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Homogeneous photo-oxidation of phenols: influence of metals [1]

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Abstract

The role of metal ions and their complexes in the photo-oxidation of phenols in homogeneous solution is reviewed and analysed. The mechanistic aspects of the data related to the photo-oxidation and photodegradation of phenols in a pure homogeneous phase, or via homogeneous pathways in a heterogeneous system, are discussed. The environmental importance (pollutant photodegradation and photomineralization) of metal-containing systems (mainly copper) is stressed (including Fenton and photo-Fenton reactions), and the future prospects in the field based on $M^{n+}/M^{(n-1)+}$ photoredox cycling are described. © 1997 Elsevier Science S.A.

Keywords: Fenton and photo-Fenton reactions; Metal complexes; $M^{n+}/M^{(n-1)+}$ photoredox cycle; Phenol photodegradation and photomineralization; Photocatalysis; Photo-oxidation

1. Introduction

The importance of phenol (photo)oxidation in industrial and environmental (photo)chemistry, as well as in biological systems, is well recognized. Oxidation reactions involving phenols and related compounds (e.g. quinones) are of interest by virtue of their important roles as antioxidants [1] and polymer photostabilizers [2]. Phenols pose a significant threat to the environment and are commonly found as dilute contaminants in groundwater and surface water [3–6]. Phenolic compounds are toxic to aquatic life and have the ability to impart tastes and odours to drinking water, even at parts per billion levels [7].

The simultaneous coupling of photolysis with an oxidant, often referred to as advanced oxidation processes (AOPs) or advanced oxidation technologies (AOTs), has demonstrated its usefulness in new routes for the photo-oxidation and photodegradation of organic substrates (OSs), as well as in promising approaches to solve environmental problems. Vigorous research has demonstrated that TiO_2 as catalyst causes the complete photo-oxidation of phenols (as well as a number of other pollutants) to innocuous products, such as water, carbon dioxide and simple mineral acids [8–12]. Interestingly, as shown in a number of studies (see, for example, Ref. [13]), the effectiveness of the catalytic photo-oxidation of pollutants in such systems is influenced significantly by the addition of metal ions and their complexes (e.g. copper). For example, the rate of phenol photo-oxidation is enhanced when cupric species are added to the heterogeneous (TiO_2 catalyst) system [14,15]. It has been suggested [16] that the enhanced rate of pollutant photo-oxidation arises from a homogeneous pathway, involving a copper complex, rather than through a TiO_2 surface process.

Therefore there are several reasons for studying the homogeneous photo-oxidation of phenol in the presence of metal ions and their complexes. Firstly, the environmental importance of phenol and phenolic compounds (also present as humic substances in aquatic systems) is increasing (toxicity; remedial measures required). Secondly, phenol oxidation has been suggested as a model reaction for the treatment of aqueous organic wastes using photochemical [17], electrochemical [18], radiolytic [19–21] and biological [22] procedures and sonochemistry [23]. Thirdly, the observation of enhanced photodegradation rates of phenol after the addition of metal ions via homogeneous pathways opens the way to new possibilities of improving the phenol degradation efficiency. In this context, metal complexes (mainly copper) are of interest due to their versatility and suitable (photo)redox properties. Finally, research devoted to the photo-oxidation of phenol in phenol–metal ion (complex) systems may lead to new and exciting findings of chemical, industrial, medical, biological and environmental importance. To our knowledge, no paper on this subject has yet been published.

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[1] Dedicated to Professor Horst Hennig.

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Table 1
TiO_2 photo-oxidation of phenols in the presence of metal ions (complexes)

System	Phenolic compound	Conditions	Metal ion (complex)	Effect of metal	Product(s)[a]	Reference
I	Phenol	TiO_2	Cu(II)	Positive/negative	CO_2	[15]
II	Monochlorophenol	TiO_2	Ag(I)	Positive	CO_2	[33]
III	Phenol	TiO_2	Ag(I), Fe(III)	Positive	CO_2	[29]
	Nitrophenol	TiO_2	Ag(I), Fe(III)	Positive	CO_2	[34]
IV	Phenol	TiO_2	Cu(II)	Negative	CO_2	[14]
V	Phenol	TiO_2	Cu(II) > 1 mM	Negative	Cu^0, Cu_2O	[35]
VI	Phenol	TiO_2	Fe(III)	Positive	CO_2	[14]
VII	Phenol	TiO_2/H_2O_2	Cu(II)	Positive	CO_2	[14,36]
VIII	Phenol	TiO_2/H_2O_2	Fe(III)	Positive	CO_2	[14,36]
IX	Phenol	TiO_2	Fe(II), Fe(III), Ag(I)	Positive	CO_2	[37]

[a] Only identified products are given.

