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Environmental preservation of emerging parabens contamination: effect of Ag and Pt loading over the catalytic efficiency of TiO$_2$ during photocatalytic ozonation

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Abstract

The aim of this study was to verify the effect of Ag and Pt with different loadings (0.1 and 0.5wt.%) as dopants on TiO$_2$for the degradation of a mixture of five parabens through photocatalytic ozonation. The effect of the treatment on the mixture toxicity over different species was also analyzed. The best catalyst in terms of parabens degradation was 0.5%Ag-TiO$_2$.The decrease of metal loading on TiO$_2$ decreased the parabens degradation efficiency as well as COD and TOC removal. Also this decrease has a slight effect over the treated solution toxicity over the different species tested.

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1. Introduction

The so called emerging contaminants encompass compounds usually used on pharmaceuticals and personal care

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products and are progressively appearing on natural aquatic resources[1]. Among these pollutants are the parabens which are widely used as preservatives and antimicrobial[2]. However, some studies point out that these compounds present carcinogenic potential[3]. Thus, their presence in rivers and wastewater treatment plants may constitute a problem for human health[2]. Bearing in mind the low efficiency of the traditional municipal wastewater treatment processes on the degradation of these compounds, scientific efforts have been made to find a suitable solution to degrade them[4,5].

Ozone is a powerful oxidant, with a high potential oxidation (E^o = 2.07 V), that can oxidize a large amount of organic compounds [6]. The presence of heterogeneous catalysts on ozonation can enhance the production of hydroxyl radicals that due to their higher potential of oxidation (E^o = 2.80 V) can react with a wider range of organic and inorganic substances. Thus, hydroxyl radicals may improve the mineralization degree achieved by ozonation. In fact, molecular ozone reactions can be a source of refractory by-products no further reactive with O_3 leading to low mineralization levels[7]. The choice of a suitable catalyst can be an important factor on catalytic ozonation performance. This choice can also be influenced by the use of UV-radiation for aiding ozone action. Titanium dioxide is the most commonly used photocatalyst[8]. The band gap is 3.2 eV for anatase TiO_2 (λ < 387 nm).Therefore, for exciting an electron from the valence band to the conduction band, UV-light is required [9]. The band gap of TiO_2 can be reduced using metal (such as Pt, Ag and Pd) or non-metal (such as N and B) dopants, which allows the production TiO_2 photogenerated electrons and holes using lower energy, such solar irradiation [9-11]. The presence of ozone on photocatalytic experiments with this kind of catalysts (semiconductors) can enhance the photogeneration of electron-hole pair because ozone adsorbed on TiO_2 surface works as electron acceptor producing ozonides radicals ($O_3{}^{\bullet-}$). Moreover, the presence of noble metals in the surface of titanium dioxide may work as scavenger of photogenerated electrons. These two situations can reduce the recombination phenomenon of electron-hole pairs[12, 13]. On the other hand, the water adsorbed on the catalyst surface can react with the photogenerated holes to produce hydroxyl radicals ($^{\bullet}OH$). The ozonide radical at acidic conditions can also enhance the production of hydroxyl radicals [14].

Rey et al. studied the degradation of ibuprofen using photocatalytic ozonation under visible light irradiation with the catalyst WO_3 and verified complete removal in less than 20 min [15]. The effect of Pt loading on TiO_2 surface was studied for the oxidation of formaldehyde and the 0.6wt.% loading showed the highest dispersion of the dopant over the surface of the catalyst [16]. Mohamed and Khairou verified that an increase of Ag loading onto TiO_2 surface can block the UV-light thus affecting the photocatalytic activity and for Ag loading of 1.6wt% the photogenerated hole trapping effect was negligible. Moreover, an increase of Ag loading can increase the photogenerated electron scavenging [17].

Bearing this in mind, the aim of the present study was to verify the effect of noble metal loading on TiO_2 surface over the efficiency of photocatalytic ozonation of a mixture of five parabens, methylparaben (MP), ethylparaben (EP), propylparaben (PP), butylparaben (BuP) and benzylparaben (BeP).For this purpose the noble metals Ag, Pt, at loadings of 0.1 and 0.5 wt.%, doped onto TiO_2 were tested using ozone and UV-A irradiation. Furthermore, the parabens are toxic compounds, so another goal of this work is to verify the ecological impact of raw and treated solutions. For this, the toxicity assessment to three different species *Vibrio fischeri, Corbicula fluminea* and *Lepidium sativum* was performed.

