Photocatalytic activity of N, S co-doped and N-doped commercial anatase TiO₂ powders towards phenol oxidation and *E. coli* inactivation under simulated solar light irradiation

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Abstract

Nitrogen and sulfur co-doped and N-doped TiO₂ anatase TKP 102 (Tayca) were prepared by manual grinding with thiourea and urea, respectively, and annealing at 400 °C. Both materials showed visible-light absorption as measured by Diffuse Reflectance Spectroscopy (DRS). Interstitial N-doping, anionic and cationic S-doping was found when the TiO₂ was doped with thiourea while TiO₂ doped with urea showed only the presence of interstitial N-doping as measured by X-ray Photo-electron Spectroscopy (XPS). The N content on the surface of N-doped TKP 102 photocatalyst was 2.85 at.% and higher than the N content in the N, S co-doped TiO₂ photocatalyst (0.6 at.%).

The photocatalytic activity of the doped catalysts was tested using phenol and *Escherichia coli* as chemical and biological targets, respectively, using N, S co-doped, N-doped TiO₂, undoped Degussa P-25 and undoped TKP 102 powders under simulated solar light. It was found that undoped Degussa P-25 was the photocatalyst with the highest photocatalytic activity towards phenol oxidation and *E. coli* inactivation. N, S co-doped powders showed almost the same photocatalytic activity as undoped TKP 102 while N-doped TKP 102 was the less active photocatalyst probably due the N impurities on the TiO₂ acting as recombination centers.
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Keywords: Heterogeneous photocatalysis; Helio-photocatalysis; Nitrogen doped TiO₂; Sulfur doped TiO₂

1. Introduction

Solar heterogeneous photocatalysis has emerged as a promissory technology to destroy toxic and/or bio-recalcitrant pollutants in water (Malato et al., 2003). Moreover, this technology has also shown the strongest potential in order to inactivate waterborne pathogen microorganisms (Rincón and Pulgarin, 2004a,b, 2005).

Photocatalysis mainly uses a semiconductor such as TiO₂ which can absorb UV light ($\lambda < 400$ nm) and can photo-stimulate redox reactions on its surface producing Reactive Oxygen Species (ROS) such as hydroxyl radical (˙OH), superoxide radical (˙O₂⁻) (Lisenbigler et al., 1995) and singlet oxygen (¹O₂) (Daimon et al., 2008).

However, the overall efficiency of TiO₂ under natural sunlight is limited to the UV-driven activity ($\lambda < 400$ nm), accounting only to ~4% of the incoming solar energy on the Earth's surface. Therefore, in recent years, shifting of the absorption spectrum of TiO₂ towards the visible-light range has attracted a lot of attention (Hashimoto et al., 2005; Thompson and Yates, 2006; Emeline et al., 2008). In particular, much progress has been achieved in the field of *visible-light-active* TiO₂ by incorporation of metallic and no-metallic dopants into its lattice (Choi et al., 1994; Anpo et al., 2005).

It is possible to increase the TiO₂ absorption towards the visible doping with non-metallic elements such as the

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Nitrogen and Sulfur. Insertion of N or S atoms on TiO_2 produces localized states within the band gap just above the valence band. Thus, when N- or S-doped TiO_2 is exposed to visible light, electrons are promoted from these localized states to the conduction band (Di Valentin et al., 2007; Yang et al., 2007).

Recently, several authors have demonstrated the photocatalytic activity of N- and S-doped TiO_2 (N, S TiO_2) in the visible part of the solar spectrum. These materials have been obtained by hydrolytic process using $TiCl_4$ or titanium tetra-isopropoxide, nitrogen, sulfur and carbon precursors (i.e. ammonia solution, thiourea, ethanol and urea) (Ohno et al., 2004; Sato et al., 2005; Kobayakawa et al., 2005; Chen et al., 2005; Kitano et al., 2007). N-doped commercial TiO_2 powders have also been prepared (Gole et al., 2004; Silveyra et al., 2005). N, S TiO_2 has been used to degrade air pollutants such as formaldehyde, acetone and NO (Yu et al., 2006; Yin et al., 2006). Most recently, we prepared N, S TiO_2 by a mechanical grinding of TiO_2 with thiourea using anatase powders Tayca TKP 102 (Rengifo-Herrera et al., 2008) and anatase–rutile powders Degussa P-25 (Rengifo-Herrera et al., 2009a) which was followed by annealing at 400 °C. These materials revealed photocatalytic activity and photo-toxicity towards *Escherichia coli* bacteria under illumination with visible light between 400–500 nm.

