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Photocatalytic degradation of 2-phenylphenol on TiO_2 and ZnO in aqueous suspensions

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Abstract

The degradation of 2-phenylphenol (OPP), commonly used as fungicide, can be photocatalysed by TiO_2 and ZnO. The latter is a little more efficient but cannot be used in acidic solution. In both cases, the main identified photoproducts are hydroquinone (HQ), *p*-benzoquinone (BQ), phenylhydroquinone (PHQ), phenylbenzoquinone (PBQ), 2,2′- and 2,3-dihydroxybiphenyls (2,2′- and 2,3-$BPh(OH)_2$). The observed minor formation of 2-hydroxydibenzofuran is due to the photocyclisation of PBQ.

The influence of various parameters is considered. The phototransformation of OPP is slightly favoured by increasing pH. It is enhanced by the addition of small amounts of H_2O_2, but it is inhibited by high concentrations of chloride, sulphate or nitrate. From the inhibiting effect of alcohols, it is deduced that the main degradation pathway involves hydroxyl radicals, but a direct oxidation by positive holes h^+ is probably not negligible. The observed slow photodegradation of ZnO in unbuffered solution is attributed to an electrochemical process. A mechanism is proposed for the photocatalytic transformation of OPP.

Keywords: 2-Phenylphenol; Photodegradation; Positive holes h^+

1. Introduction

Many phenolic compounds are commonly used as solvents or reagents in industrial processes and therefore they are the common contaminants in industrial waste water [1,2]. In the past several years, many studies have been reported concerning the photocatalytic transformation of phenolic compounds using suspensions of semiconductors [3–6].

Absorption of light by TiO_2 or ZnO promotes an electron (e^-) from the valence band to the conduction band, creating a positive hole (h^+) in the valence band. Most often, oxygen play the role of electron trap [7,8]. In aerated aqueous suspension, oxygen is reduced to $O_2^{\bullet -}$ by electrons promoted in the conduction band. Positive holes oxidize HO^- or H_2O with the formation of hydroxyl radicals. These species has been identified by electron spin resonance (ESR) [9]. From available results, it can be suggested that the majority of organic substrate is oxidized by $HO^{\bullet}$, it has also been suggested that direct oxidation of the substrate by positive hole (h^+) can occur [10,11].

2-Phenylphenol (OPP) is commonly used as a fungicide and its fate in the environment is an important question. A few papers have appeared in the last decade on its transformation. In air-saturated unbuffered solution, the main photoproducts are phenylhydroquinone (PHQ), phenylbenzoquinone (PBQ) and 2-hydroxydibenzofuran resulting from the photocyclisation of PBQ [12,13]. Two other photoproducts favoured by acidic medium result from the opening of the phenolic ring [14]. In the absence of oxygen, no photoproducts could be detected.

The oxidation of OPP can also be photoinduced: the excitation of azidopentaamine cobalt(III), ($[Co(NH_3)_5N_3]^{2+}$) in neutral solution leads to the formation of adducts (dihydroxytetraphenyls) [15], whereas the excitation of nitrate ions, the main photoproducts initially formed, are dihydroxybiphenyls and hydroxynitrobiphenyls [16]. Actually the photolysis of NO_3^- excited near 300 nm leads to the formation of hydroxyl radicals and nitrogen dioxide. To our knowledge the photocatalytic transformation of OPP was not reported in literature.

The aim of the present work is the study of the photocatalyzed transformation of OPP in the presence of ZnO and TiO_2 irradiated between 300 and 450 nm and the determination of the influence on the degradation of various parameters, such as pH, initial OPP concentration, the presence of inorganic ions or hydrogen peroxide. The inhibiting influence of alcohols, namely ethanol and *tert*-butanol, commonly used to quench hydroxyl radicals, brings

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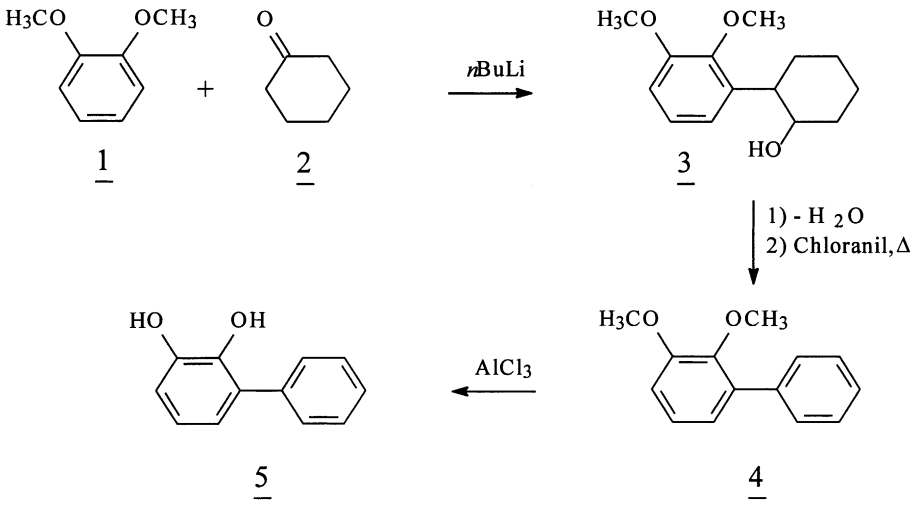


Scheme 1. Synthesis of 2,3-dihydroxybiphenyl.

informations about reactive species involved in the reaction. A mechanism is proposed.

