



Phenol photodegradation with oxygen and hydrogen peroxide over TiO₂ and Fe-doped TiO₂

C. Adán*, J. Carbajo, A. Bahamonde, A. Martínez-Arias*

Instituto de Catálisis y Petroleoquímica, CSIC, C Marie Curie 2, Cantoblanco, 28049 Madrid, Spain

ARTICLE INFO

Article history:

Available online 21 November 2008

Keywords:

Photocatalyst
Titanium dioxide
Iron doping
Sol-gel/microemulsion synthesis
Phenol degradation
Hydrogen peroxide

ABSTRACT

Photodegradation of phenol was investigated with two types of oxidant agents in water, oxygen and hydrogen peroxide, at two different reaction pH with a series of nanosized iron-doped anatase TiO₂ catalysts with different iron contents. The catalysts have been prepared by a sol-gel/microemulsion method. Firstly, iron-doped titania catalysts were studied with respect to their activity behavior when oxygen was used as oxidant agent in the photocatalytic degradation of aqueous phenol in comparison with un-doped reference catalysts. Secondly, two catalysts (TiO₂ and 0.7 wt.% Fe-doped TiO₂) were selected to extend the study for the employment of hydrogen peroxide as oxidant at different concentrations and two initial reaction pHs. An enhancement of the photocatalytic activity is observed only for relatively low doping level (ca. 0.7 wt.%) in catalyst calcined at 450 °C preferably using hydrogen peroxide as oxidant agent which is attributable to the partial introduction of Fe³⁺ cations into the anatase structure. Nevertheless, it has been demonstrated that catalyst surface properties can play an important role during phenol photodegradation process on the basis of the analysis of differences found in the photoactivity as a function of reaction pH.

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1. Introduction

Nowadays the use of conventional biological treatments to remove phenolic compounds is limited to low phenol concentration waste streams, given that phenol is a bactericide at concentrations above 0.2 kg/m³ [1]. The destruction of these toxic and recalcitrant pollutants must be therefore demanded to methods which totally remove it [2]. Consequently, the implementation of novel and improved cost-effective techniques for the industrial wastewater treatment is a demand nowadays because of the growing incidence of hazardous pollutants and the stringer discharge limits. The great potential of heterogeneous catalyst provides important opportunities in this field. So, new advanced options based on catalytic processes point at being an important goal in wastewater treatments with lower organic contents, being specially promising the so called advanced oxidation processes (AOPs) [3], which usually operate at or near ambient temperature and pressure. Therefore the use and development of heterogeneous catalysts will be an important answer to the perspective of tightening regulations in the treatments of aqueous waste, such as European Directive 2000/60/CE [4] or EPA [5] forcing the need to

adopt measures against water pollution and searching novel methods in the near future.

In this sense, novel and economical advanced oxidation techniques based on catalytic photo-oxidation are emerging as a promising alternative [6–8]. During the last decades heterogeneous photocatalysis based on titanium dioxide (TiO₂) has been identified as a potential alternative because of its ability to photodegrade aqueous and atmospheric pollutants [9,10].

One of the more important drawbacks that present TiO₂ catalysts is attributable to the high recombination rate of its photogenerated electron and holes [11]. To try to enhance its photoactivity, titania doped with transition metal cations had been revealed as a good strategy to reduce electron–hole recombination rates [12–15] improving final photocatalytic efficiency.

Additionally, experimental factors like initial reaction pH employed in the solution, type and concentration of oxidation agent employed, wavelength light irradiation or even reactor geometric configuration can play important roles in the pollutant photodegradation in aqueous medium [10]. These external factors could be the origin of the discrepancies found in the literature when dealing with iron-doped catalysts, also considering that no particular activity enhancement for relatively low doping level can be found [16].

On the other hand, in the photocatalytic process it is common to use oxygen from the air as TiO₂ electron acceptor, which is due to the good efficiency, availability and low cost. However, the use of

* Corresponding authors. Tel.: +34 915 854 776; fax: +34 915 854 760.

