Degradation of nitroaromatic compounds by the UV–H₂O₂ process using polychromatic radiation sources

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The UV–H₂O₂ process, a standard advanced oxidation process (AOP) for water treatment, has been applied to the degradation of a series of nitroaromatic compounds (nitrobenzene, 1-chloro-2,4-dinitrobenzene, 2,4-dinitrophenol, 3-nitrophenol, 4-nitrophenol and 4-chloro-3,5-dinitrobenzoic acid) using polychromatic radiation sources. The optimal concentration of hydrogen peroxide ($[H_2O_2]_{OPT}$) leading to the fastest degradation rate of a given substrate (S) was determined experimentally and estimated using a simplified kinetic model based on the main reactions involved in the first stages of the oxidation. We have shown that, under conditions of monochromatic irradiation, the ratio R_{OPT} (= $[H_2O_2]_{OPT}/[S]_0$) is given by a simple mathematical expression containing only a few parameters, whereas, under conditions of polychromatic irradiation, R_{OPT} is expressed by a complex mathematical equation (involving the spectral distribution of the lamp emission and the absorption spectra of H_2O_2 and the substrate). Two numerical analysis procedures are proposed for obtaining the bimolecular rate constants for the reaction of hydroxyl radicals with a substrate (k_S) from this equation. The rate constants, k_S, determined for the substrates investigated in this work are in agreement with the expected reactivity trend, taking into account the effects of substituents on the distribution of electron density in the aromatic ring. The methods proposed in this work offer a double advantage: i) a standard AOP may be used to evaluate the rate constants of reaction of substrates with hydroxyl radicals under polychromatic as well as under monochromatic irradiation, ii) optimal amounts of additive may be obtained using only a few parameters as predictive tools.

Introduction

The photo-initiated oxidation of pollutants in aqueous solution in the presence of hydrogen peroxide, commonly abbreviated as the UV–H₂O₂ process, is one of the well-known advanced oxidation process (AOPs) available for the degradation and eventual mineralization of organic pollutants.[1–5] Most of these processes are based on the production of hydroxyl radicals as the primary oxidizing species. In the UV–H₂O₂ process, hydroxyl radicals are produced by photolysis of H₂O₂ [reaction (1)].

$$H_2O_2 \xrightarrow{h\nu} 2\,HO^\bullet \qquad (1)$$
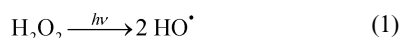
Hydrogen peroxide does not absorb radiation at wavelengths longer than 300 nm and, although it increases steadily at shorter wavelengths, its molar absorption coefficient (ε_{HP}) at 254 nm is only 18.7 L mol⁻¹ cm⁻¹.[6] Low-pressure mercury arcs with a quasi-monochromatic emission at 253.7 nm are commonly employed for H₂O₂ photolysis.[1–2,7] However, the limited radiant power of these lamps[8] explains the frequent use of polychromatic light sources, such as medium- and high-pressure mercury arcs,[3,5,8–10] in the laboratory, as well as in pilot and industrial applications.[11] Therefore, it is of interest to extend the relatively simpler kinetic analyses of experiments performed with monochromatic lamps to the cases where polychromatic light sources are employed.[6]

We have recently reported on the efficiency of the degradation of nitroaromatic derivatives by means of the UV–H₂O₂ technique.[2,12,13] The optimal concentration of hydrogen per-oxide could be evaluated using a simplified expression based on the main reactions involved in the first stages of the oxidation process. In this work, we analyzed the effect of the spectral distribution of a medium-pressure mercury arc on the kinetics of degradation of the same series of nitroaromatic derivatives [1-chloro-2,4-dinitrobenzene (CDNB), 2,4-dinitrophenol (DNP), 3-nitrophenol (MNP), 4-nitrophenol (PNP), nitrobenzene (NBE) and 4-chloro-3,5-dinitrobenzoic acid (CDNBA)].