Thus the photosensitivity of systems containing metal complexes and organic molecules may lead to many interesting phototransformations of organic molecules [24]. This paper focuses on one class of photoreaction: the photo-oxidation of phenols in the presence of metal ions and their complexes. The emphasis is on the homogeneous photo-oxidation of phenols within the Cu(II)/Cu(I) photocatalytic redox cycle developed in our laboratory. We also evaluate data on the homogeneous pathways of phenol photo-oxidation in heterogeneous systems containing M^{n+} ions.

2. Effect of metal ions in TiO_2–phenol systems

Polycrystalline TiO_2 (anatase) is an excellent catalyst in the non-aqueous [25] and aqueous photo-oxidation of a variety of aromatic substrates, such as phenol and its derivatives (for a review, see Ref. [26]). In the oxidation of phenol by photoactivated TiO_2 in aqueous medium, hydroquinone and catechol are the major products, together with smaller quantities of pyrogallol, 1,2-trihydroxybenzene and hydroxylbenzoquinone [15,27]. Similar hydroxylated species are identified in the photo-oxidation of 3-fluorophenol [28]. In addition to these hydroxylated compounds, often regarded as intermediates, the total photo-oxidation (photomineralization to CO_2) of phenol, cresols, fluorinated phenols [26] and nitrophenols [29] has been reported. The major oxidizing species in the photo-oxidation of most OSs (phenols included) is the $^{\cdot}OH$ radical [30,31], formed after the primary photochemical step (photogeneration of electron–hole pairs from illuminated TiO_2 particles). It has been suggested, for example, that when H_2O_2, O_2 and phenol are present in an aqueous dispersion containing TiO_2 (anatase), oxygen acts mainly as an electron trap and H_2O_2 acts mainly as a hole trap [29]. Both of these processes generate radical species capable of oxidizing phenol; as a consequence, phenol degradation can occur mainly through two parallel reaction pathways. Thus the photomineralization of many organic pollutants is greatly accelerated by H_2O_2. For example, it has been shown that 60 mM H_2O_2 leads to a ninefold increase in the rate of mineralization of 2-chlorophenol in the presence of TiO_2 [32]. There are also many examples in the literature in which the photo-oxidation of phenols is noticeably affected by the presence of metal ions. These systems (including TiO_2) are listed in Table 1.

The cupric ion can act as a positive or negative catalyst at different concentrations in the photocatalytic decomposition of phenol over TiO_2 powder [15] (system I in Table 1). The observed increase in the rate of photo-oxidation over TiO_2 after the addition of Cu^{2+} ions [15] has been attributed to electron trapping by the metal ions [38], which prevents electron–hole recombination and results in an increased concentration of $^{\cdot}OH$ radicals. The addition of Ag^+ to a TiO_2 (P25) suspension greatly increases the initial photocatalytic decomposition rates of monochlorophenols [33]. This increase is consistent with decreased hole–electron recombination due to electron localization on the adsorbed Ag^+ ions (system II). Moreover, the addition of Ag^+ ions [29] (system III) leads to the successful photocatalytic activity of originally inactive TiO_2 (rutile) dispersions (only the anatase form of TiO_2 is active towards phenol) [34]. The negative effect of Cu^{2+} in the absence of H_2O_2 [14] has been attributed [15] to severe short circuiting of the cupric ion, as the Cu(I)/Cu(II) couple creates a cyclic process without generating active hydroxyl radicals (systems I and IV). The observed inhibitory effect of dissolved Cu^{2+} ions at higher concentrations ($c(Cu^{2+}) > 1$ mM) on the photodegradation of phenol in the presence of TiO_2 (initial phenol concentration, 1 mM) has been explained by the photodeposition of metallic copper and Cu_2O onto the TiO_2 surface, which modifies the generation and recombination processes of charge carriers and radical intermediates [35] (system V). Added ferric ions induce, in the absence of H_2O_2 (system VI), the enhancement of phenol removal from 23% to 33% due to the photo-Fenton reaction within 8 h (total organic carbon (TOC) removal, 11%) [14]. However, in the presence of H_2O_2, both ferric and cupric ions enhance the rate of phenol photo-oxidation markedly [14,36] (systems VII and VIII). A solution of the same phenol concentration was completely photomineralized within 1 h and TOC removal reached 80%. This observation was explained in terms of the role played by metal ions as catalysts to decompose H_2O_2 [14,36,39].