2. Experimental

2.1. Chemicals

Analytical standards: PHQ Janssen; PBQ Eastman; 2,2′-dihydroxybiphenyl Merck; 2-phenylphenol 99%, Aldrich. 2-Hydroxydibenzofuran was isolated in the transformation of PBQ [13].

Most of the experiments were carried out with zinc oxide which was provided by Vieille Montagne SA (France). Its specific area is $9.4\,m^2\,g^{-1}$. The main impurities are Cd (3.5×10^{-3}), Fe (2×10^{-4}) and Pb (10^{-4}). Titanium dioxide Degussa P25 was also used for comparison. It is predominantly anatase (80% anatase, 20% rutile), with a surface area of $50\pm5\,m^2g^{-1}$ and small amounts of SiO_2 and Al_2O_3 [17].

For quantitative measurement (specially in HPLC analysis, monitored by UV spectroscopy) an authentic sample of 2,3-dihydroxybiphenyl was needed. It was synthesized according to the following procedure.[1] The four-stage synthesis is summarized in Scheme 1. Condensation of 2,3-dimethoxyphenyl-lithium (obtained by reaction of *n*-butyl-lithium with Veratrole **1**) with cyclohexanone **2** yield 2-(2,3-dimethoxyphenyl)-cyclohexan-1-ol, **3** as intermediate to the corresponding unsaturated compound, after splitting off a molecule of water, according to the method of Bergmann et al. [18]. Subsequent dehydrogenation, with chloranil in boiling xylene, afforded the dimethoxybiphenyl compound **4**. From this product, the desired compound **5** was obtained in good yield by demethylation with aluminium chloride in chlorobenzene, as described by Bruce and Sutcliffe [19]. Obtention of analytical sample could be achieved by sublimation. M.p.: 114°C (hexane). λ_{max} (dioxane): 253 and 292 nm. The structures of the synthetic products as well as photoproducts were controlled by ^{1}H- and ^{13}C-NMR on Bruker AC 400 spectrometer (Blaise Pascal University).

2.2. Reactors and light sources

The experimental device used for irradiation has been described elsewhere [6]. The reaction mixture consists of 20 ml of OPP (5×10^{-4} M) and 0.04 g of ZnO or TiO_2 ($2\,g\,l^{-1}$) stirred for 30 min before being irradiated. The initial pH of the suspension was 6.6 with ZnO and 5.9 with TiO_2 P25. Light intensity received by the reactor were evaluated with potassium ferrioxalate to be about 4×10^{15} photons $cm^{-3}\,s^{-1}$.

2.3. Analyses

UV spectra were recorded on Secoman 1000 PC. After irradiation, solutions were filtered through 0.45 μm Millipore filter to remove ZnO and TiO_2 and analysed with HPLC and GC–MS. A Waters HPLC chromatograph equipped with a μ-Bondapack 250 mm × 4.6 mm C_{18}-type column was used. Eluent was a mixture MeOH/H_2O 50:50 (v/v). Products were detected at 280 nm with an LC Spectrometer Lambda-Max 481. For GC–MS analyses, the products were extracted with ether and the resulting solution were injected in a capillary column FS SE 30 length 25 m, i.d. 0.25 mm. The spectrometer was Nermag service 32 equipped with FID detection.

The electrochemical measurements were performed with a three-electrode system. The collector electrode was a Pt foil (area, 0.1 cm^2). The counterelectrode was a Pt wire separated from the compartment containing the semiconductor

[1] Subsequent detailed data on request.

suspension by a glass-frit. A calomel electrode (CSE) was used as reference. Potential control of collector electrode was achieved with a Tacussel model potentiostat.

The concentration of Zn^{2+} was determined polarographically by a Tacussel polarograph. Before each polarographic analysis, ZnO was removed by filtration through 0.45 μm Millipore filter. The concentrations of H_2O_2 were measured according to an adaptation of the method suggested by Petruj and Marchal [20] for the titration of hydroperoxides.

3. Results and discussion

3.1. Kinetics of OPP disappearance in the presence of TiO_2 and ZnO

A comparative study of the photocatalytic transformation of OPP ($C_0 = 5 \times 10^{-4}$ M) in the presence of ZnO and TiO_2 (2 g l^{-1}) in aqueous suspensions was carried out. Suspensions were irradiated at $\lambda > 300$ nm. As it appears in Fig. 1, the kinetics of disappearance of OPP is faster with TiO_2 than with ZnO. It was initially controlled that in both cases, no photocatalytic degradation was observed in absence of radiation. The slow transformation observed in the absence of photocatalyst is due to the absorption of OPP near 300 nm when there is no screen effect by TiO_2 or ZnO. This direct phototransformation can be neglected in the presence of photocatalyst.