Nomenclature

COD	Chemical Oxygen Demand
GI	Germination index
HPLC	High Performance Liquid Chromatography
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis
TOC	Total Organic Carbon
TOD	Transferred Ozone Dose
XRD	X-Ray diffraction

2. Material and methods

2.1. Chemical and Catalyst preparation

Methylparaben (MP), ethylparaben(EP), propylparaben (PP), benzylparaben (BeP), were obtained from Sigma-Aldrich. Butylparaben (BuP) was purchased from Fluka. Titanium (IV) isopropoxide was purchased from Aldrich Chem and was used as TiO_2 precursor. The photo-deposition method using UV-reduction of Pt^{4+}, Ag^+ ions in the titanium dioxide suspension was applied to prepare $Pt-TiO_2$ and $Ag-TiO_2$. A solution of isopropanol containing H_2PtCl_6 (0.1 and 0.5 wt.%) and a solution of ethanol containing $AgNO_3$ (0.1 and 0.5 wt.%) was degassed with nitrogen and irradiated by UV-Vis light (1000 W Xe lamp) for 6 hand for 100 min, respectively. Afterwards the solids were separated by centrifugation and dried at 65 - 120 ºC for 12 h.

2.2. Experimental procedure

The photocatalytic ozonation experiments were carried out in a 2L glass photoreactor equipped with 3 lamps (Philips TL 6W BLB) for UV-A irradiation (main emission 365 nm), at controlled temperature (25±1 ºC) by a thermostatic bath. The photon flux was obtained using ferrioxalate actinometer [18] and was calculated at 5.75×10^{-7} einstein/Ls. To test the adsorption capacity of catalyst it was placed in the reactor with the solution of parabens 5 min before ozone being fed and turning on the light irradiation. The stirring speed was previously optimized at 700 rpm to ensure chemical regime [6]. Along the reaction, samples were withdrawn and immediately centrifuged at 3500 rpm (Nahita 2655 Centrifuge) to remove the catalyst. Ozone was produced (802N, BMT) from pure oxygen stream (99.9%) and the inlet ($[O_3]^{in}$) and outlet ($[O_3]^{out}$) ozone concentration were measured by ozone analysers (BMT 963 and 964 vent, BMT), for determination of TOD according to eq. 1.

$$TOD = \int_0^t \frac{Q_{Gas}}{V_{Liquid}} \times ([O_3]^{in} - [O_3]^{out}) \times dt \qquad (1)$$

Where Q_{Gas} represents the gas flow rate (0.2 L/min), V_{Liquid} is the volume of the effluent used (2 L). The TOD was expressed in mg O_3/L. The remaining ozone leaving the reactor was trapped by a 2% of KI (Panreac) solution.

2.3. Analytical methods

The analysis of structure, elemental characterization and metal dispersion on catalyst surface were performed with SEM-EDS a TESCAN VEGA 3 SBH - Easy Probe equipped with a Bruker QUANTAX system that includes the Bruker Nano XFlash® detector. The EDS analysis was performed for randomly points selected from SEM analysis, and was carried out using an accelerating potential of 20 kV. Energy-Channel calibration was used with a copper standard (Kα 8.0463 keV).The crystalline structure of the catalysts powders was evaluated by XRD analysis, through a diffractometer (Bruker D8 Advance). The diffractometer works with Cu Kα radiation (2.2kW ceramic tube). The determination of each paraben concentration was made by HPLC (UFLC, Shimadzu). The detection occurred at 255 nm, with a C18 (SiliaChrom) column at 40 ºC. The injection volume of samples was 20 μL and the mobile phase (0.5 mL/min) consisted in a mixture of 50:50 methanol: acidic water (0.1% orthophosphoric acid). The TOC for initial and final treatment was determined using a TOC analyser (TOC-V CPN model, Shimadzu, Japan) coupled to an autosampler (model V-ASI, Shimadzu, Japan). COD was measured according to the standard method 5220D [19] using a calibration curve obtained for potassium hydrogen phthalate (Panreac). The samples absorbance was measured at 445 nm (WTW photolab S6 photometer) after 2h of digestion at 150 ºC (ECO25 – Velp Scientifica).

2.4. Toxicity assessment

The luminescence inhibition for *V. fischeri* bacteria was determined for initial mixture of parabens and treated solutions using a LUMIStox 300 apparatus from Dr. Lange. The bacteria luminescence after 15 min of incubation with blank (NaCl solution of 2%) was compared with the one obtained when *V. fischeri* were in contact with the samples. *C. fluminea* individuals with shell length in the range 20-30 mm were collected from a canal in Mira, Portugal (N40°25'06.90''/W8°44'13.18''). Mortality tests were performed in two replicates for treated samples with

a blank control (dechlorinated water). The effluents were dosed after 24h acclimation period in a ratio of effluent volume to clams number of 1:20. The test occurred at constant temperature (20 ± 2 °C), under a cycle of 16 h[Light]: 8h[Dark] and with continuous aeration. The mortality of clams was assessed every 24h based on resistance to valve opening when forced with a blunt dissection needle or siphoning activity evidence[20]. The number of *L. sativum* germinated seeds and the radicle growth were measured to calculate the GI[21]. Seeds were placed on petri dishes in contact with sample volume of 5 mL. The number of seeds germinated and radicle growth with treated samples and blank were recorded, and the GI was calculated for each one. The Trautmann and Krasny criteria based on GI was used for sample phytotoxic classification [21].