However, there are few publications reporting the use of non-metallic-doped TiO_2 prepared by chemical methods under simulated or direct solar light.

Liu et al. (2006) claimed that N-doped TiO_2 nanoparticles prepared by sol–gel method showed a higher photocatalytic activity than undoped Degussa P-25 towards *E. coli* inactivation and Acid Orange 7, an organic dye, under simulated solar light. In addition, Wawrzyniak and Morawski (2006) have reported the preparation of N-doped TiO_2 from the calcination of metatitanic acid in gaseous NH_3 atmosphere at different temperatures. In latter study, two azo dyes, Reactive Red 198 and Direct Green 99, were degraded under simulated solar exposition using N-doped TiO_2. No comparison was carried out between their own photocatalyst and TiO_2 Degussa P-25.

Furthermore, Nieto et al. (2008) reported that N-doped TiO_2 prepared by sol–gel method showed higher photocatalytic activity than undoped powders towards flumequine degradation upon simulated solar light. On the other hand, Lee et al. (2008) prepared C-doped TiO_2 by sol–gel method with higher photocatalytic oxidation of phenol than Degussa P-25.

The most part of these studies have used as chemical probe consisting of an organic dye, Yan et al. (2006) have suggested that the using of visible-light-absorbing dyes chemical is not suitable especially to evaluate the photocatalytic activity under visible light. They recommend the use of chemical probes compounds to be degraded that do not absorb the incoming light.

We hereby present the photocatalytic activity of N-doped and N, S co-doped commercial anatase powder, Tayca TKP 102, towards the *E. coli* inactivation and phenol oxidation which is a chemical substance not absorbing visible light under simulated solar light. Their photocatalytic activity was compared with undoped TKP 102 and undoped Degussa P-25 a commercial TiO_2 powder commonly used as a reference in photocatalytic reactions.

2. Experimental

2.1. Materials

Tayca Corporation kindly supplied commercial TiO_2 nanoparticles. TKP 102 (96% anatase, primary crystallite particle size of 15 nm). Degussa P-25 nanoparticles (70% anatase, 30% rutile) were supplied by Degussa AG. Phenol (99% Fluka chemicals), thiourea and urea (99% Sigma–Aldrich) were used as received.

2.2. Preparation of doped Tayca TKP 102

The N, S co-doped and N-doped TiO_2 powders were prepared by manual grinding of thiourea and urea, respectively, with TKP 102 TiO_2 sample in a 4:1 (w/w) ratio. The material was annealed under air atmosphere during 1 h at 400 °C with a heating rate of 10 °C for minute and then cooled at room temperature. After heating the materials were washed with Milli-Q water three times, dried at 70 °C and then crushed in an agate mortar into a fine powder before use.

2.3. Powder characterization

2.3.1. Diffuse Reflectance Spectroscopy (DRS)
DRS spectra of TiO_2 powders were measured with a Varian Cary 1E spectrophotometer equipped with a diffuse reflectance accessory.

2.3.2. X-ray Photo-electron Spectroscopy (XPS)
XPS analyses were carried out on a XPS Analyzer Kratos model Axis Ultra with a monochromatic $AlK\alpha$ and charge neutralizer.

The deconvolution software program was provided by Kratos. This software is the standard program used and is accepted as reference in the field.