3.2. Effect of the initial concentration

It appears in Fig. 2 that the initial rate r_0 increases with increasing C_0. This variation has been treated according to a Langmuir–Hinshelwood-type relation [21,22]

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{kKC_0}$$

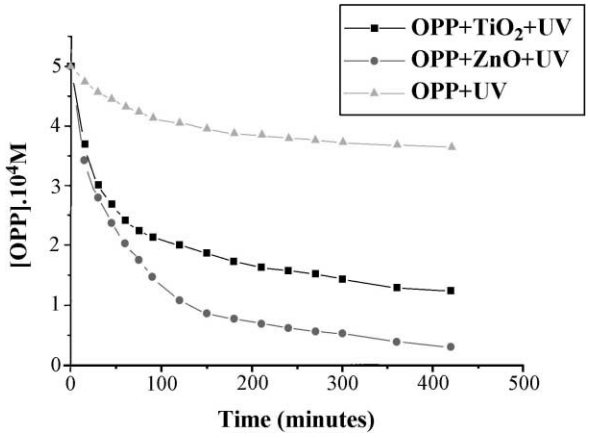


Fig. 1. Kinetic of the photocatalytic transformation of OPP (5×10^{-4} M) with ZnO, TiO_2 (2 g l^{-1}) and without photocatalyst. Irradiation in the range 300–450 nm.

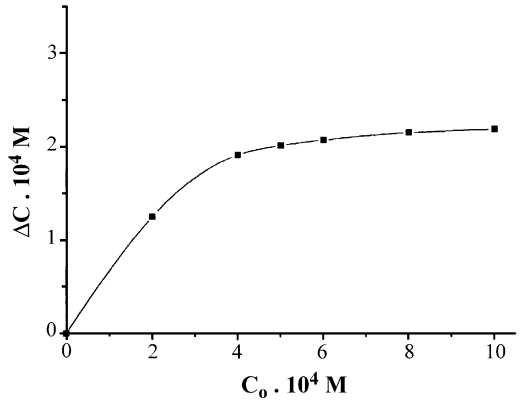


Fig. 2. Influence of the initial concentration on the phototransformation of OPP after 20 min irradiation in the presence of ZnO 2 g l^{-1}.

Table 1
Rate constants and adsorption constants on ZnO and TiO_2

	K (mol^{-1} l)	k (mol^{-1} l s^{-1})	θ
ZnO	7370	9.7×10^8	0.78
TiO_2	6205	18.2×10^8	0.75

where k and K are the rate and adsorption constants, respectively, and θ the fraction of the surface of photocatalyst covered by the substrate. The plot $1/r_0$ vs $1/C_0$ enables the determination of K. The results are given in Table 1.

3.3. Intermediate photoproducts

The photocatalytic transformation of OPP on ZnO leads to a mixture of photoproducts (Fig. 3). The formation of HQ, BQ, PHQ, PBQ and 2,2′-dihydroxybiphenyl (2,2′-$BPh(OH)_2$) was deduced from the comparison of HPLC retention times with those of authentic samples. The formation of PHQ, PBQ and 2,2′-$BPh(OH)_2$ was confirmed by GC/MS coupling. Besides, the presence of 2,3-$BPh(OH)_2$ has been identified by GC/MS and confirmed by NMR. 2-Hydroxydibenzofuran (2-DBFOH) is a minor secondary photoproduct resulting from the photocyclisation of PBQ formed in the first stage of the reaction. It has been identified by comparison with an irradiated solution of PBQ in acetonitrile. Actually it was previously reported that the irradiation of PBQ in acetonitrile leads to the formation of 2-DBFOH with a good yield [13]. It appears after long irradiations (≥420 min). The photoproduct characterized by a retention time equal to 4.70 min was not identified. The quantification of the main identified products formed in the photocatalytic transformation of OPP in ZnO and TiO_2 suspensions is given in Table 2.

In aqueous ZnO suspension, HQ, BQ, PHQ, PBQ and 2,3-$BPh(OH)_2$ were the main products obtained; 2,2′-$BPh(OH)_2$ was also formed in appreciable amounts (Fig. 4). With TiO_2, the main products were PBQ, PHQ,