Experimental

Chemicals

1-Chloro-2,4-dinitrobenzene (CDNB, Aldrich, 99%), 2,4-dinitrophenol (DNP, Riedel de Häen, 99%), 3-nitrophenol (MNP, Riedel de Haën, >99%), 4-nitrophenol (PNP, Fluka and Riedel de Haën, >99%) and nitrobenzene (NBE, May & Baker, >95%) were used without further purification. 4-Chloro-2,5-dinitrobenzoic acid (CDNBA, Aldrich, >95%) was purified as recommended in the literature.[14] When required, solubilization of the nitroaromatic derivatives was facilitated by sonication with cooling. The concentrations of the substrates ranged between 20 and 90 mg L⁻¹. Hydrogen peroxide (30% H₂O₂ w/w in aqueous solution) was purchased from Merck (30% perhydrol). The concentrations of H₂O₂ (5.5×10^{-3} to 0.6 mol L⁻¹) were checked by titration with KMnO₄ and spectrophotometrically. The pH of the solutions (2.5) was adjusted by adding H₂SO₄ (Merck) before irradiation.

Spectrophotometric measurements

Absorption spectra were recorded on a double beam spectro-photometer (Cary 3). An Ocean Optics Inc. Model SD2000 spectrophotometer was also employed. Measurements were made using quartz cells of 0.2 cm optical path length. Solutions whose absorbance was higher than 1.25 were diluted to avoid linearity losses. Solutions of H_2SO_4 of the same concentration were employed as references for the absorbance measurements.

HPLC measurements

HPLC analyses were carried out using a HP1100 Ti-series equipment with a LiChrospher 100 RP-18 column (length: 125 mm, diameter: 4 mm, film thickness: 5 mm); the eluent was a mixture of acetonitrile and water (40 : 60). The aqueous phase contained 3.75 mL of triethanolamine and 2 mL of H_3PO_4 dissolved in 1 L of water. A flow rate of 1 mL min^{-1} was used. Calibration curves for CDNB, DNP, MNP, PNP, CDNBA and NBE were established under identical conditions.

Photochemical reactor

The photochemical experiments were performed at 25.0 ± 0.5 °C in an annular reactor (DEMA, Mangels, Bornheim-Roisdorf, Germany) with a capacity of 750 mL (internal radius = 1.75 cm, external radius = 4.0 cm and height = 20.0 cm). The reactor was equipped with a medium-pressure mercury arc lamp (Philips HPK 125 W) of 4 cm height and 0.65 cm radius, positioned in the axis of the reactor. The HPK125 emission spectrum in the region from 200 to 500 nm, measured in our laboratory with a spectrometer Ocean Optics Inc. Model SD2000,[15] agreed with the spectrum supplied by Philips. The relative emission spectrum of the HPK125 lamp is shown in Fig. 1.
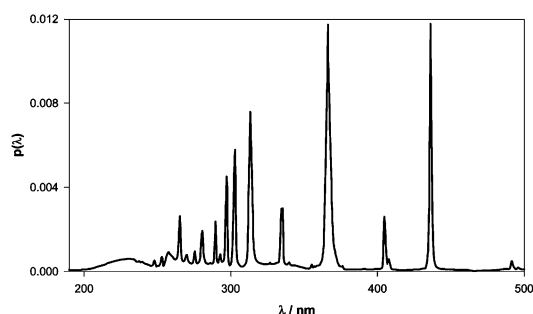

Fig. 1 Probability density function of the photonic emission of the HPK125 lamp between 200 and 500 nm (total area under the curve = 1).

Polychromatic actinometry

Potassium ferrioxalate(III), $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ was used as an actinometer.[8] 1,10-Phenanthroline (Phen) was used as a complexing agent of the Fe^{2+} formed during irradiation of the actinometer, and the absorbance of the complex was measured at 510 nm. To ensure total absorption of the radiation by the actinometric solution in the UV region, a 0.019 mol L^{-1} solution of potassium ferrioxalate was used, the pH being adjusted to a value of 3.0 with H_2SO_4. The incident photon rate, P_0, defined as the total number of photons entering the solution per unit time and unit volume, was calculated using eqn. (2). A

$$P_0 = \frac{d[Fe^{2+}]/dt}{\sum_i p_i(1-10^{-A_i})\Phi_i} \qquad (2)$$

value of 1.3×10^{-5} einstein L^{-1} s^{-1} (absolute photon flow = 9.8 $\times 10^{-6}$ einstein s^{-1}) was obtained for the HPK125 lamp used. Subscript i refers to a very small finite wavelength interval, $d[Fe^{2+}]/dt$ is the rate of Fe^{2+} production (measured as the slope of the plot of $Fe(Phen)_3^{2+}$ vs. time), p_i is the probability mass