All the binding energies were referenced to the C 1s peak at 285 eV of carbon. Powder samples were prepared by deposition of catalyst on carbon type stuck to sample holder. The powder samples were analyzed with a very large spot (0.3×0.7 mm). Therefore, it was assumed that the recorded spectrum is characteristic of "average" particles. Using a large spot the signal/noise ratio was improved significantly. The atomic concentrations were determined with an increased sensitivity factor because in general the signal/noise ratio observed was weak. This analysis was carried out: (a) taking a larger area (b) the signal accumulation time was increased and (c) the elements analyzed like N did not have a weak sensitivity. The detection limit was

not 0.1 at.% but 0.03 at.%. Typical error is lower than 5% of the calculated value for higher atomic surface concentration and around 10% in the case of the lowest signal to noise conditions.

2.4. Photocatalytic activity

Cylindrical Pyrex bottles (50 ml) were used, a TiO_2 concentration of 1.0 mg mL^{-1} was selected and oxygen (present in the air) was the electron acceptor. The suspension was kept under magnetic stirring and illuminated by a Hanau Suntest (AM-1) solar simulator (Total intensity: 550 W m^{-2}, UV intensity: 20–30 W m^{-2}). The lamp has a spectral distribution with about 0.5% of emitted photons at wavelengths shorter than 300 nm (UV-C range), and about 4% between 300 and 400 nm (UV-B and UV-A ranges). The distribution of the photons emitted between 400 and 800 nm follows the solar spectrum. The radiant flux was monitored with a Kipp & Zonen (CM3) power meter (Omni instruments Ltd., Dundee, UK). Temperature of the experiments was never superior to 38 °C. Samples were periodically collected to follow the reaction kinetics. Results represent the average of three experimental runs and their standard deviations were equal or lower than 15% for the microbiological analysis and less of 8% for HPLC analysis.

2.4.1. Bacterial inactivation

Photocatalytic bactericidal activity was measured by sampling *E. coli* strain K12 MG 1655 from the photoreactor. Before the experiment, bacteria were inoculated into nutrient broth (Oxoid No. 2, Switzerland) and grown overnight at 37 °C. During the stationary growth phase, bacteria cells were harvested by centrifugation at 5000 rpm for 10 min at 4 °C. The bacterial pellet was then washed three times with a saline solution (8 mg mL^{-1} NaCl and 0.8 mg mL^{-1} KCl in Milli-Q water, pH 7 by addition of HCl or NaOH). A suitable cell concentration (10^6 colony forming units (CFU) per mL^{-1}) was inoculated in the reactor's saline solution. Then, the inoculated Pyrex bottles with the catalyst added were illuminated during 4 h and samples (1.0 mL) were taken at different time intervals. Serial dilutions were performed in saline solution and 100 µL volumes were inoculated in a plate count agar (PCA, Merck, Germany) growth medium. The number of colonies was counted 24 h after inoculation at 37 °C. Control experiments (*E. coli* and UV or visible light without catalyst) and (*E. coli* + catalyst without light) were also performed.

2.4.2. Phenol photocatalytic oxidation

The procedure was the same used in the *E. coli* inactivation. Phenol solution containing 1×10^{-4} M was added to the Pyrex glass reactors. Samples were taken and filtered by 0.2 µm membranes. Phenol oxidation was followed by HPLC (Hewlett–Packard series 1100) and with a reverse phase Spherisorb silica column (Macherey–Nageland). As mobile phase was used acetonitrile: water (60:40). Phenol and *p*-benzoquinone detection was carried out by Diode Array Detector (DAD) at 220 and 244 nm, respectively.

3. Results and discussion

3.1. Characterization of doped TiO_2 TKP 102

Fig. 1 shows the DRS spectra transformed to (K/S) by the Kubelka–Munk relationship of undoped TKP 102 and thiourea and urea treated TKP 102 powders (Th and U-TKP 102, respectively). It is possible to observe that annealing at 400 °C of anatase TKP 102 powders with thiourea and urea increased the absorption of TKP 102 anatase nano-powders towards the visible region (400–550 nm). It was also observed that urea treated TKP 102 showed a higher visible absorption than thiourea treated titania powder. In addition, it is possible to observe that Degussa P-25 shows absorption at wavelength below 410 nm.