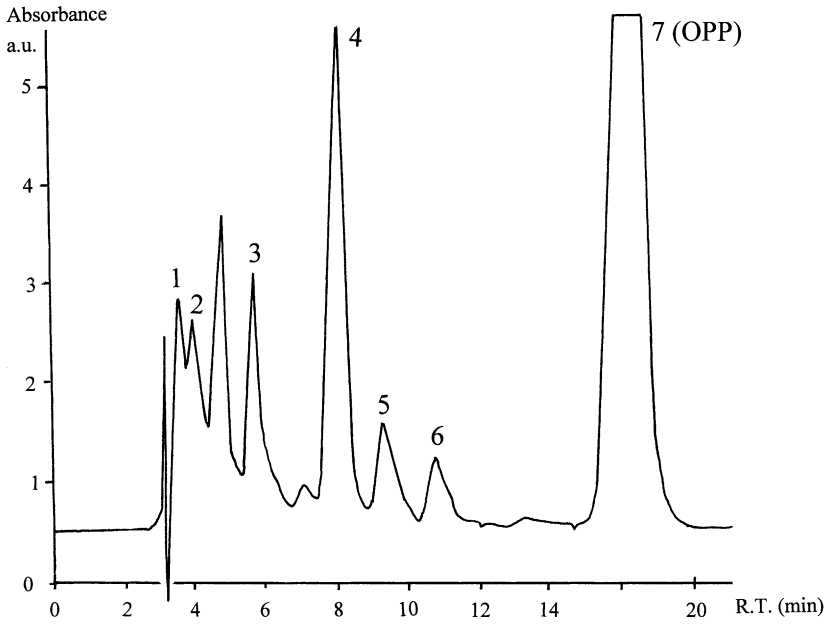


Fig. 3. HPLC chromatogram of an aqueous solution of OPP irradiated during 90 min HPLC Eluent: MeOH/H_2O 50:50 (v/v). Detection at 280 nm. 1: HQ; 2: BQ; 3: PHQ; 4: 2,3-BPh$(OH)_2$; 5: 2,2′-BPh$(OH)_2$; 6: PBQ; 7: OPP. A minor formation of 2-DBFOH was detected at 19.2 min in solutions irradiated during 7 h (not represented here).

Table 2
Photoproducts quantitatively identified in the photocatalytic transformation of OPP (5×10^{-4} M) after 30 min irradiation

	Conversion extent	HQ (%)	BQ (%)	PHQ (%)	PBQ (%)	2,2′-BPh$(OH)_2$ (%)	2,3-BPh$(OH)_2$ (%)
ZnO	0.346	18.44	10.33	11.89	8.44	1.01	23.58
TiO_2 (P25)	0.263	Traces	Traces	3.34	7.07	0.23	1.15

2,2′-BPh$(OH)_2$ and 2,3-BPh$(OH)_2$ (Fig. 5). In these conditions, only traces of HQ and BQ were detected. It is noteworthy that HQ is the main product in aqueous ZnO suspension, but a minor product in aqueous TiO_2 suspension. After 30 min under irradiation, the concentration of PHQ was eight times higher in aqueous ZnO suspension than TiO_2.

3.4. Influence of various factors on the photocatalytic degradation of OPP

3.4.1. pH

pH of the suspension is an important parameter in the reaction taking place on semiconductor particle surfaces, since it is related to the surface charge properties of the

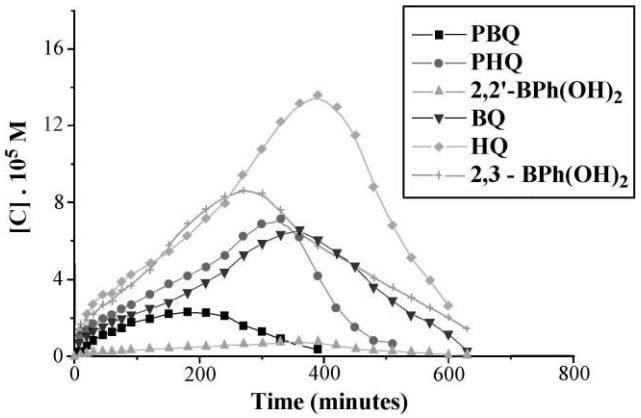


Fig. 4. Concentration of identified photoproducts formed in a solution of OPP (5×10^{-4} M) irradiated in presence of ZnO vs irradiation time.

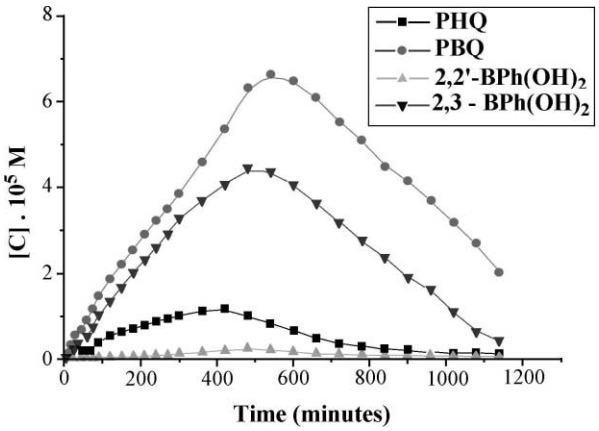


Fig. 5. Concentration of identified photoproducts formed in a solution of OPP (5×10^{-4} M) irradiated in presence of TiO_2 vs irradiation time.