E-mail addresses: cadan@icp.csic.es (C. Adán), amartinez@icp.csic.es (A. Martínez-Arias).

hydrogen peroxide has been also addressed due to its high oxidising efficiency as a consequence of its high oxidation potential, comparable with fluor, with a value of 1.78 eV at 25 °C [17]. Hydrogen peroxide works as an electron acceptor and can promote an increase in the production of active $\cdot\text{OH}$ radicals able to attack the organic matter [18].

Therefore, the aim of this work has consisted in studying the influence of type and concentration of oxidant agent on phenol photocatalytic degradation with titania and iron-doped titania-based catalysts. The oxidant agents used were oxygen and hydrogen peroxide, and other operating conditions such as reaction pH were also analyzed to try to determinate the best photocatalytic conditions to get good performance in the photo-degradation of phenol.

2. Experimental

2.1. Materials and synthesis

The photocatalysts were prepared using a combined sol–gel/microemulsion preparation method by the addition of Ti tetra-isopropoxide to a reverse microemulsion containing in its aqueous phase a solution (between 0.01 and 0.1 M) of iron(III) nitrate nonahydrate dispersed in *n*-heptane, using Triton X-100 (Aldrich) as surfactant and hexanol as co-surfactant [13,19]. The resulting mixture was stirred for 24 h, centrifuged, decanted, rinsed with methanol and dried at room temperature for 12 h. Then, the amorphous mixed oxides were calcined under air for 2 h at 450 °C using a temperature ramp of 1 °C/min. Iron-doped TiO_2 and iron-free TiO_2 samples were prepared by using the same method, dissolving in the aqueous phase the necessary amount of iron(III) nitrate nonahydrate in each case or just using distilled water. Table 1 includes the nomenclature employed for all the catalysts along with some basic characteristics and preparation parameters. A second iron-free catalyst ($\text{TiO}_2\text{-A}$) was prepared under acid conditions similar to the one present in the iron solution employed to prepare iron-doped catalysts; for this purpose, the aqueous phase was acidified to pH 1.8 with HNO_3 , see Table 1.

2.2. Characterization

The chemical composition of the samples was analyzed by ICP-OES; Fe content obtained during such analyses was employed to label the samples (see Table 1). The chemical analysis evidences, within experimental error, quantitative precipitation of the iron in all cases, except for the most loaded sample. BET surface areas (S_{BET}) were obtained from nitrogen adsorption at -196°C using a Micromeritics Tristar apparatus; samples were previously out-gassed overnight at 140°C to a vacuum of $<10^{-4}$ Pa, to ensure a dry clean surface, free from any loosely held adsorbed species. The specific surface areas were determined by the application of the

BET equation [20]. XRD patterns were obtained with a Siemens D-500 apparatus using nickel-filtered $\text{Cu K}\alpha$ radiation operating at 40 kV and 40 mA, with a 0.04° step size and accumulating a total of 5 s per point. UV–vis transmission experiments, useful in the determination of the semiconductor band-gap [21,22], were performed with a UV–vis Varian 2300 apparatus. The analysis of the direct band-gap transition of the samples was made using equations developed elsewhere [22].

The pH of the aqueous slurry of the solid catalysts dispersed in distilled water (referred to as pH slurry) is a good measure of the acid/basic character of the TiO_2 catalysts overcoat, particularly when it operates in aqueous solutions. pH slurry reflects pH changes in the bulk liquid interacting with a saturated solid suspension after a prolonged contact, as a consequence of the exchange of protons to or from the surface of the oxide [23]. For this purpose, 0.5 g of TiO_2 was added to 10 mL of CO_2 -free distilled water kept in a bottle at room temperature and continuously stirred for 1 day until the corresponding pH was stabilized.