Figs. 2 and 3 show the XPS measurements to identify the species responsible for the visible absorption. In previous works, we reported that undoped TKP 102 did not reveal any presence of N or S impurities on its surface (Rengifo-
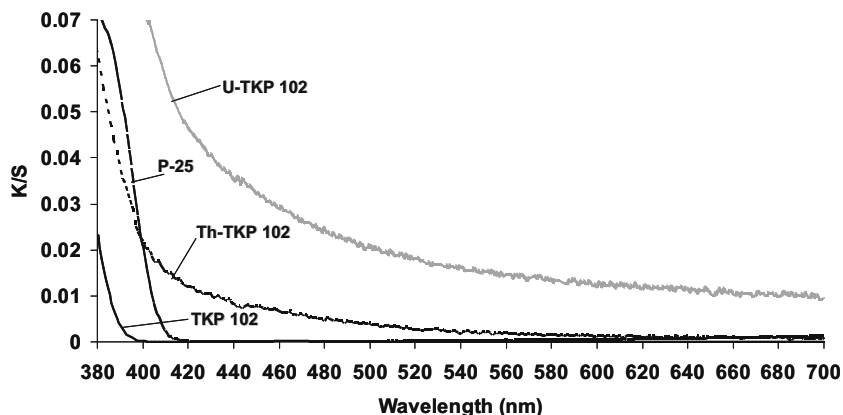

Fig. 1. DRS spectra of undoped TKP 102, undoped Degussa P-25, TKP 102 treated with thiourea at 400 °C and TKP 102 treated with urea at 400 °C.
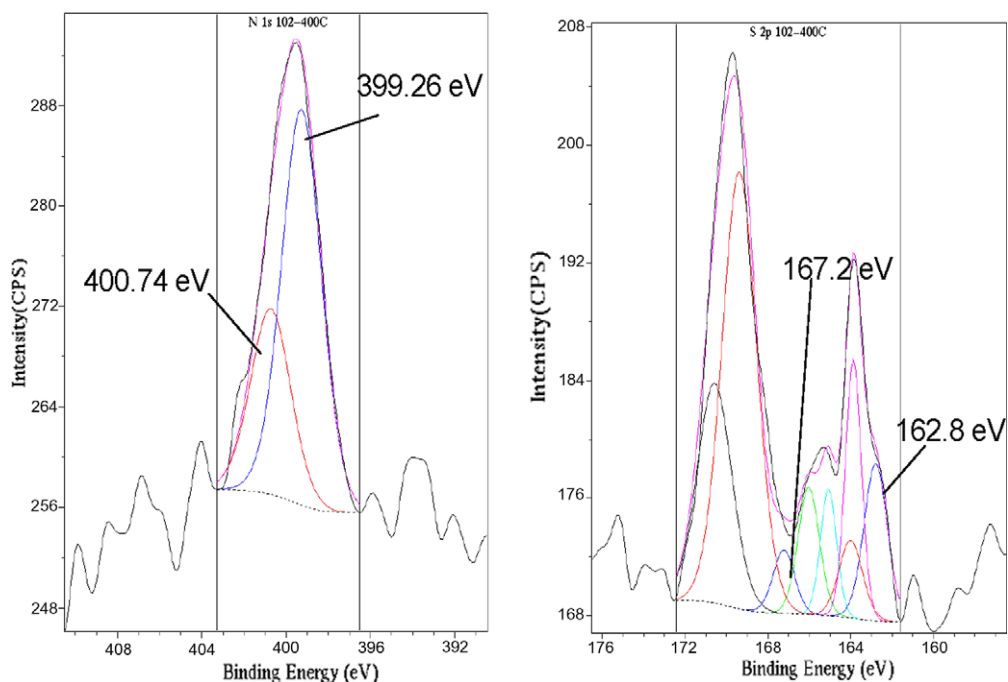
Fig. 2. N 1s, and S 2p XPS peaks acquired for N, S co-doped TKP 102 powder.
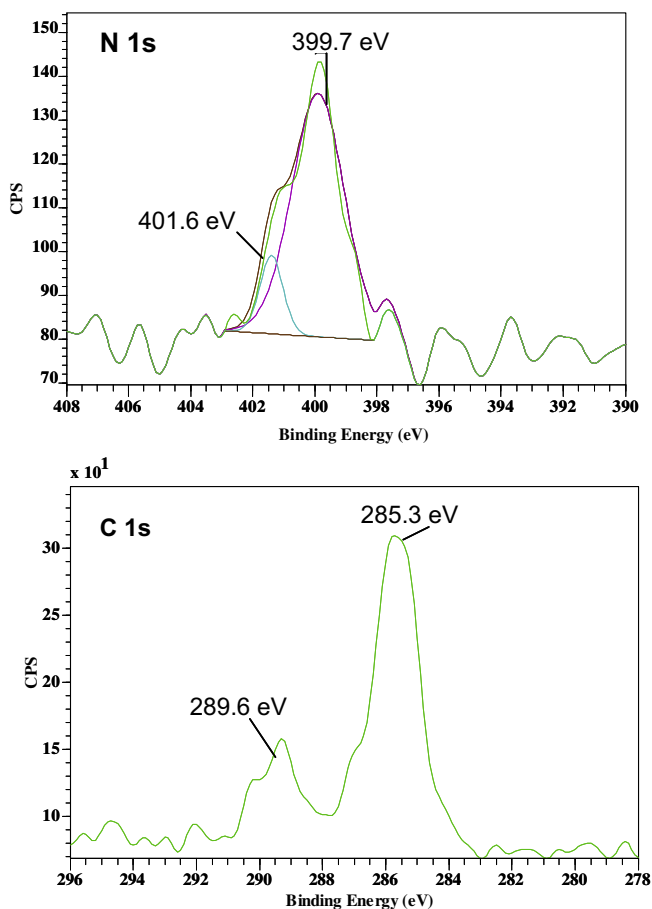