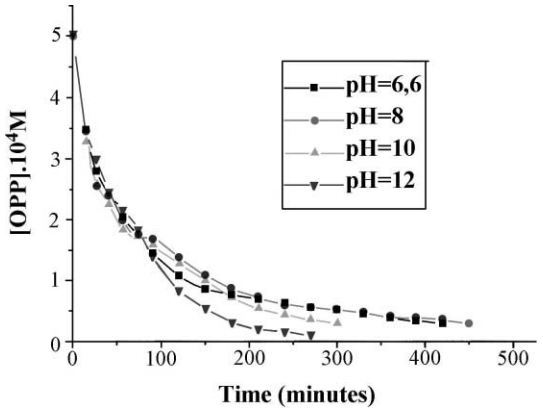


Fig. 6. Influence of pH on the phototransformation of OPP (5×10^{-4} M) in presence of ZnO.

photocatalyst. The effect of pH on the rate of photodegradation of OPP was examined in the range 6.6–12 in an aqueous ZnO suspension. The results are depicted in Fig. 6. The enhancing effect of increasing pH was due to a more efficient formation of $HO^{\bullet}$ from HO^{-} than from H_2O, or to a higher oxidability of the anionic form of OPP in comparison with the molecular form.

3.4.2. Inorganic ions

Solutions of OPP (5×10^{-4} M) were irradiated between 300 and 450 nm in the presence of various amounts of sodium chloride, sulphate and nitrate. Results are presented in Fig. 7. It clearly appears that a large amount of these anions negatively affects the degradation rate of OPP. This inhibition can be attributed to a competitive adsorption on the ZnO of these anions and molecules of substrate.

3.4.3. Addition of alcohol

Alcohols such as ethanol or *tert*-butanol are commonly used to quench hydroxyl radicals. The rate constant of the reaction between $HO^{\bullet}$ and ethanol ($1.9 \times 10^{9}\,M^{-1}\,s^{-1}$) is higher than the rate constant with *tert*-butanol ($6.0 \times 10^{8}\,M^{-1}\,s^{-1}$) [23]. It was observed that small amounts of ethanol or *tert*-butanol inhibit the photocatalytic transformation of OPP (Fig. 8). It can be deduced that hydroxyl radicals play a major role in the transformation.

The inhibition is more efficient with ethanol than with *tert*-butanol that is consistent with the different rate constants. However, the efficiency of the inhibition decreases with increasing concentration. With 0.6% (or more) of ethanol, the photocatalytic reaction is 84% inhibited (Fig. 9). In other words the inhibition does not obey the Stern–Volmer law

$$\frac{\phi_0}{\phi} = 1 + k\tau\,[\text{alcohol}]$$

where ϕ_0 and ϕ are the quantum yields of the transformation in the absence and in the presence of quencher, respectively, k the rate constant of the quenching and τ the lifetime of the reacting species.

Thus the transformation is not only due to hydroxyl radicals. Another reactive species, which does not react with alcohols, is necessarily involved. This species are most

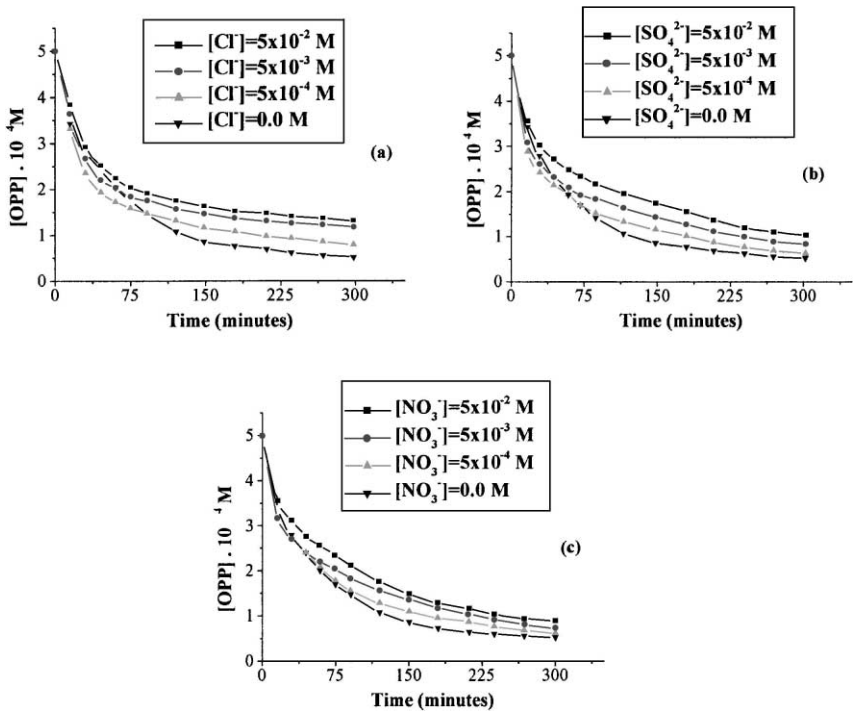


Fig. 7. Influence of inorganic salts on the phototransformation of OPP (5×10^{-4} M) in presence of ZnO ($2\,g\,l^{-1}$): (a) chloride; (b) sulphate; (c) nitrate.