2.3. Catalytic activity

Phenol photo-oxidation runs were done with a Pyrex batch-photoreactor of cylindrical shape, supplied by Helios Italquartz company. A high-pressure Hg lamp (500 W) immersed within the suspension and cooled by water circulating through a Pyrex jacket, was used for the illumination. This lamp has an emission range between 260 and 420 nm, with an intense emission band centered at 366 nm and two weaker ones at 318 and 303 nm. The photoreactor was provided with three ports in its top section for sampling the solution and/or flowing air current as required. When experiments were performed with hydrogen peroxide, no air was admitted to the reactor vessel. A magnetic stirrer was used to achieve uniform conditions in the reacting mixture. Operation conditions were chosen on the basis of minimizing light scattering by the photocatalyst particles and avoiding appreciable saturation by the substrate; in this respect, 500 mg L^{-1} of the catalysts, 1-L volume reactor, 50 mg L^{-1} of phenol and $100\text{ N cm}^3\text{ min}^{-1}$ of oxygen flow were selected as most optimum working conditions; in turn, two different hydrogen peroxide concentrations (250 and 500 mg L^{-1}) at two different reaction pH (3 and 6) were studied in this report. Small portions of the irradiated reactor were extracted at different reaction times to monitor TOC contents using a $\text{TOC-V}_{\text{CSH/CSN}}$ Shimadzu analyser.

3. Results and discussion

Data estimated from analysis of the XRD patterns along with other relevant chemical analysis and surface properties of the catalyst are collected in Table 1. All XRD patterns evidenced the presence of mainly the anatase crystal form of titania [24]. To increase iron content inside Fe–titania catalysts a maximum of anatase crystal size,

Table 1
Physico-chemical properties of Titania and TiFe catalysts.

Catalyst	Fe content (wt.%)		Synthesis pH	$\text{pH}_{\text{slurry}}$	S_{BET} (m^2/g)	Particle size ^b (nm)	Band-gap (eV)
	Nominal	Chemical analysis ^a					
TiO_2	0.00	–	6.0	8.4	119	7.7	3.17
TiFe-0.4	0.35	0.37	2.9	6.9	105	10.6	3.12
TiFe-0.7	0.70	0.74	2.7	6.7	83	12.7	3.10
TiFe-1.5	1.40	1.49	2.4	4.9	77	13.3	3.00
TiFe-3.5	3.50	3.48	2.2	5.6	107	10.5	2.71
TiFe-5.1	6.91	5.14	1.9	5.3	85	7.7	2.58
$\text{TiO}_2\text{-A}$	0.00	–	1.8	5.6	107	10.8	3.06

^a ICP-OES measurements.

^b Anatase crystal size determined by using the Scherrer equation.

at the same time that a minimum of surface area, can be observed with TiFe-1.5 catalyst. All of that can be attributed to the fact that this iron content is close to the maximum of solubility of iron cations inside anatase structure [23], where the maximum attained in the elongation of the lattice parameter and in the cell volume for the tetragonal cell of anatase was close to 0.74 wt.% of iron content (TiFe-0.7 catalyst) [25].

UV–vis spectra (not shown here) revealed contributions at wavelength lower than 380 nm (ca. 3.2 eV) which can be assigned to the intrinsic band-gap absorption of pure anatase TiO₂ [24]. The presence of iron in this iron-doped titania catalysts gave place to absorption bands in the visible region below ca. 400 nm, which increased iron content and being in agreement with the observed changes in the color of the samples from white to yellow or light brown. The direct band-gap values (Table 1) also decrease when iron content increases in TiO₂, which means that lower excitation wavelength could form e[−]/h⁺ pairs in the doped semiconductor.

On the other side, an important factor that could be most relevant to the photoactivity is related to the surface acid/base characteristics of the catalysts [26]. The obtained values for pH_{slurry} of iron-doped titania materials suggest an enhancement of surface acidity upon doping the titania catalyst with iron at very low pH. This parameter may give a good indication about the surface oxygen groups and the electronic surface charges of the samples, given that can be related to point of zero charge (PZC) of the solid [27]. In this line, pure titania usually presents isoelectric point values in the pH range of 6.0–6.5 [28] that correspond to the materials with surface acid character. Nevertheless, it is known that surface acid/basic character can depend on changes of certain factors such as preparation method parameters or sample preconditioning employed. Therefore, shifts in isoelectric points can occur in response to changes in cation coordination, crystallinity, hydration state, surface composition and structural charge or ion exchange capacity among others. These factors can explain the significant decrease observed for the pH_{slurry} of the iron-doped titania catalysts up to 1.40 wt.% of iron. Nevertheless, again higher iron contents did not generate any significant change in the catalyst surface acidity. Doping of titania with a transition metal like iron led to decrease pH of synthesis increasing their surface acid characters as un-doped TiO₂-A catalyst synthesized at pH 1.8.