3. Results and discussion

3.1. Catalysts characterization

The XRD analysis reveals that the predominance phase is anatase (results not shown), and the presence of the doping metals on TiO_2 do not change the XRD pattern. The explanation for the absence of diffractive peak of noble metals is due to the low doping dose. The EDS analysis detected the presence of Ti and O for the both catalysts, whereas the noble metal does not appear, this can be explained by the low amount of dopant used and its good dispersion. The SEM analysis (Fig.1.b) show that the catalyst reveal a certain roughness on their surface, the morphology is not well-clean and the shape is not well-designed. No significant differences are found between the catalysts prepared with different metal loadings in what regards SEM images.
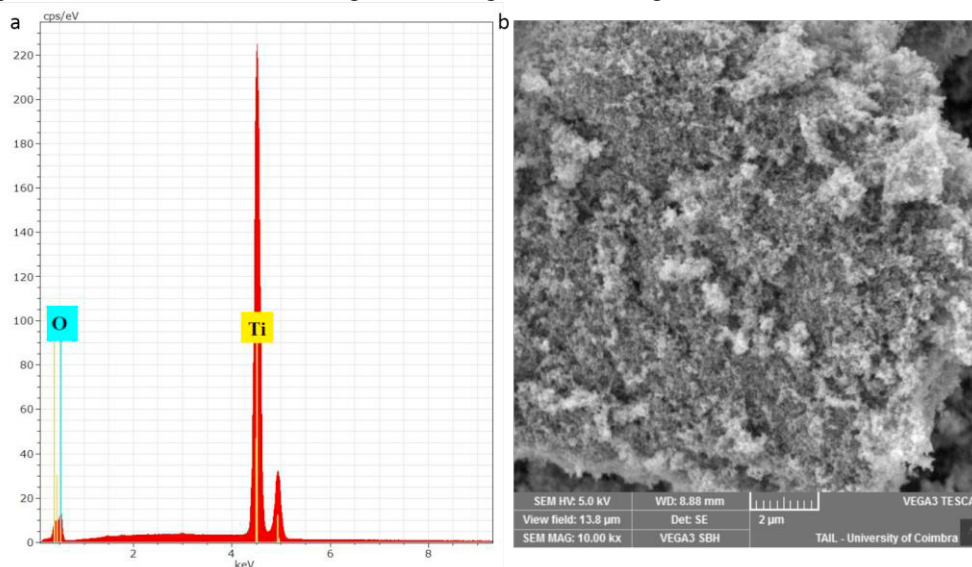

Fig. 1. EDS-analysis (a) and SEM Analysis (b) for 0.1% Ag-TiO2.

3.2. Effect of metal loading on parabens degradation

Fig. 2 shows the degradation of parabens with the different catalysts tested as function of TOD. As it can be seen the parabens with higher molecular weight (BuP and BeP) were the first ones to be totally degraded using a low amount of TOD, below 35 mg/L for BeP. This may be explained by ozone reactive preference for high electronic density groups such as benzenic rings. The high molecular weight of these compounds leads to a larger number of sites available for reaction. On the other hand, for the parabens with lower molecular weight the degradation rate was slower, so higher amount of ozone was necessary for total removal. The results clearly show that for photocatalytic ozonation the worst catalyst was 0.1% Pt-TiO_2. For example for total MP degradation with this catalyst it was necessary a TOD of 63 mg/L while for the best catalyst (0.5% Ag-TiO_2) it was just needed a TOD of 39 mg/L. The decrease on metal loading in Pt-TiO_2 leads to lower efficiency towards parabens removal. This means