function of the photonic emission of the lamp (total integral surface of the lamp emission equal to 1, Fig. 1), A_i is the average absorbance of the solution during irradiation and Φ_i is the quantum yield of the actinometric reaction in the ith wavelength interval. Φ_i varies little between 254 and 415 nm (from 1.24 to 1.12), then decreases regularly to a value of 0.01 at 580 nm.[8] As far as we know no data are reported in the literature for this quantum yield below 254 nm, therefore a constant value of 1.24 was assumed for Φ_i between 200 and 254 nm.

Results and discussion

UV photolysis

Aqueous solutions of the nitroaromatic derivatives investigated (CDNB, DNP, MNP, PNP and NBE) were photolyzed at pH 2.5 using an HPK125 medium-pressure mercury arc lamp (see Experimental section). In all cases, less than 4% of the substrates was degraded and no significant changes in the absorption spectra (not shown) were detected under continuous irradiation during two or three hours in the absence of H_2O_2. Very low polychromatic quantum efficiencies η_S of 4.9×10^{-4}, 1.3×10^{-4}, 4.3×10^{-4}, 7.8×10^{-4} and 4.6×10^{-4} for the degradation of CDNB, DNP, PNP, NBE and MNP respectively were obtained using eqn. (3),

$$\eta_S = \frac{dc_S/dt}{P_0 \sum_i p_i(1-10^{-A_i})} \qquad (3)$$

where dc_S/dt is the substrate degradation rate obtained from the slope of c_S as a function of the irradiation time. P_0 and p_i are defined in eqn. (2) (see Experimental section).

The quantum yields of photolysis of various aromatic compounds have been determined to be between 10^{-3} and 10^{-4}.[2,16]

UV–H_2O_2 method: effect of filters

We have investigated the effect of the wavelength range of the incident radiation in the UV region by carrying out a series of experiments on solutions of PNP and NBE, in the presence of H_2O_2. The incident wavelength range was selected by placing different liquid cut-off filters between the lamp and the inner wall of the photoreactor. The solutions employed as filters were the following: a) water (cut-off at $\lambda < 190$ nm), b) solution of acetic acid (25%) in water (cut-off at $\lambda < 230$ nm), c) pure acetic acid (cut-off at $\lambda < 240$ nm), d) solution of toluene (1%) in isooctane (cut-off at $\lambda < 260$ nm), e) solution of toluene (12.5%) in isooctane (cut-off at $\lambda < 270$ nm), f) pure toluene (cut-off at $\lambda < 275$ nm).

The results obtained using different filter solutions are shown in Fig. 2. Initial degradation rates are listed in Table 1.

A significant decrease in the degradation rate was observed when an increasing part of the UV-C emission was absorbed by the cut-off filter solutions. The values shown in Table 1 suggest that, although the fraction of radiant power emitted by the lamp below 245 nm is less than 20%, in both cases more than 70% of the photo-assisted degradation takes place due to radiation from this region of the UV spectrum. This is related to the increase of the molar absorption coefficient of hydrogen peroxide, from a value of around 28.6 L mol^{-1} cm^{-1} at 240 nm up to 196.2 L mol^{-1} cm^{-1} at 200 nm.

UV–H_2O_2 method: effect of the H_2O_2 concentration on the photodegradation rates under polychromatic irradiation

Solutions of the various substrates were irradiated in the absence of cut-off filters (water cooling). The effect of the initial H_2O_2 concentration ($[H_2O_2]_0$) on the initial rates of substrate disappearance ($r_S = -dc_S/dt$) was studied. In all cases

Table 1 Initial rates of degradation of PNP and NBE by the UV–H_2O_2 process using various filter solutions ($[PNP]_0 = 2.86 \times 10^{-4}$, $[NBE]_0 = 2.46 \times 10^{-4}$, $[H_2O_2]_0 = 0.01$ mol L^{-1}, HPK125 Hg arc)[a]