Therefore, doping titania with iron contents lower than 1.4 wt.% seems to lead to minimum values in their acidity surface character and S_{BET} at the same time that a higher anatase crystal size was found by using Scherrer equation, which could well be related to the effective introduction of Fe³⁺ inside titania-anatase structure and the lower pH of synthesis.

3.1. Photocatalytic activity with oxygen

Fig. 1 shows the phenol photodegradation results with oxygen as oxidant at two reaction pH (3 and 6) over TiO₂ and TiO₂-A catalysts. In all cases photoreaction process was initiated after an initial equilibration period (≈30 min) during which relatively negligible amounts of phenol was chemisorbed on the catalyst surface, always lower than 3–4%. No iron lexiates to the reaction medium were detected along photocatalytic process at the two reaction pH studied here.

In any case, higher TOC removals were always found to increase with irradiation time, however some significant differences can be observed for the bare titania catalyst as a function of the reaction pH. Thus, the highest TOC conversions (ca. 40% at 300 min) as well as lowest final photoactivity (16% TOC conversion after 300 min irradiation time) were obtained with TiO₂ catalyst at pH 6.0 and 3.0, respectively. In contrast, TiO₂-A photoactivity did not seem to be affected to reaction pH, given that very similar final TOC

removals (25 and 29% for pH 3.0 and 6.0, respectively) can be observed. This fact could be due to some significant differences in their catalytic surface properties given that their structural properties, surface area and band-gap are apparently quite similar.

Taking into account that these titanium dioxides were prepared at two different acid pH values and calcined at 450 °C different values of pH of the slurries can be addressed. Thus, titania prepared at lower pH (TiO₂-A at pH 1.8) presented a lower pH_{slurry} 5.6 than titania prepared at pH 6.0 (TiO₂), pH_{slurry} 8.4, which is related to an important acid surface character in TiO₂-A sample, as it could be expected. On the other side, to acidify the synthesis medium probably affects reorganization of amorphous aggregates during the preparation method [29], leading to increase the anatase crystal size in titania prepared at lower pH, TiO₂-A.

Therefore, the differences found in the photocatalytic activity of these two titania-based catalysts as a function of reaction pH employed suggests that different surface properties are playing important roles during phenol photo-oxidation.

The initial pH of the aqueous solution employed to prepare the materials (Table 1) strongly affects the surface acid/basic character of this catalysts by modifying its surface acidity (0.201 and 0.580 mmol g^{−1} for TiO₂ and TiO₂-A, according to the previous ammonia chemisorption measurements [24]) which is also reflected in pH slurry values (Table 1). The differences found in the photoactivity of these two catalysts as a function of the initial pH employed suggests that different surface entities could be present in TiO₂, in contrast to TiO₂-A, which would affect the electrostatic interaction between catalyst surface and phenol molecule in each case. It must be noted that the PZC of pure TiO₂ anatase lies in the range of 5.0–6.0 [30]. In this sense, the un-doped TiO₂ sample can most likely present differences in its surface charging characteristics between the two operating pH employed, which would be somewhat damped for the modified TiO₂-A sample.

In the same line, in our previous work the activity of iron catalysts for phenol photodegradation showed an optimum value of iron content in the doped titania samples around 0.7 wt.% when reaction pH was 3.0 [24]. This was attributed to the fact that substitutional incorporation can be maximized at such relatively low dopant content, in line with literature reports displaying maximum photoactivity in organics photo-oxidation reactions for dopant contents close to that value [26].