that for achieving total parabens removal with lower amount of Pt onto TiO_2 surface was necessary a higher TOD. For Ag based catalysts, the effect of metal loading was not so sharp regarding parabens degradation. The increase of Ag loading from 0.1wt.% to 0.5wt.% allows reducing about 10 mg/L of TOD needed for total parabens degradation. Ag presents a lower electronegativity compared with Pt (1.93 to 2.28 according Pauling scale). On this way, lower amounts of electrons can be scavenged by Ag, so even using high Ag loads, the photogenerated electrons are still available to reduce ozone to produce ozonide and hydroxyl radicals. This larger amount of hydroxyl radicals may be helpful for parabens degradation, reducing the amount of TOD needed.
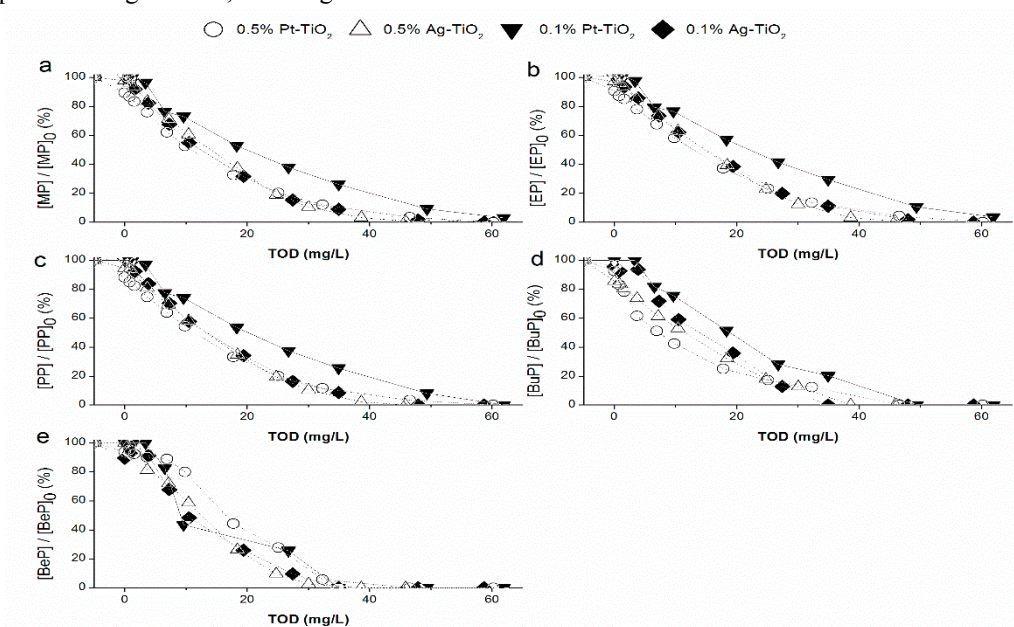

Fig. 2. Normalized concentration of individual parabens (a) – MP; (b) – EP; (c) – PP; (d) – BuP and (e) – BeP during photocatalytic ozonation of the mixture as a function of TOD.

3.3. COD and TOC removal

Table 1 summarizes COD and TOC removal after 120min of photocatalytic ozonation for different catalysts. All catalysts lead to similar COD and TOC removals but when 0.5% Ag-TiO_2 was applied, TOD used was lower which can be economically more interesting.

Table 1. Summary results of TOC and COD removal in function of TOD

Catalyst	TOD (mg/L)	$TOC_{removal}$ (%)	$COD_{removal}$ (%)
0.5% Pt-TiO_2	60	37	50
0.5% Ag-TiO_2	46	37	44
0.1% Pt-TiO_2	63	43	48
0.1% Ag-TiO_2	59	37	45

3.4. Toxicity assessment

The luminescence inhibition of *V. fischeri* and the mortality of *C. fluminea* strongly decrease when the individuals are in contact with the treated solutions (120 min of photocatalytic ozonation) when compared when in contact with the initial mixture of parabens. Also the GI increases, which means that initial toxicity was reduced. Moreover, it seems that the decrease of Ag loading in the catalyst leads to a slightly more toxic treated mixture (Table 2). No significant differences regarding the toxic effect are found between 0.1%Pt-TiO_2 and 0.5%Pt-TiO_2.

The best result in terms of lower toxicity on organisms tested was 0.5% Ag-TiO$_2$ (Table 2).

Table 2. Summary results of toxicity tests with different species tested

Catalyst	*V. fischeri* light inhibition	Mortality *C. fluminea* (%)	GI (%)
Initial mixture Parabens	96 ± 0	100	42 ± 11
0.5% Pt-TiO$_2$	61± 1.2	0	107 ± 11
0.5% Ag-TiO$_2$	43 ± 1.5	0	112 ± 1
0.1% Pt-TiO$_2$	58 ± 4.6	7 ± 7	112 ± 19
0.1% Ag-TiO$_2$	69 ± 8.5	21 ± 7	99 ± 0

4. Conclusions

All conditions tested in this work proven efficient on total parabens degradation, COD and TOC removal, as well as toxicity reduction compared with the initial mixture. The decrease on metal loading doped onto TiO$_2$ reveals also a decrease on parabens degradation efficiency. Besides the 0.5%Ag-TiO$_2$ presents the best result for the photocatalytic ozonation of the parabens mixture, 0.1%Ag-TiO$_2$ also reveals a good performance.

Acknowledgements

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