Cut-off/nm	$-d[PNP]/dt$/mol L^{-1} min^{-1}	$-d[NBE]/dt$/mol L^{-1} min^{-1}
190	$(7.6 \pm 0.4) \times 10^{-5}$	$(8.4 \pm 0.3) \times 10^{-5}$
230	$(4.7 \pm 0.3) \times 10^{-5}$	$(3.8 \pm 0.1) \times 10^{-5}$
240	$(2.2 \pm 0.1) \times 10^{-5}$	$(2.60 \pm 0.08) \times 10^{-5}$
260	—	$(1.00 \pm 0.03) \times 10^{-5}$
270	$(2.7 \pm 0.2) \times 10^{-6}$	—
275	$(2.3 \pm 0.1) \times 10^{-6}$	$(5.1 \pm 0.2) \times 10^{-6}$

[a] The indicated error values correspond to one standard deviation.
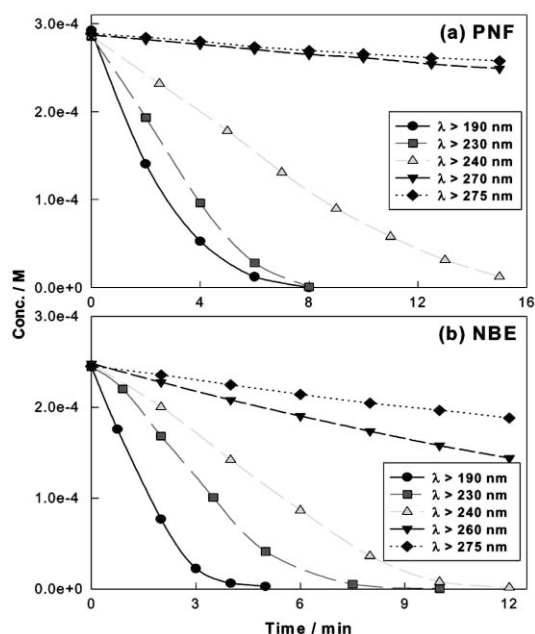
Fig. 2 Kinetic profiles obtained for the degradation of PNP and NBE in the presence of H_2O_2 using different cut-off filters ($[PNP]_0 = 2.86 \times 10^{-4}$, $[NBE]_0 = 2.46 \times 10^{-4}$, $[H_2O_2]_0 = 0.01$ mol L^{-1}, HPK125 medium-pressure Hg arc).
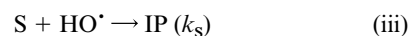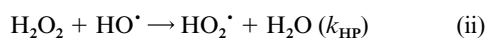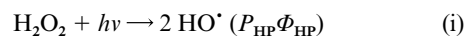
a similar trend was observed: when the $[H_2O_2]_0$ increases, r_S increases until it reaches a maximum value ($r_{MAX,S}$), then slowly decreases. Such behaviour has been reported in the literature for different types of organic compounds.[17–21] Moreover, we also observed similar trends when monitoring the formation of inorganic nitrogen or the depletion of dissolved organic carbon (DOC) (not shown).[12] When the substrate load was increased, the optimal H_2O_2 concentration ($[H_2O_2]_{OPT}$, defined as the initial hydrogen peroxide concentration at which $r_{MAX,S}$ was reached) increased proportionally.

Fig. 3 shows the normalized initial photodegradation rates ($r_S/r_{MAX,S}$) for each compound as a function of the parameter R (defined as the ratio of initial concentrations of H_2O_2 and substrate, $[H_2O_2]_0/[S]_0$). The observed values of R_{OPT} ($[H_2O_2]_{OPT}/[S]_0$) are independent of the initial substrate concentration, being only dependent on the nature of the substrate. Values of R_{OPT} of 138 ± 9, 61 ± 7, 98 ± 15, 148 ± 12, 159 ± 10 and 188 ± 17 were obtained for DNP, CDNBA, CDNB, NBE, PNP and MNP, respectively, using the experimental data and specially developed software based on an algorithm that combines a Taylor series around each experimental point with polynomial regression analysis.[22]

Simplified reaction scheme

In previous papers,[2,13] we deduced a simple and general expression for predicting the optimal hydrogen peroxide concentration when monochromatic radiation sources were employed in the UV–H_2O_2 process.[2] The main hypotheses and corresponding equations are presented below.

