the results obtained after modelling the MCPA photocatalytic degradation in the presence of 0.5 g L<sup>-1</sup> of Degussa P25. As observed, the model does an adequate job when simulating the evolution profile of the parent compound. Additionally, given the complexity of the system and the excessive number of unknown rate constants, the trends observed in H<sub>2</sub>O<sub>2</sub> accumulation and 4-chloro-2-methyl phenol generation are also acceptably calculated. It is obvious that the model is not complete and additional reactions leading to ring opening and low molecular weight compounds formation should be considered.

In spite of the system complexity, the proposed mechanism is also capable of simulating the effect of different scavengers. As observed in Fig. 8 (bottom), the model adequately predicts the MCPA profiles after addition of 0.25 M of TBA or  $3 \times 10^{-4}$  M of I<sup>-</sup> by just considering their reactions with free hydroxyl radicals (rate constants  $6 \times 10^8$  and  $1.3 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>, respectively).

When the addition of 2-propanol was modelled, reactions 3–5 led to a lineal MCPA degradation, different from the curved profile experimentally observed. However, if MCPA removal by organic radicals generated after HOattack to 2-propanol is considered, the MCPA conversion acquires the observed curvature. A value of 20  $M^{-1}s^{-1}$ given to this constant allows for obtaining the theoretical profile observed in Fig. 8 (bottom). It should be noticed the similar magnitude of the adopted value and the rate constant corresponding to the reaction between C<sub>3</sub>H<sub>6</sub>OH· and 2-propanol.

The total deactivation of the process in the presence of 0.01 M in sodium azide was theoretically obtained by just considering the reaction of this species with hydroxyl radicals.

The effect of oxalate was also adequately simulated by considering its degradation by direct attack of holes and further generation of hydroperoxyl radicals. Similar results could be obtained by taking into account the direct attack of  $CO_2^{--}$  to MCPA.

Finally, theoretical calculations conducted at low oxygen concentration  $(2.5 \times 10^{-6} \text{ M})$  could also acceptably





Fig. 9 Sensitivity analysis of some of the rate constants in the proposed reaction mechanism

simulate the results obtained in the experiment carried out by bubbling nitrogen (the reactor was open to the atmosphere, so oxygen concentration was not considered zero).

As stated previously, the mechanism here presented is not complete and probably lacks of some reactions. Accordingly, the optimized rate constants used should be taken with caution. Nevertheless, the reaction mechanism reveals the importance of HO· in MCPA photodegradation and also the presumably important role played by organic radicals and hydroperoxyl radicals. A sensitivity analysis of different parameters is shown in Fig. 9.

From Fig. 9, it has to be highlighted the obvious influence of the holes/electrons generation rate. Oxygen addition to radicals R1· and R2· affects MCPA conversion profiles only for rate constant values well below the normal ones  $(10^8-10^9 \text{ M}^{-1}\text{s}^{-1})$ . In a similar way, the rate constant in Eq. 29 only influences MCPA degradation when low values are used. The effect of k<sub>Hydroperoxyl</sub> confirms the hypothesis previously suggested of the role played by the pair HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>.

### Conclusion

From the experiments completed in this investigation, the following conclusions can be withdrawn:

- MCPA can be photocatalytically degraded in the presence of powdered titania.
- Doping of bare titania with nitrogen enhances the MCPA removal rate. An optimum in doping percentage can be foreseen.
- Calcination temperature at the time of catalyst preparation is a crucial variable.
- In spite of the high number of attempts, in no case the results obtained improve those obtained by using the commercial P-25.
- A mechanistic approach to the process reveals the importance of free radicals in MCPA photocatalytic oxidation.
- Other minor degradation routes include the role played by organic and hydroperoxyl radicals.



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