In Fig. 2, it can be observed that the evolution of TOC over iron-doped titania catalysts at reaction pH 6.0, where a gradual activity

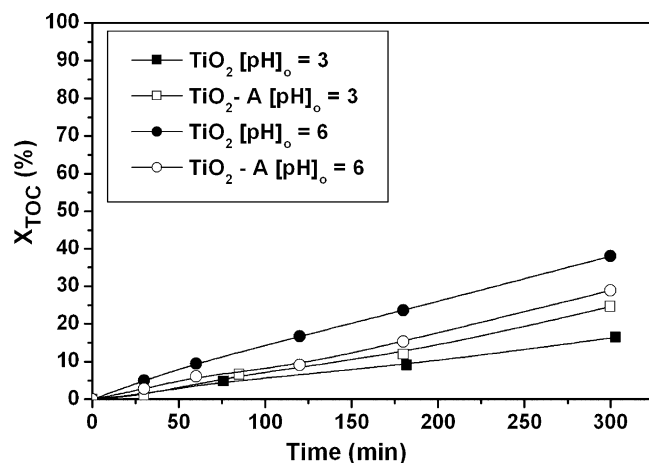


Fig. 1. Influence of reaction pH on TOC evolution in phenol photodegradation with TiO₂ and TiO₂-A catalysts. Operating conditions: [phenol]_o = 50 ppm; [O₂]_o = 100 N mL min^{−1}; pH_{reaction} 6.0.

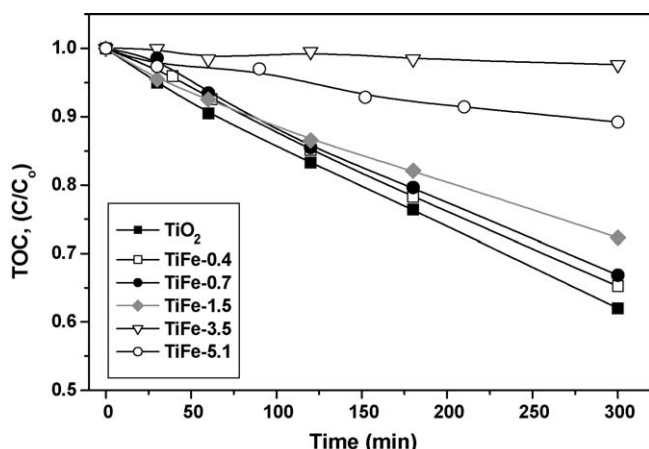


Fig. 2. Evolution of TOC during phenol photo-oxidation over TiFe catalysts. Operating conditions: $[\text{phenol}]_0 = 50 \text{ ppm}$; $[\text{O}_2]_0 = 100 \text{ N mL min}^{-1}$; $\text{pH}_{\text{reaction}} = 6.0$.

reduction was always detected with increasing the iron content. It must be noted that no traces of iron lixivates were detected along this photocatalytic process at the studied operating conditions. Although no appreciable enhancement in the photoactivity results upon doping with iron the titania catalysts for systems tested at reaction pH 6.0, a maximum TOC removal was achieved for 0.3–0.7 wt.% iron content at reaction pH 3.0 in a previous work [24]. However, a relative good phenol photodegradation can be obtained over the lowest iron content catalysts (0.3–0.7 wt.%) at reaction pH 6.0.

The general decrease detected in the photoactivity with increasing iron content above ca. 0.7 wt.% can be attributed, in agreement with UV–vis results reported in a previous work [24], to the formation of segregated oxidic phases of iron for which electron–hole recombination processes can be the dominant route [31].

Therefore significant differences in photocatalytic behavior can be obtained as a function of the reaction pH when comparing undoped titania with iron-doped titania catalysts.

In general, TOC removals with iron-doped catalyst presented lower differences upon changing the initial pH whereas with undoped samples (Figs. 1 and 2), higher conversion values were achieved at reaction pH 6.0.

Overall, this suggests an important role of surface properties in the same sense as pointed out above for the un-doped samples while the balance with bulk characteristics (determining electron–hole dynamics and activity, which can be apparently optimized for the TiFe-0.7 specimen [24]) can determine the activity trends observed. In any case, among the studied series, TiO_2 and TiFe-0.7 catalysts apparently exhibit optimized phenol photodegradation activity at both pHs and for this reason they are chosen for an extension of the study employing hydrogen peroxide as oxidant.