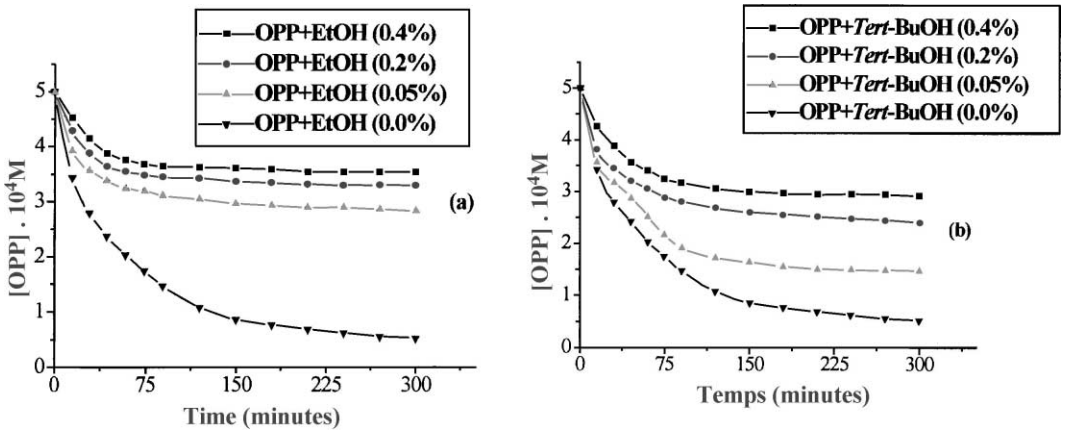


Fig. 8. Inhibition of the photocatalytic transformation of OPP (5×10^{-4} M) by alcohols: (a) ethanol; (b) *tert*-butanol (%, v/v).

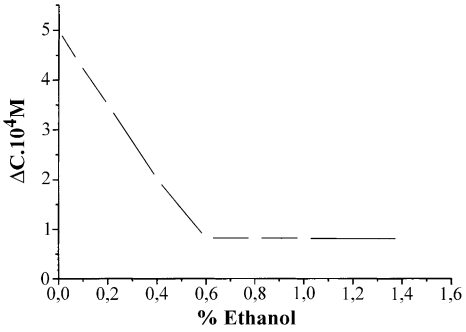


Fig. 9. Limit point of inhibition of photocatalytic transformation of OPP (5×10^{-4} M) by ethanol.

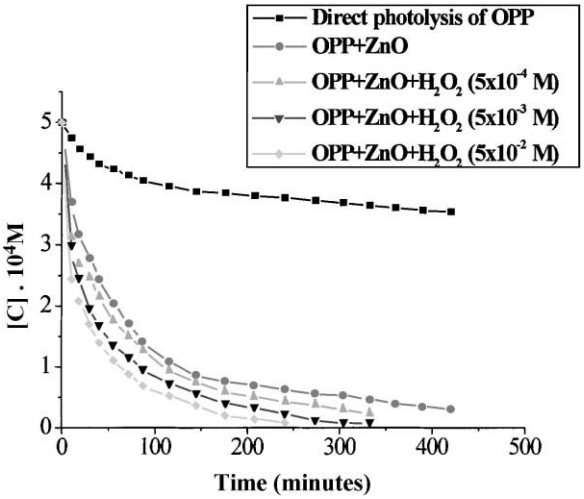


Fig. 10. Influence of H_2O_2 on the photocatalytic transformation of OPP (5×10^{-4} M) in the presence of ZnO.

probably positive holes h^+ formed on the irradiated photocatalyst, which react with the adsorbed molecules. Similar phenomenon was previously reported in the cases of monochlorophenols and 2,4-dichlorophenol — the reaction is 60–70% inhibited whatever be the concentration of ethanol in the range 0.1–2% and it was concluded that h^+ accounts for 30–40% of the transformation [24,25]. In contrast, it was reported that the photocatalytic transformation of dichlorobenzenes is completely inhibited by ethanol 1% (i.e. 0.17 M) indicating that the reaction is only due to hydroxyl radicals [26].

The concentrations of the main quantified photoproducts formed in the presence or in the absence of alcohols are given in Table 3. It appears that the formation of PBQ is less inhibited by alcohols than the formation of the other photoproducts. It can be deduced that h^+ plays a more significant role in the formation of PBQ than in the formation of hydroxylated products.