Table 2
Homogeneous photo-oxidation of phenols in the presence of metal ions (complexes)

System	Phenolic compound	Conditions	Metal ion (complex)	Effect of metal	Product(s)^a	Reference
I	2-Nitrophenol	H_2O_2	Fe(III)	Positive	CO_2	[43]
	4-Nitrophenol	H_2O_2	Fe(III)	Positive	CO_2	[43]
II	4-Nitrophenol	H_2O_2	Fe(II)	Positive	HNO_3	[44]
III	4-Chlorophenol	H_2O_2	Fe(III)	Positive	CO_2	[45]
IV	Phenol	ACN/O_2	$CuCl_2$	Positive	Cu(I), pbq, dhb	[46]
V	Methyl-substituted phenols	ACN/O_2	$CuCl_2$	Positive	Cu(I), mbq	[47,48]
VI	Phenol	ACN/O_2	CuL_n	Positive	Cu(I), pbq	[49]
VII	Phenol	Water/O_2	$[Cr(bpy)_3]^{3+}$	Positive	pbq	[50–52]
VIII	Phenol	Water/O_2	$[Ru(bpy)_3]^{2+}$	Positive	pbq	[52]
IX	Phenol	Water	$[Ru(bpz)_3]^{2+}$	Positive	hpd	[52]
X	4-Chlorophenol	Water	$[Ru(bpz)_3]^{2+}$	Positive	hpd	[52]
XI	Phenol	Water/O_2	AlSPC, ZnSPC	Positive	pbq	[53]
XII	4-Chlorophenol	Water/O_2	AlSPC, ZnSPC	Positive	pbq	[53]
XIII	Catechol	Water/O_2	AlSPC, ZnSPC	Positive	n.d.	[53]
XIV	Phenol	ACN/water/O_2	CuL_n	Positive	Cu(I), CO_2, pbq	[54,55]
XV	Phenol	Water/O_2	CuL_n, $CuCl_2$	Positive	pbq, CO_2	[56]
XVI	Phenol	Water/O_2	CuL_n	Positive	pbq, CO_2	[57,58]

^{a}Only identified products are given.

Abbreviations used: ACN, acetonitrile; hpd, hydroxyphenyl dimers; pbq, *p*-benzoquinone; bpz, 2,2′-bipyrazine; dhb, dihydroxybenzene; AlSPC, sulphonated chloroaluminium phthalocyanine; ZnSPC, sulphonated zinc phthalocyanine; L = bpy, phen; bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; mbq, monomeric benzoquinones; n.d., not determined.

At the same time, the generation of ·OH radicals from the TiO_2 surface becomes less important [36].

The increase in the phenol and nitrophenol photo-oxidation rate after the addition of Fe^{3+} ions has also been explained in terms of the catalytic decomposition of H_2O_2 present in another system [29]. Thus the Fe^{3+} ion can be considered as a cocatalyst and mediator via the production of ·OH radicals in the homogeneous Fenton reaction (system III). The ions Fe^{2+}, Fe^{3+} and Ag^+ react very easily with the peroxo species produced on the catalyst surface and/or in solution, and thus positively influence the photodegradation of phenol in aqueous polycrystalline TiO_2 dispersions (system IX) [37].

The study of the effect of TiO_2 doping with transition metals on the photoactivity of the TiO_2 pigment has resulted in contradictory conclusions [40–42]. Doping with Mo, V, Al and Pb leads to a decrease in the photoactivity of TiO_2 (polycrystalline rutile powder) [40]. This effect was explained (based on surface photovoltage spectroscopy and photochemical measurements) by the fact that the d electrons of Mo(4d) and V(3d), as majority carriers in TiO_2, can effectively quench the photogenerated holes, at the impurity levels introduced by doping, within the bandgap of TiO_2 [40]. In contrast, the addition of copper to TiO_2 (anatase) increases the rate of phenol [41] and chlorophenol [42] decomposition due to facilitation of electron emission at the surface of the TiO_2 semiconductor [41].