3.2. Photocatalytic activity with hydrogen peroxide

According to the literature, there is an optimum molar ratio between concentrations of hydrogen peroxide and pollutant $[\text{H}_2\text{O}_2/\text{pollutant}]$, for which $\cdot\text{OH}$ radicals concentration photo-generated at the surface becomes enough to oxidize all the organic matter present in the reaction medium. It must be noted that an excess of $\cdot\text{OH}$ radicals formation could result detrimental to the photoactivity as a consequence of hydrogen peroxide being disproportionated to water and molecular oxygen. The optimum molar ratio described in literature was around 10–100 [32–34]. For this reason, the selected initial $\text{H}_2\text{O}_2/\text{phenol}$ molar ratios used in

this study were 14 and 28, which correspond to stoichiometric and double stoichiometric amount of hydrogen peroxide for complete oxidation of phenol, respectively.

The results from the study of the influence of pH (3.0 and 6.0) on the photodegradation of phenol with the stoichiometric amount of H_2O_2 for TiO_2 and TiFe-0.7 catalysts are given in Figs. 3 and 4, respectively.

The final TOC conversion for TiO_2 catalyst, independently of reaction pH, was significantly lower than TOC conversion achieved when oxygen was used as oxidant agent. In this sense, Tryba et al. [35], in studies of a similar type, have detected the formation of hydroxyl radicals over the surface of the catalyst and have attributed the decrease of the activity to the depletion of $\cdot\text{OH}$ radicals concentration. This behavior could be probably due to the inherent capacity of hydroxyl radicals to react with hydrogen peroxide and give rise to the formation of H_2O and O_2 . This is in agreement with the results exhibited in Fig. 3, where hydrogen peroxide conversions were 60 and 75% at pH 3.0 and 6.0, respectively, which did not correlate with TOC conversion values (reaching only $\sim 10\%$). On the other hand, the inhibiting effect observed over TiO_2 catalyst could arise as a consequence of surface modification of titania upon interaction with H_2O_2 [36]. This could be related to the yellow color of the catalyst observed at the end of the reaction, in contrast to initial white color, likely due to

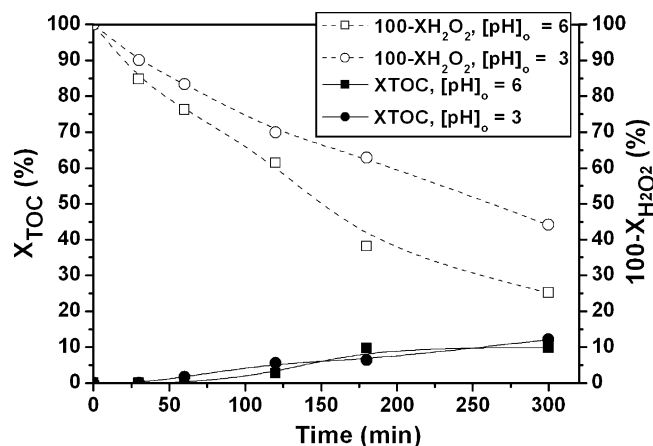


Fig. 3. Influence of reaction pH on TOC and H_2O_2 conversions in phenol photodegradation over TiO_2 catalyst. Operating conditions: $[\text{phenol}]_0 = 50 \text{ ppm}$; $[\text{H}_2\text{O}_2]_0 = 250 \text{ mg L}^{-1}$.

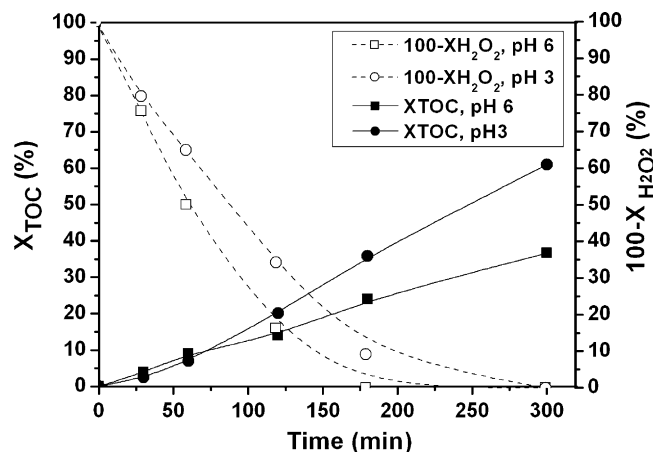


Fig. 4. Influence of reaction pH on TOC and H_2O_2 conversions in phenol photo-oxidation with TiFe-0.7 catalyst. Operating conditions: $[\text{phenol}]_0 = 50 \text{ ppm}$; $[\text{H}_2\text{O}_2]_0 = 250 \text{ mg L}^{-1}$.