Taking into account the first minutes of the reaction, where only small amounts of substrate and H_2O_2 are consumed, the following scheme can be considered:[2,3,11,12,23,24]

$$H_2O_2 + h\nu \longrightarrow 2\,HO^{\bullet} \quad (P_{HP}\Phi_{HP}) \qquad (i)$$

$$H_2O_2 + HO^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O \quad (k_{HP}) \qquad (ii)$$

$$S + HO^{\bullet} \longrightarrow IP \quad (k_S) \qquad (iii)$$

where P_{HP} is the rate of photon absorption by H_2O_2 at a given wavelength of irradiation, Φ_{HP} is the quantum yield of H_2O_2 photodissociation, k_{HP} and k_S are the bimolecular rate constants for the reactions of hydroxyl radicals with H_2O_2 and the substrate(s), respectively.

In the reaction scheme [eqns. (i)–(iii)] above, reactions of the hydroperoxyl radical $HO_2^{\bullet}$ or its conjugate base $O_2^{\bullet -}$ are not considered as their reactivity is much lower than that of the $HO^{\bullet}$ radicals.[25–28] Similarly reactions associated with the intermediate products were neglected (their concentrations in the first minutes of irradiation are very low). The UV photolysis of the nitroaromatic derivatives investigated is very slow under our experimental conditions (see UV photolysis section), therefore degradation of the substrate by UV photolysis may also be neglected.

According to the simplified reaction scheme given above [eqns. (i)–(iii)], the rate of substrate consumption r_S is given by eqn. (4),

$$r_S = \frac{-dc_S}{dt} = k_S c_S c_{HO^{\bullet}} \qquad (4)$$

where c_S and $c_{HO^{\bullet}}$ are the substrate and $HO^{\bullet}$ radical concentrations.

Equation for the initial rate of substrate degradation under monochromatic irradiation

Under conditions of monochromatic irradiation and if a steady-state concentration of hydroxyl radicals is assumed, their concentration ($c_{HO^{\bullet},SS}$) is given by eqn. (5),

$$c_{HO^{\bullet},SS} = \frac{2P_0(1-10^{-A})\Phi_{HP}F_{HP}}{k_{HP}c_{HP} + k_S c_S} \qquad (5)$$

where A represents the total absorbance of the solution and F_{HP} is the fraction of photons absorbed by H_2O_2 at the irradiation wavelength; during the first minutes of irradiation most of the incident radiation is absorbed by the substrate and H_2O_2, thus $F_{HP} = \varepsilon_{HP}c_{HP}/(\varepsilon_{HP}c_{HP} + \varepsilon_S c_S)$ where ε_{HP} and ε_S are the molar absorption coefficients of H_2O_2 and the substrate at the irradiation wavelength.