3.4.4. Addition of hydrogen peroxide

The photocatalytic degradation of OPP has been studied at three different hydrogen peroxide concentrations (5×10^{-4}, 5×10^{-3}, 5×10^{-2} M). Results are given in Fig. 10. The rate of photocatalytic degradation of OPP on ZnO

Table 3
Concentrations, in mol l^{-1}, of OPP (5×10^{-4} M) and photoproducts in presence and absence of alcohol after 90 min reaction (% v/v)

	HQ	BQ	PHQ	2,2′-BPh(OH)$_2$	PBQ	OPP transformed
0% alcohol	4.26×10^{-5}	2.15×10^{-5}	2.69×10^{-5}	0.31×10^{-5}	1.76×10^{-5}	3.53×10^{-4}
0.05% ethanol	0.91×10^{-5}	0.45×10^{-5}	0.59×10^{-5}	0.05×10^{-5}	1.32×10^{-5}	2.08×10^{-4}
0.4% ethanol	0.59×10^{-5}	0.27×10^{-5}	–	–	0.44×10^{-5}	1.54×10^{-4}
0.05% *tert*-butanol	1.93×10^{-5}	1.07×10^{-5}	1.14×10^{-5}	0.28×10^{-5}	1.65×10^{-5}	3.0×10^{-4}
0.4% *tert*-butanol	0.91×10^{-5}	0.45×10^{-5}	0.36×10^{-5}	0.06×10^{-5}	0.4×10^{-5}	1.65×10^{-4}

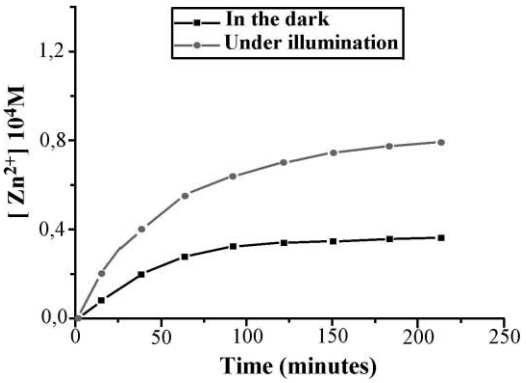


Fig. 11. Evolution of the concentration of Zn^{2+} produced from ZnO decomposition as a function of irradiated time in an aqueous solution of OPP (5×10^{-4} M) in the presence of ZnO ($2\,g\,l^{-1}$) in the dark and under irradiation.

increases with increasing hydrogen peroxide concentration. This effect is explained by radical mechanism. The added H_2O_2 accelerates the reaction by scavenging electrons and producing additional hydroxyl radicals [27].

$$ZnO + h\nu \rightarrow ZnO + e^- + h^+ \quad (1)$$

$$H_2O_2 + e^- \rightarrow HO^\bullet + HO^-, \quad k = 10^{10}\,M^{-1}\,s^{-1} \quad [23] \quad (2)$$

3.5. Photostability of ZnO

In the dark, some dissolution of ZnO was noted in stirred aqueous suspensions (0.04 g per 20 ml of a solution of OPP (5×10^{-4} M, pH = 6.6)), yielding an equilibrated concentration of Zn^{2+} equal to 0.35×10^{-4} M (Fig. 11). A larger concentration of Zn^{2+} was found when the samples were illuminated and Zn^{2+} concentration increases with increasing irradiation time. In air-saturated solution, a simultaneous formation of H_2O_2 was also observed. Photodecomposition of ZnO also occurs in the absence of oxygen, under argon bubbling. Under these conditions, no traces of H_2O_2 were detected. It was also noted that the concentration of Zn^{2+} increases with increasing amount of semiconductor. At pH = 10, no photocorrosion of ZnO takes place. At pH lower than 4.0, the dissolution of ZnO is complete, but it is due to a classical chemical process.

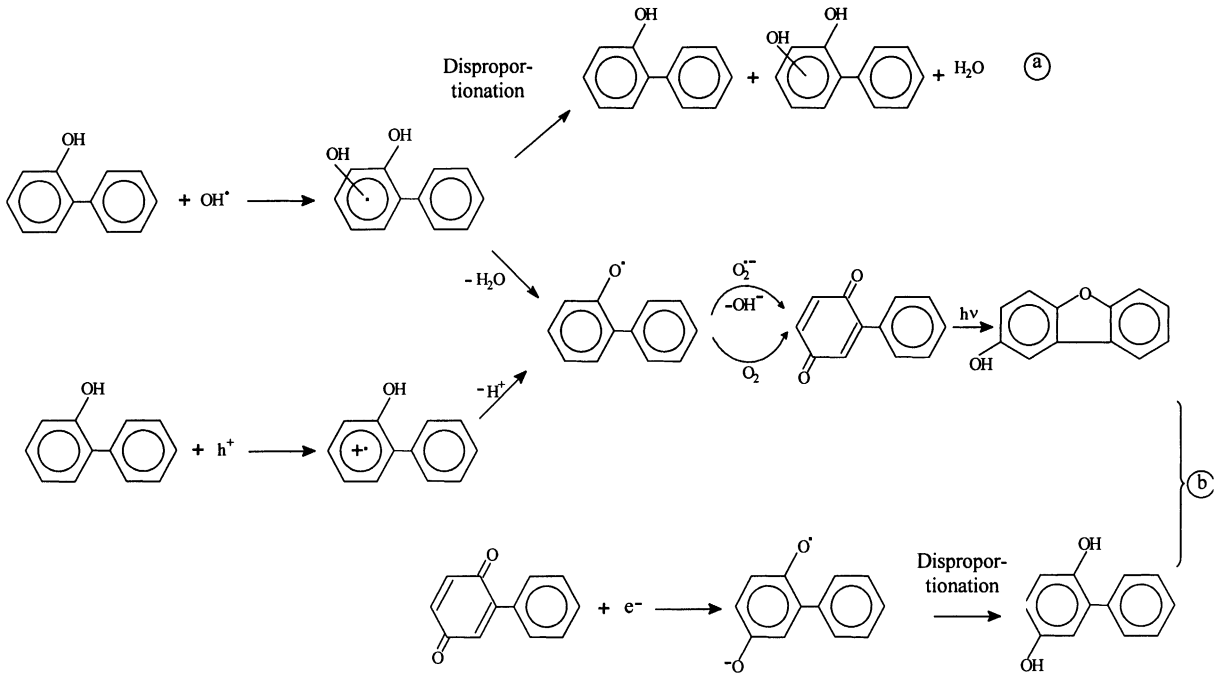
The dissolution of ZnO induced by light in neutral solution can be explained by the following mechanism. Absorption of light by ZnO promotes an electron (e^-) in the conduction band creating a positive hole (h^+) in the valence band (reaction (1)). In the presence of oxygen, e^- reduces O_2 into $HO_2^\bullet$ which disproportionate into O_2 and H_2O_2 (reactions (3)–(5)). In the absence of oxygen, e^- is assumed to reduce H^+ into H_2 or another organic species in the solution. The formation of Zn^{2+} is attributed to the oxidation of ZnO by h^+ as suggested by Fujishima et al. [28]. The intermediate oxygen species, O^* is assumed to oxidize some organic compounds in the solution.