3. Homogeneous phenol–metal ion (complex) systems

Heterogeneous and/or homogeneous reaction pathways have not always been distinguished unambiguously in the TiO_2 systems discussed above; there are many examples in which the photo-oxidation of phenols proceeds exclusively homogeneously. These systems include Fenton- and/or photo-Fenton-type reactions, photosensitization and photoredox cyclic processes (see Table 2).

The importance of the chemical oxidation of various substrates by hydroxyl radicals generated by Fenton's reagent and the utilization of this reaction in chemistry, biochemistry, environmental science and biology are well recognized [59]. Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron (Fe^{2+}) which produces ·OH radicals

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \qquad (1)$$

Other metal cations can be used in a lower oxidation state (e.g. Cu^+ [60]) giving a more general expression

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH^- + {}^{\cdot}OH \qquad (2)$$

The ·OH radicals produced in Eqs. (1) and (2) are capable of reacting with a variety of OSs resulting in their oxidation (degradation or mineralization).

A modification of the classical Fenton reaction, leading to an increase in yield, involves the so-called photo-Fenton reaction in non-aqueous [61,62] and aqueous [30,44,63] media. The main goal of the photo-Fenton reaction is the photochemical regeneration of Fe^{2+} (which is consumed in the classical Fenton reaction and leads to its termination) by the photoreduction of Fe^{3+} ions (complexes) present in the system.

The results of a study with 4-nitrophenol (systems I and II in Table 2) [43] have shown that the photo-Fenton reaction is a suitable method for the removal of nitrophenols (complete mineralization) in waste treatment plants. The degradation of 2-nitrophenol (3.6×10^{-3} mol dm^{-3} solution degraded in 3 h in the dark and 1 h under photo-Fenton conditions) proceeds at about half the rate of its homologue 4-nitrophenol (system I). This observation was explained [43] by the fact that, in the case of hydroxylated 4-nitrophenol, the two bonds between the adjacent OH groups can undergo easy oxidative scission, but only one bond of this type is found in hydroxylated 2-nitrophenol (because the withdrawing effect of the nitro group is greater in the ortho and para positions). It has been shown [44] that irradiation of 4-nitrophenol (1×10^{-4} mol dm^{-3}) in the presence of Fenton's reagent (3.5×10^{-5} mol dm^{-3} $FeCl_2+8\times10^{-3}$ mol dm^{-3} H_2O_2) accelerates the degradation of phenol significantly (total decomposition in approximately 100 min) compared with the rate in the dark Fenton system (system II) (total decomposition after approximately 250 min). The Fenton reaction has been suggested as the preferred method for the elimination of 2-nitrophenol and 2,4-dinitrophenol from water and wastewater [64]. The positive photoirradiation effect has been explained in terms of the different (increased in comparison with the ground state) reactivity of the 4-nitrophenol molecule in the excited state (which is more susceptible to electrophilic substitution by hydroxyl radicals), the direct photolysis of H_2O_2 (more $^{\cdot}OH$ formed) and the photo-Fenton reaction. The photo-Fenton reaction has also been used for the photomineralization of 4-chlorophenol (system III) in water [45]. The total mineralization of a solution of 1.01×10^{-3} mol dm^{-3} 4-chlorophenol (containing 2.5×10^{-4} mol dm^{-3} Fe^{2+} + 1.01×10^{-2} mol dm^{-3} H_2O_2) was reached in 30 min. Although the nature and composition of the photochemically active Fe(III) species leading to Fenton-active Fe(II) were not determined, the increased efficiency and advantage of the photo-Fenton reaction (small amount of iron used, accelerated degradation by irradiation, TOC value significantly reduced) in comparison with the classical Fenton reaction were clearly demonstrated in this study.

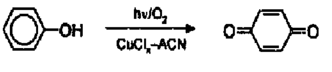
In recent decades, a large number of investigations have been carried out on the photochemical transformations of phenolic compounds by direct [65–70] and indirect (in the presence of a photosensitizer) irradiation. The role of singlet molecular oxygen as an agent for the environmental degradation of aquatic phenolic pollutants (predominantly in metal-free systems) has recently been reviewed [71].