Fig. 3. N 1s, C 1s XPS peaks acquired for N-doped TKP 102 powder.

stitial N-doping (Diwald et al., 2004) and substitutional anionic and cationic S-doping (Umebayashi et al., 2002; Cong et al., 2007) (Fig. 3) with N 1s signals at 399.2 and 400.7 eV and S 2p peaks at 162.8 and 167.2 eV. On the other hand, urea treated TKP 102 revealed the presence of interstitial N-doping with signals at 399.7 and 401.6 eV (Fig. 4). C 1s signal revealed the presence of adventitious carbon at 285.3 eV and carbonates with a signal at 289.6 eV (Sano et al., 2004; Sun et al., 2006).

Regarding the atomic concentration of N and S species on the TiO_2 surfaces, it was found that N-doped TKP 102 showed higher N content that N, S co-doped TKP 102 (Table 1). This latest fact could be the responsible of the highest visible-light absorption present on N-doped TKP 102 (urea treated powders).
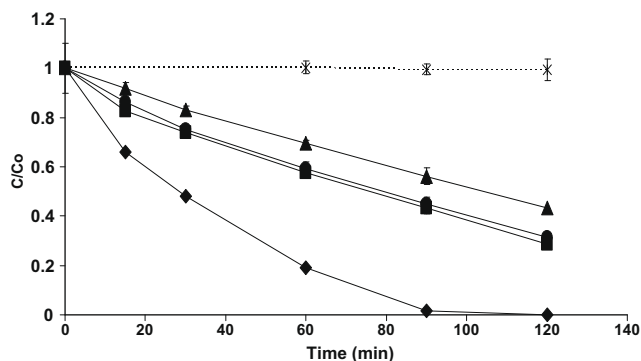

Fig. 4. *E. coli* inactivation under simulated solar light. (-♦-) undoped Degussa P-25. (-■-) undoped TKP 102. (-●-) N, S co-doped TKP 102 (-▲-) N-doped TKP 102. (-x-) Light only without catalyst. Experimental conditions: pH 7.0, Total intensity: 550 W m^{-2}. UV intensity 20–30 W m^{-2} and concentration of TiO_2 powders of 1 g L^{-1}.