Table 2First-order constants for H₂O₂ decomposition and TOC degradation during phenol photodegradation at stoichiometric peroxide conditions.

Catalyst	H ₂ O ₂ decomposition				TOC degradation			
	[pH] ₀ 3		[pH] ₀ 6		[pH] ₀ 3		[pH] ₀ 6	
	<i>k</i> (min ^{−1})	<i>r</i> ²	<i>k</i> (min ^{−1})	<i>r</i> ²	<i>k</i> (min ^{−1})	<i>r</i> ²	<i>k</i> (min ^{−1})	<i>r</i> ²
TiO ₂	2.7 × 10 ^{−3}	0.99	4.7 × 10 ^{−3}	0.98	0.4 × 10 ^{−3}	0.98	0.3 × 10 ^{−3}	0.99
TiFe-0.7	12.9 × 10 ^{−3}	0.94	15.2 × 10 ^{−3}	0.98	3.2 × 10 ^{−3}	0.99	1.5 × 10 ^{−3}	0.99

formation of surface peroxo-complexes like Ti(O)₂(OH)₂ and Ti(OOH)(OH)₃, which are known to inhibit the photocatalytic activity [37–39]. In contrast, when TiFe-0.7 catalyst was examined under the same operating conditions, Fig. 4, the found TOC conversions were excellent in comparison with un-doped titania catalyst. To analyze the effect of reaction pH on phenol photodegradation a very best performance can be seen at pH 3.0. Nevertheless, no significant differences in TOC degradation rate could be seen at reaction pH 6.0 with this titania-doped catalyst, when either of the two oxidant agents were employed, hydrogen peroxide (Fig. 4) or oxygen (Fig. 2) giving similar final TOC conversions, 37 and 33%, respectively, after 300 min of irradiation time. Iron lixiviates to the reaction medium were considered negligible during phenol photodegradation at the two reaction pH studied here.

Taking into account the obtained results, it could be assumed that the decomposition reaction rate of H₂O₂ follows a first-order rate. In the same way, kinetic constants have been calculated for TOC degradation at both reaction pH, considering that TOC degradation rate also follows a first-order rate equation.

In Table 2 are summarized the values of the first-order rate constants for H₂O₂ decomposition and TOC degradation values obtained by least squares method with TiO₂ and TiFe-0.7 catalysts when the stoichiometric amount of H₂O₂ was used. In both cases, kinetic constants for H₂O₂ decomposition were much higher than the corresponding TOC kinetic constants, which could be correlated with the fact that a part of the oxidant was consumed in this process without producing reactive hydroxyl radicals to promote total phenol oxidation, i.e. directly decomposing to water and molecular oxygen. This negative or undesirable effect of H₂O₂ decomposition could be reduced when working at acid pH (3.0),

where more efficient generation of hydroxyl radicals capable to efficiently oxidize organic matter were attained [40], as can be confirmed from the highest TOC kinetic constants obtained under this condition with both catalysts.

Also, to try to improve the efficiency of the H₂O₂ decomposition into more reactive hydroxyl radicals, the use of larger amounts of hydrogen peroxide concentration could lead to improve the final TOC removal. Therefore, double stoichiometric amount of H₂O₂ was employed with TiFe-0.7 catalyst and the obtained results were contrasted with those when oxygen and stoichiometric amount of H₂O₂ were used as oxidant agents at reaction pH 3.0. The comparison study is shown in Fig. 5 (note that the irradiation time is now longer than those shown in the previous figures.). Again iron lixiviates to the reaction medium can be neglected. From Fig. 5 results it can be concluded that the use of double of stoichiometric amount of hydrogen peroxide for phenol photodegradation at lower reaction pH is more efficient in the generation of reactive hydroxyl radicals during organic matter oxidation. In this operating condition final TOC conversion was almost 1.4 higher than when oxygen was used as oxidant agent [41,42].