The catalytic and non-catalytic thermal oxidations of phenols by transition metal oxidants (e.g. complexes of Mn, Co [72], Ru [73], Cr [74,75], etc.) have been studied in detail [76,77]. For example, the oxidation of phenol by the pentaaquachromium(IV) ion ($(H_2O)_5CrO_2^+$) in acidic aqueous solution yields *p*-benzoquinone (pbq) as a major product [75]. The oxidation of substituted phenols by dioxygen in the presence of copper complexes as catalysts has been the subject of several studies (for a review, see Ref. [78]). These phenol oxidations usually lead to a mixture of quinones, dimers and polymers (e.g. polyphenylene oxides). Copper halides in acetonitrile (ACN) have been claimed [79] to be particularly effective for pbq production from phenol in good yield, but only at pressures greater than 10 100 kPa (100 atm) of dioxygen [80] or at elevated temperature [79].

It should be noted that the majority of such systems have been studied mainly in the dark (thermal oxidation), and very little attention has been paid to the photochemistry of phenol oxidation in the presence of copper catalysts.

In order to extend the application of copper complexes [81–84] as catalysts in the oxidation of OSs [85–87], we undertook a study of a novel route of phenol photochemical oxidation under very mild experimental conditions (room temperature, atmospheric pressure) within the photocatalytic Cu(II)/Cu(I) redox cycle developed in our laboratory [88].

This photoredox cyclic process is based on the photoreduction of the Cu(II) metal centre [89] (visible irradiation in the region of the lowest, spin-allowed, charge transfer excited state of the $CuCl_x$ complex in ACN) and the concomitant oxidation of the Cl^- ligand to the $Cl^{\cdot}$ radical (strong oxidizing agent towards OSs). When O_2 is present, the photochemically formed Cu(I) is re-oxidized to Cu(II), thus closing the cycle. Moreover, a strong dependence of the yield of photo-oxidized OS on the composition of the CuL_x catalyst has also been observed [90–93]. For example [91], the oxidation driving force of chlorocopper(II) complexes in ACN decreases with increasing number of chloro ligands in the coordination sphere of $CuCl_x$. This observation opens up the possibility of the useful control and tailoring of copper catalyst properties. It was found [46,92–95] that the irradiation of a homogeneous solution of phenol–CuL_x–O_2–ACN (typical experimental conditions: $c(CuCl_x)=10^{-1}$–10^{-3} mol dm^{-3}, phenol in excess, medium-pressure Hg lamp, $\lambda_{irr}>315$ nm) leads to the formation of pbq



(3)

A substantial enhancement of the pbq yield (system IV in Table 2) in irradiated systems (by two- to fourfold with respect to the dark reaction [46,94]) has been found.

The photocatalytic redox cycle can be represented by a sequence of equations

$$Cu(II)Cl_x \xrightarrow{h\nu} Cu(I)Cl_{x-1} + Cl^{\cdot} \tag{4}$$

$$Cu(I)Cl_{x-1} + O_2 \xrightarrow[(H^+)]{L} Cu(II)Cl_x + O_2^{\cdot -} \tag{5}$$

$$Cl^{\cdot} + PhOH \rightarrow PhO^{\cdot} + HCl \tag{6}$$

$$PhO^{\cdot} + O_2^{\cdot -}(O_2) \xrightarrow{(H^+)} \text{quinone (hydroxo derivatives)} \tag{7}$$

The continuous irradiation of an ACN solution of cuprous chloro complexes [47,48] in the presence of *o*-cresol, *m*-cresol, *p*-cresol, 2,4-dimethylphenol and 2,5-dimethylphenol (system V) leads to a very effective (98% yield, 98% selectivity and 100% conversion) phototransformation of phenol to monomeric quinones

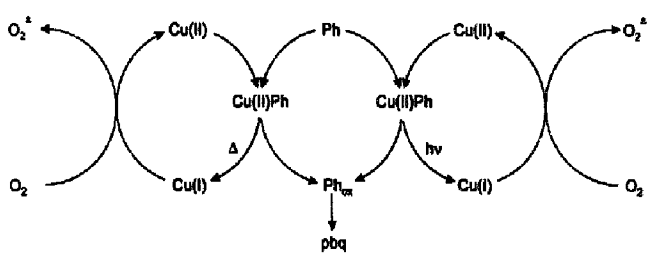
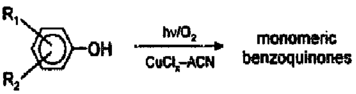


Fig. 1. Phenol-to-pbq (photo)transformation in the presence of CuL$_2$ complexes (λ_{irr} > 315 nm) (Ph, phenol; Ph$_{ox}$, phenoxy radical; pbq, *p*-benzoquinone; L ≡ phen or bpy).