Herrera et al., 2008). It was also mentioned that thiourea treated TKP 102 powders showed typical features of inter-

Table 1
Atomic concentration determined by XPS in at.% of N, C and S present on the surface of N-doped and N, S co-doped TKP 102 powders.

Powder	N 1s (at.%)	C 1s (at.%)	S 2s (at.%)
N, S TKP 102	0.54	21.41	0.71
N-TKP 102	2.85	15.96	0.0

Thus, in summary, it is possible to point out that annealing with thiourea of anatase commercial powders lead the presence of N and S species linked commonly to N- and S-doping which produces visible-light absorption. In the case where urea was used instead of thiourea, commercial anatase powders with visible-light response were also achieved but principally due to N-doping.

3.2. Photocatalytic oxidation of phenol and E. coli inactivation upon simulated solar light

Figs. 4 and 5 show the phenol oxidation and *E. coli* inactivation, respectively, under simulated solar light exposition in presence of undoped Degussa P-25, undoped TKP 102, N, S co-doped TKP 102 and N-doped TKP 102. Results revealed that undoped TKP 102 and N, S co-doped TKP 102 showed almost the same photocatalytic activity during *E. coli* inactivation and phenol oxidation. In contrast, N-doped TKP 102 showed a decrease in the photocatalytic inactivation to inactivate *E. coli* cells and oxidize phenol. Degussa P-25 showed the highest degradation rate for phenol oxidation and *E. coli* cells inactivation under simulated solar light. The photocatalytic activity of Degussa P-25 is due mainly to the presence of anatase and rutile. Mixed-phase materials such as TiO_2 Degussa P-25 present low e^-/h^+ recombination since the photo-produced electrons on the anatase phase transfer to lower lying to lower trapping sites in rutile (Bickley et al., 1991). How-
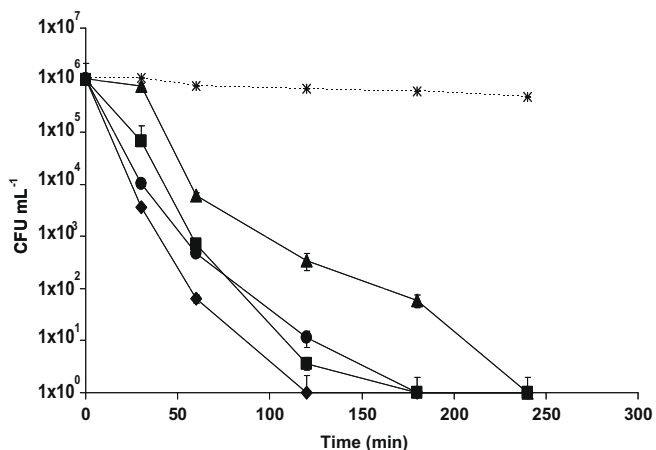
Fig. 5. Phenol oxidation under simulated solar light. (-◆-) undoped Degussa P-25. (-■-) undoped TKP 102. (-●-) N, S co-doped TKP 102 (-▲-) N-doped TKP 102. (-x-) Light only without catalyst. Experimental conditions: pH 7.0, Total intensity: 550 W m^{-2}. UV intensity 20–30 W m^{-2} and concentration of TiO_2 powders of 1 g L^{-1}.
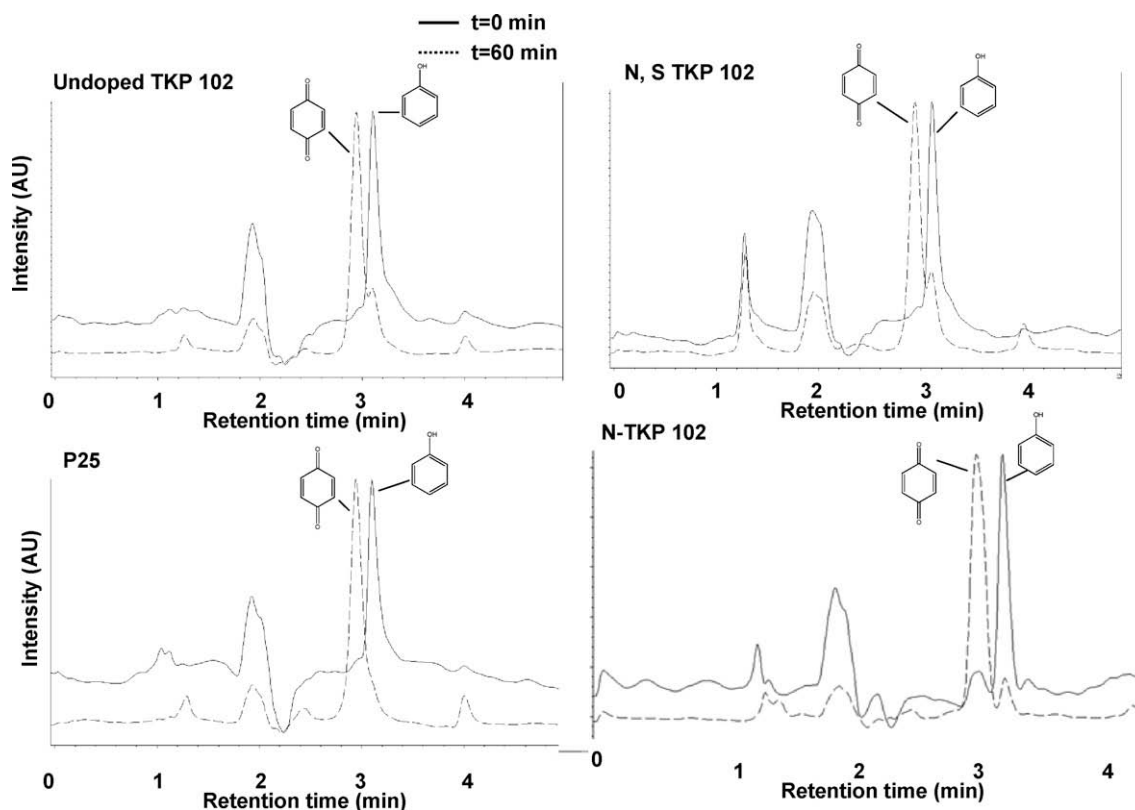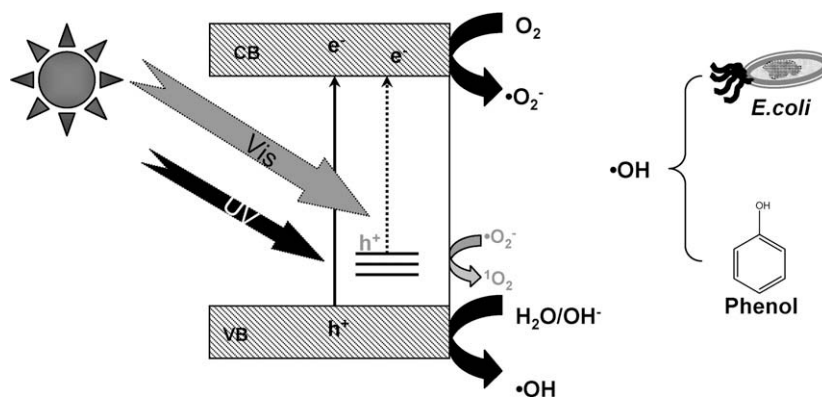
Fig. 6. Chromatograms using Diode Array Detector (DAD) at 244 nm revealing the formation of *p*-benzoquinone upon simulated solar light (a) undoped Degussa P-25, (b) undoped TKP 102 (c) N, S co-doped TKP 102 and (d) N-doped TKP 102.