Combining eqns. (4) and (5) under conditions of total absorbance [i.e. $(\varepsilon_{HP}c_{HP} + \varepsilon_S c_S)\, l \geqslant 2$, where l is the optical path inside the reactor and has a minimum value of 2.25 cm], it can easily be shown that the degradation rate of the substrate as a function of R is expressed as,
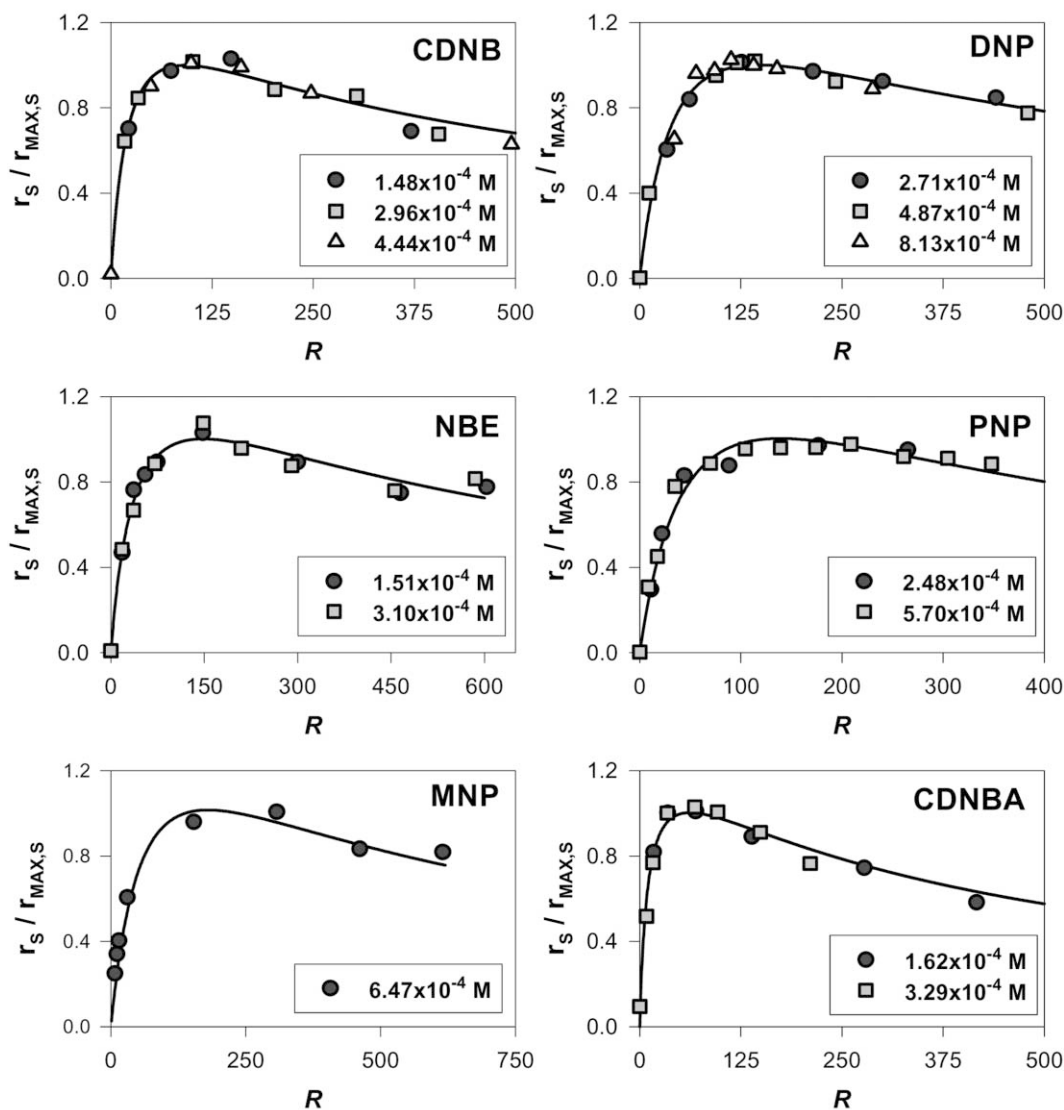
Fig. 3 Normalized initial rates of substrate disappearance $r_S/r_{MAX,S}$ *vs.* R ($[H_2O_2]_0/[S]_0$) for the photodegradation of CDNB, DNP, NBE, PNP, MNP and CDNBA in aqueous solution in the presence of hydrogen peroxide. The curves were calculated using eqn. (11).

$$r_S = \frac{2k_S P_0 \Phi_{HP} \varepsilon_{HP} R}{(k_{HP} R + k_S)(\varepsilon_{HP} R + \varepsilon_S)} \quad (6)$$

According to eqn. (6), r_S exhibits a maximum at a given value of R (R_{OPT}), as experimentally observed (Fig. 3). The observed behavior of r_S as a function of R is due to two contradictory effects. On the one hand, as the value of R increases, the fraction of photons absorbed by H_2O_2 increases, leading to an increase in the production of $HO^{\bullet}$ radicals. On the other hand, at high values of R, reaction (ii) (the trapping of $HO^{\bullet}$ by H_2O_2) competes more effectively with reaction (iii) (oxidation of the substrate by $HO^{\bullet}$).