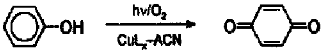


(8)

where R$_1$, R$_2$ ≡ H and/or CH$_3$.

Although the importance of the presence of chloride in the copper catalyst [46,93,94,96] has been emphasized, the formation of pbq from phenol has also been observed in the absence of chloride using, for example, Cu(II) sulphate or copper complexes with 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) [49,97–100].

Continuous irradiation of a mixture of cuprous bpy (or phen) complex and phenol in ACN solution in the presence of dioxygen with visible light (system VII) leads to the formation of pbq [49,100–102]



(9)

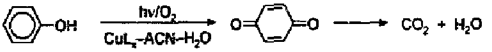
where L ≡ bpy or phen.

The amount of pbq formed was estimated to be approximately ten times higher than the corresponding stoichiometric concentration of Cu(I) catalyst used under dark and photolysis conditions. The enhancement of pbq formation [49,100] on photolysis (with respect to dark conditions) was found to be 161% and 214% using $[Cu(bpy)_2]^+$ and $[Cu(phen)_2]^+$ complexes respectively. The overall reaction scheme of phenol-to-quinone aerobic oxidation, catalysed by Cu(I) bpy and phen complexes, involves dioxygen activation, phenoxy radical formation and at least one photochemical step (Fig. 1).

As shown in Fig. 1, phenoxy radical formation due to Cu(II)–phenol bond breaking (Cu(II) being reduced to Cu(I)) is followed by the interaction of this radical with "activated dioxygen" (probably originating from the Cu(I)–O$_2$ moiety, as observed in analogous cobalt systems [103]) and re-oxidation of the Cu(I) metal centre by molecular dioxygen, thus closing the cycle. The enhancement of phenol-to-quinone photo-oxidation on irradiation is explained by the enhanced rate of Cu(II) to Cu(I) photoreduction and by the photoformation of phenoxy radicals from the excited Cu(II)–phenolate complex. When CuCl$_x$ complexes are present instead of CuL$_x$ in the system, the yield of pbq is positively influenced by Cl$^{\cdot}$ radical formation from the CuCl$_x$ species in a purely photochemical step [104] (also demonstrated as $Cl_2^{\cdot -}$ anion radical [90,105]). These Cl$^{\cdot}$ radicals interact with phenol molecules (hydrogen abstraction [106,107]) leading to increased phenoxy radical concentration and thus to increased quinone formation. This is why the difference between the product formation in irradiated and dark systems is much higher for CuCl$_x$ than for CuL$_x$.

Interestingly, the aqueous photo-oxidation of phenol in the presence of air, sensitized by the bpy complexes $[Cr(bpy)_3]^{3+}$ [50–52] (system VII in Table 2) and $[Ru(bpy)_3]^{2+}$ [52] (system VIII), also leads to pbq as the only photoproduct formed through the mediation of singlet oxygen $^1O_2$ [50,52]. The intermediacy of $^1O_2$ was supported by the higher Φ_{pbq} in D$_2$O (a factor of approximately three higher) than in H$_2$O due to the shorter lifetime of $^1O_2$ during solvent-mediated deactivation in H$_2$O (2.0 μs) relative to D$_2$O (33 μs) [108]. The yield of pbq increases linearly with irradiation time without any induction period, indicating that pbq appears as a primary product. In contrast, the reductive quenching of excited $[Ru(bpz)_3]^{2+}$ (bpz, 2,2′-bipyrazine) by phenol (system IX) and 4-chlorophenol (system X) in the absence of air yields hydroxyphenyl dimers which arise via redox quenching (and not via a $^1O_2$ pathway) [52]. These results demonstrate how the products of the photosensitized oxidation of phenol can be tuned through the utilization of alternative mechanisms which take advantage of the excited state properties of the metal complex. Using sulphonated aluminium (AlSPC) and zinc (ZnSPC) phthalocyanines as sensitizers, phenol (system XI) and 4-chlorophenol (system XII) are oxidized mainly to pbq [53] in the presence of oxygen. The photosensitized oxidation of catechol (system XIII) was also observed under the same experimental conditions [53]. The quenching of ^{3}AlSPC by oxygen leads to the formation of $^1O_2$ with a high quantum yield (Φ = 0.34) [73], but the rate constant of reaction of ^{1}AlSPC with phenols is greater than that with $^1O_2$. It was concluded [53] that the interaction of phthalocyanines in the singlet excited state with phenol leads to the formation of the phthalocyanine anion radical and phenoxy cation radical, both of which can react with O$_2$. This reaction represents a parallel pathway in the mechanism of the photosensitized activation of dioxygen.