Scheme 1. Photocatalytic phenol oxidation and *E. coli* inactivation mechanism suggested under simulated solar exposition on N, S co-doped and N-doped TKP 102 powders.

ever, from Electronic Paramagnetic Resonance (EPR) measurements, Hurum et al. (2003) have proposed an interwoven network of anatase and rutile crystallites facilitating the electron transfer between anatase and rutile.

In addition, the HPLC chromatograms (Fig. 6) recorded using a Diode Array Detector (DAD) show the presence of a phenol peak before to turn-on the light. After 60 min of irradiation, this peak decreased and a new peak corresponding to *p*-benzoquinone appeared when undoped and doped powders were irradiated with simulated solar light. Some authors (Ilisz and Dombi, 1999; Sobczynski et al., 2004) have mentioned that the first step in the phenol degradation on TiO$_2$ is the electrophilic attack of the ·OH radicals on the aromatic moiety producing hydroquinone or *p*-benzoquinone. Previously, we reported that phenol oxidation in presence of N, S-doped TKP 102 under UV-light exposition leaded to the production of *p*-benzoquinone as the main oxidative by-product due to the reaction of ·OH produced by water or/and OH ions oxidation by holes photo-produced on the semiconductor valence band (Rengifo-Herrera et al., 2009b).

Even though the N-doped TKP 102 showed an intense visible-light absorption, its photocatalytic activity was low. This behavior could be due to the highest N concentration on its surface acting as recombination centers (Irie et al., 2003).

The N, S co-doped and the N-doped commercial anatase powders having visible-light response did not enhance the photocatalytic activity respect to TiO$_2$ Degussa P-25 and undoped TKP 102 under simulated solar irradiation.

These results could be supported by the fact that in a former study published by Mrowetz et al. (2004), authors gave evidences about the oxidation power of N-doped TiO$_2$ is reduced since under visible-light irradiation, N-doped TiO$_2$ powders were not able to oxidize formate. We also suggested in a previous publication that under visible-light exposure, the photocatalytic *E. coli* inactivation mechanism did not involve the hydroxyl radical production since probably, the hole photo-generated by visible-light irradiation on the midgap levels induced by N and S co-doping have not the suitable redox potential to oxidize water, organics or OH$^-$ ions. It was found evidence showing the possible formation of singlet oxygen, a less oxidative ROS (Rengifo-Herrera et al., 2009b). This singlet oxygen would be the ROS responsible of cells abatement. Furthermore, under neutral conditions, the singlet oxygen did not lead the phenol oxidation.

Thus, in spite that visible light would induces less oxidative ROS formation such as singlet oxygen on N, S co-doped commercial TiO$_2$ powders, photocatalytic activity enhancement under simulated solar light irradiation was not observed. So, hydroxyl radicals with higher oxidation power generated by valence band holes under UV light could be the main active species able to phenol oxidation and *E. coli* inactivation (Scheme 1).

4. Conclusions

The N, S co-doped and the N-doped commercial anatase powders with visible-light response were synthesized by a simple method adding thiourea or urea to the anatase and then annealing at 400 °C during 1 h.

However, these novel materials did not present an enhancement on their photocatalytic activity towards phenol oxidation and *E. coli* inactivation under simulated solar light. Undoped Degussa P-25 was the commercial reference powder used in this work with highest photocatalytic activity.

We suggest that UV-induced photocatalytic process where ·OH radicals are produced mainly by hydroxyl ions or water oxidation with photo-induced valence band holes prevails upon simulated solar light exposition. Localized states induced by N- or S-doping and responsible of visible-light absorption would not play an important role on the photocatalytic activity of these novel materials under the experimental conditions reported here.

spectra, and O. Masaaki from Tayca Corp (Japan) and S. Jansen from Mitsubishi Corp. (Germany) for kindly supplied the samples of TiO_2 powders Tayca.

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