$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (3)$$

$$O_2^{\bullet -} + H^+ \rightleftharpoons HO_2^\bullet \quad (4)$$

$$HO_2^\bullet + O_2^{\bullet -} + H^+ \rightarrow H_2O_2 + O_2 \quad (5)$$

$$ZnO + 2h^+ \rightarrow Zn^{2+} + O^* \quad [28] \quad (6)$$



Scheme 2. Proposed mechanism for the photocatalytic transformation of OPP.

The photodecomposition of ZnO (reaction (6)) is thermodynamically possible since the anodic dissolution potential of ZnO (+0.65 V vs SCE [29]) lies inside the semiconductor band-gap and is lower than redox potential for water oxidation.

4. Mechanism

The main pathway in the photocatalytic transformation of OPP involves an oxidation by hydroxyl radicals. The formation of the main primary photoproducts result from *ortho* and *para* hydroxylation with respect to phenol function. This orientation is consistent with the electrophilic behaviour of hydroxyl radicals.

The first step of the photocatalytic degradation of OPP in the presence of ZnO or TiO_2 is the formation of an intermediate adduct between OPP and $HO^{\bullet}$. The formation of such an adduct was suggested by Land and Ebert [30] in the radiolysis of phenol. This adduct (OPP–$HO^{\bullet}$) can disproportionate into OPP and dihydroxybiphenyl, as it was proposed by Cercek and Ebert [31] in the case of nitrophenol. It can also release a molecule of water with formation of a phenoxyl radical. This radical is probably involved in the formation of PBQ. The latter absorbs near UV and visible light and in a second stage it is photocyclized into 2-hydroxydibenzofuran. PBQ can also be reduced on the photocatalyst into PHQ by e^- promoted in the conduction band. Such a reaction was previously observed with BQ and methylbenzoquinone [32].

The formation of unsubstituted BQ is explained by the reaction of the hydroxyl radical in position 1 (junction of rings), leading to pyrocatechol and benzyl radical oxidized into BQ. It was experimentally proved that pyrocatechol is spontaneously oxidized on ZnO and consequently it cannot be detected in the solution.

In the presence of ethanol, $HO^{\bullet}$ are scavenged and the reaction is partly inhibited, but similar oxidations can be generated by positive holes h^+ as it was proposed by Peral et al. [11] and Hashimoto et al. [33], with this difference that $HO^{\bullet}$ and h^+ have sligthly different specificities [34]. The proposed mechanism is summarized in Scheme 2.

5. Conclusion

OPP can be photocatalytically degraded on both ZnO and TiO_2. The reaction is slower with TiO_2. Similar reactions were observed on both photocatalysts, but the mass balance was better with ZnO and the proportion of product different.

The main photoproducts initially formed result from hydroxylation of the phenolic ring or from the scission between both rings. Hydroxylations occurs preferentially in *ortho* and *para* position with respect to the phenol function in good agreement with the electrophilic properties of hydroxyl radicals. The photocyclisation of PBQ into 2-hydroxydibenzofuran has also been observed.

The efficiency of photocatalytic oxidation rate increases with increasing pH and by addition of small amounts of H_2O_2, but it is reduced by high concentration of inorganic salts (chloride, sulphate and nitrate).

Hydroxyl radicals are the main reactive species, but positive holes h^+ are probably also involved, since the inhibition by alcohols does not obey Stern–Volmer law.

ZnO cannot be used at pH lower than 4, and in unbuffered solution some photodecomposition of ZnO was observed.

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