Thus the aerobic photo-oxidation of phenol in the presence of CuX and CuL$_2$ complexes (where X ≡ OCl$^-$; L ≡ bpy, phen) in ACN results in pbq formation and, more interestingly, in the total decomposition of phenol to CO_2 when working in aqueous or H_2O–ACN solution [54,55] (system XIV). The addition of water to the ACN system leads to an increased degree of phenol photodegradation to CO_2 [54]



(10)

where L ≡ Cl^-, bpy or phen.

On the basis of these experiments, it can be assumed that the photo-Fenton reaction is operative (Eqs. 11-16), and the $^{\cdot}OH$ radicals produced via Cu(I)–H_2O_2 interaction [60] are responsible for the total photodegradation of phenol (photomineralization to CO_2 and H_2O). This observation opens up new perspectives for the use of copper complexes as catalysts (system XV) for phenol degradation in pure aqueous medium [56,109].

$$Cu(II)Cl_x \underset{ACN}{\overset{h\nu}{\rightarrow}} Cu(I)Cl_{x-1} + Cl^{\cdot} \qquad (11)$$

$$Cu(I)Cl_{x-1} + O_2 \underset{(H^+)}{\overset{Cl^-}{\rightarrow}} Cu(II)Cl_x + O_2^{\cdot -}\ (H_2O_2) \qquad (12)$$

$$Cu(I) + H_2O_2 \underset{H_2O}{\overset{ACN}{\rightarrow}} Cu(II) + {}^{\cdot}OH + OH^- \qquad (13)$$

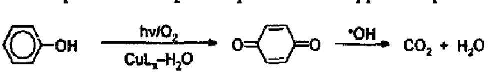
$$PhOH + {}^{\cdot}OH \rightarrow \text{degradation products}\ (CO_2 + H_2O) \qquad (14)$$

$$Cl^{\cdot} + PhOH \rightarrow PhO^{\cdot} + HCl \qquad (15)$$

$$PhO^{\cdot} + O_2^{\cdot -}(O_2) \overset{(H^+)}{\rightarrow} \text{quinone (hydroxoderivatives)}$$

$$\overset{OH}{\rightarrow} CO_2 + H_2O \qquad (16)$$

It has been found [57,58] that the photo-oxidation of phenol in aqueous solution (system XVI) leads to the degradation of phenol to CO_2 in the presence of copper complexes



(17)

where L ≡ bpy.

Recent studies [58] performed in nanopure water have shown that phenol is readily photodegraded in the system $[Cu(bpy)_2]^{2+}$–phenol–O_2–water ($\lambda_{irr} > 290$ nm). The phenol disappearance rate constants k_p increase and the corresponding $t_{1/2}$ values decrease with decreasing pH of the system. The strong pH dependence of the phenol disappearance rate constant k_p can be explained in terms of the excited state properties of the free protonated bpy ligand [58]. Chemical scavenging and kinetic isotope studies, supported by thermodynamics [58], demonstrate the involvement of $^{\cdot}OH$ radicals in the rapid photodisappearance of phenol in highly acidic aqueous medium. It has been shown [110] (using dimethylsulphoxide as molecular probe) that $^{\cdot}OH$ radicals are also formed in neutral aqueous solutions (pH 7) of cuprous bipyridine complexes in the presence of H_2O_2.