Moreover, when double amount of H₂O₂ is employed an increase in the final conversion value around 90% of TOC together with 100% of H₂O₂ decomposition conversions at 430 min of irradiation time were detected. This is only slightly higher than the final conversions achieved under stoichiometric H₂O₂ conditions. All of that is also in agreement with the slightly higher kinetic constant values obtained for TOC constants, (3.2 and 5.2) × 10^{−3} min^{−1} for stoichiometric and double stoichiometric amount of hydrogen peroxide, respectively, whereas the TOC kinetic constant calculated when O₂ was used as oxidant was lower, 2.0 × 10^{−3} min^{−1}.

4. Conclusions

Two oxidant agents (O₂ and H₂O₂) have been employed for the photodegradation of phenol over TiO₂ and Fe-doped TiO₂ catalysts. It has been demonstrated that the reaction conditions employed are crucial for the efficient generation of reactive hydroxyl radicals capable to oxidize organic matter.

In this sense, when O₂ was used as oxidant agent at reaction pH 6.0 it could be clearly observed a TOC maximum conversion with titania un-doped catalyst. However, in spite of the fact that TiFe-0.7 catalyst has demonstrated to be less efficient for the degradation of phenol at reaction pH 6.0 when oxygen was used as oxidant, it displays an optimum iron doping level inside anatase structure that introduces important changes in its catalyst properties favoring phenol photodegradation with hydrogen peroxide.

Significant differences in the catalyst surface acid/basic character were detected as a consequence of the lower pH employed during the reverse microemulsion preparation method. In this sense, iron-doped titania catalyst with acid surfaces favor phenol photodegradation at lower reaction pH used when hydrogen peroxide was employed as oxidant agent.

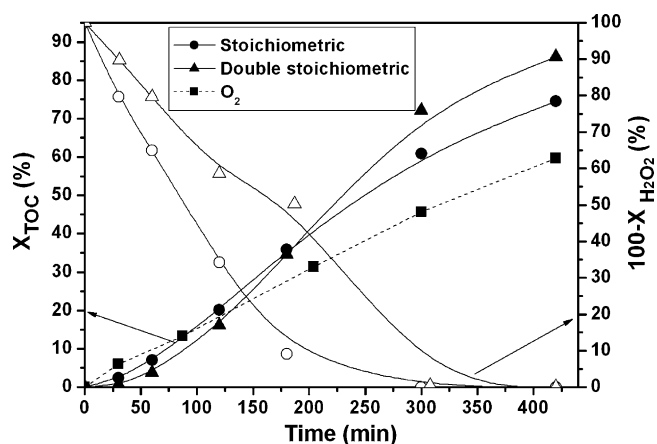


Fig. 5. Influence of type and concentration of oxidant agent on phenol photodegradation with TiFe-0.7 catalyst. TOC conversions (full symbols) and H₂O₂ conversions (open symbols). Operating conditions using H₂O₂—stoichiometric: [phenol]₀ = 50 mg L^{−1}; [H₂O₂]₀ = 250 mg L^{−1}; pH_{reaction} 3. Double stoichiometric: [phenol]₀ = 50 mg L^{−1}; [H₂O₂]₀ = 500 mg L^{−1}; pH_{reaction} 3. Operating conditions using O₂: [phenol]₀ = 50 ppm; [O₂]₀ = 100 N mL min^{−1}; pH_{reaction} 3.

Finally, an iron-doped titania catalyst, TiFe-0.7, with a lower surface area, a relatively higher anatase crystal size and slight acid surface has demonstrated to be very active in the photodegradation of phenol when H₂O₂ was used as oxidant agent with double stoichiometric amount of oxidant at reaction pH 3.0.

Acknowledgements

The authors would like to thank the MEC projects CTQ2004-03409/BQU, CTQ2006-15600/BQU and CTM2007-60577/TECNO and CSIC (project PIF 200420F0280) for financial support.

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