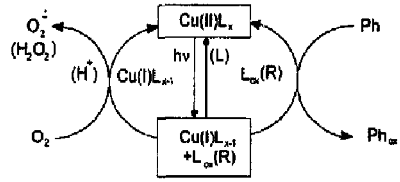


Fig. 2. Environmentally interesting phenol (Ph) photo-oxidations based on the Cu(II)/Cu(I) photocatalytic redox cycle in the Cu(II)/Cu(I)–L(Ph)–O_2 homogeneous system (L ≡ Cl^- and/or Ph, phenol (pollutant); R ≡ L_{ox} or R ≠ L_{ox} (oxidant)).

These results lead to the suggestion of a generalized scheme (Fig. 2) of environmentally interesting photo-oxidations of phenols based on the Cu(I)/Cu(II) photocatalytic redox cycle.

The first photochemical event in the cyclic process (Fig. 2) is the photoreduction of the Cu(II) metal centre to Cu(I) and the concomitant oxidation of the ligand L to L_{ox}. The oxidized ligand L_{ox} (or other strong oxidant R formed during the course of L_{ox} secondary thermal reaction) may participate further in the oxidation of phenol to environmentally acceptable species (H_2O, CO_2). The photoproduced Cu(I) is reoxidized by dioxygen to Cu(II) which is important for the closing of the catalytic cycle, as well as for the formation of the $O_2^{\cdot -}$ anion radical leading to hydrogen peroxide H_2O_2. The H_2O_2 produced is needed for $^{\cdot}OH$ radical formation (species responsible for the photodegradation of phenol via Cu(I)–H_2O_2 interaction (Fenton reaction [111])) or direct H_2O_2 photolysis [39]. This type of reaction, referred to as the "photo-Fenton reaction" [112], was used for the photooxidation of several agrochemicals in freshwater [113] and as an effective photochemical wastewater treatment process (novel photochemical degradation method for organic contaminants) [45]. This cycle only works in the presence of sufficient ligand L (L ≡ Ph or L ≠ Ph) concentration in the system as an electron donor for Cu(II) to Cu(I) reduction. The main decisive electron donor for Cu(II) recovery from photochemically formed Cu(I) is the dioxygen molecule which is always present in sufficient concentration in the system under aerobic conditions. Such redox cycling enables a copper metal catalyst concentration several magnitudes lower than the actual amount of phenol photodegraded to be used, thus making this approach very advantageous.

4. Conclusions

The homogeneous photo-oxidation of phenols in the presence of metal ions (complexes) has been demonstrated to be of importance both theoretically and practically. It has been shown that the presence of metal ions profoundly influences the course and effectiveness of phenol phototransformation (photodegradation or photomineralization). From a mechanistic point of view, the role of the M^{n+} metal ion in the homogeneous photo-oxidation of phenols can be summarized as follows.

1. The presence of the M^{n+} ion positively influences (mainly at low concentrations relative to the phenol substrate) the rate of phenol photo-oxidation due to its electron trapping efficiency, thus preventing electron–hole recombination in TiO_2 suspensions.
2. The positive effect of the metal ion in the presence of O_2 can be explained by $^{\cdot}OH$ radical formation (within pure homogeneous systems and homogeneous pathways of heterogeneous TiO_2 systems) from the thermal or photo-Fenton reaction and/or from H_2O_2 photolysis (photocatalysed or direct).
3. Another explanation for the enhancement of the phenol photo-oxidation rate may be the (photo)chemical reactivity of the ternary complex present in homogeneous solutions (between the copper ion, OS and dioxygen-derived species (O_2, $O_2^{\cdot -}$, $HO_2^{\cdot -}$, H_2O_2)). This possibility, although suggested for other OSs (e.g. toluene in the presence of TiO_2 [16]), may be of importance for phenol photo-oxidation. It is supported by the fact that the homogeneous photo-oxidations of phenols [52,53] and of several other OSs [13] are strongly dependent on the nature of the metal catalyst (or sensitizer [52,53]), which opens up new possibilities for the tailoring of the active complex in such systems. Thus a detailed study of the composition and reactivity of the complexes involved in homogeneous phenol photo-oxidation (often omitted) deserves special attention.
4. It was demonstrated that, in addition to photosensitization, the use of the photocatalytic Cu(II)/Cu(I) redox cyclic process is very important for homogeneous phenol photo-oxidation. The exploitation of such photoredox cycling may lead to environmentally interesting phenol phototransformations (photodegradation and/or photomineralization) and to applications in processes of technological and biological importance.

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