By differentiating eqn. (6) ($dr_S/dR = 0$), we obtain an expression for R_{OPT} (*i.e.* the optimal concentration ratio that allows a maximum value for the initial degradation rate r_S), under monochromatic irradiation,

$$R_{OPT} = \sqrt{\frac{k_S \varepsilon_S}{k_{HP} \varepsilon_{HP}}} \quad (7)$$

Since the value of k_{HP} is known (2.7×10^7 L mol^{-1} s^{-1} [29]) and molar absorption coefficients are easy to obtain, this relationship can be used either to evaluate the optimal hydrogen peroxide concentration if k_S is known, or to calculate k_S if the optimal H_2O_2 concentration has been experimentally determined.

Eqn. (7) provides a method for evaluating rate constants for the reaction of substrates with hydroxyl radicals that is easier to implement in technical applications than pulse radiolysis experiments (most of the information available in the literature was obtained using this latter technique).

Equation for the initial rate of substrate degradation under polychromatic irradiation

Eqn. (7) holds for the UV–H_2O_2 process under monochromatic irradiation. However, this expression can be extended to processes occurring when polychromatic irradiation sources are employed.

A typical HPK125 lamp exhibits a continuous background and various emission lines (Fig. 1). Therefore, the rate of photon absorption by hydrogen peroxide, P_{HP}, is described by eqn. (8),

$$P_{HP} = P_0 \int_{\lambda} \frac{(1-10^{-A(\lambda)})\varepsilon_{HP}(\lambda)c_{HP}}{\varepsilon_{HP}(\lambda)c_{HP} + \varepsilon_S(\lambda)c_S} p(\lambda)d\lambda \quad (8)$$

where the quantities $A(\lambda)$, $\varepsilon_{HP}(\lambda)$ and $\varepsilon_S(\lambda)$ retain their previous meaning, at a given wavelength λ, and $p(\lambda)$ is the probability density function of the photonic emission (see Experimental section, Fig. 1).

This integral cannot be solved in a simple way. However, the

calculation of P_{HP} can be carried out as a discrete sum for intervals of 1 nm. In the present study the wavelength range between 200 and 500 nm was considered for solving eqn. (8),

$$P_{HP} = P_0 \sum_i p_i (1 - 10^{-A_i}) \frac{\varepsilon_{HP'} c_{HP}}{\varepsilon_{HP'} c_{HP} + \varepsilon_{S'} c_S} \quad (9)$$

where subscript i refers to a very small finite wavelength interval and p_i is the probability mass function of the photonic emission of the lamp [eqn. (2)].

Thus, the pseudo-stationary concentration of HO• radicals ($c_{HO•,SS}$) can be expressed as

$$c_{HO•,SS} = 2P_0 \sum_i \frac{p_i (1 - 10^{-A_i}) \Phi_{HP'} \varepsilon_{HP'} c_{HP}}{(k_{HP} c_{HP} + k_S c_S)(\varepsilon_{HP'} c_{HP} + \varepsilon_{S'} c_S)} \quad (10)$$

and r_S is given by

$$r_S = \frac{2 k_S c_S P_0}{(k_{HP} c_{HP} + k_S c_S)} \sum_i \frac{p_i (1 - 10^{-A_i}) \Phi_{HP'} \varepsilon_{HP'} c_{HP}}{(\varepsilon_{HP'} c_{HP} + \varepsilon_{S'} c_S)} \quad (11)$$

Under conditions of total absorbance over the considered wavelength range (*i.e.*, $\lambda < 350$ nm) and by denoting the ratio $\varepsilon_{HP}/\varepsilon_{S'}$ as ε_i and the ratio k_{HP}/k_S as k, eqn. (11) can be rewritten as:

$$r_S = \frac{2 P_0}{(kR + 1)} \sum_i \frac{p_i \Phi_{HP'} \varepsilon_i R}{(\varepsilon_i R + 1)} \quad (12)$$

This expression is the equivalent of eqn. (6) under polychromatic irradiation. As already indicated, r_S exhibits a maximum at a given value of R ($= R_{OPT}$) for which $dr_S/dR = 0$

$$\frac{dr_S}{dR} = \frac{2 P_0}{(kR + 1)^2} \sum_i \frac{p_i \Phi_{HP'} \varepsilon_i (1 - k\varepsilon_i R^2)}{(\varepsilon_i R + 1)^2} = 0 \quad (13)$$

thus,

$$\sum_i \frac{p_i \Phi_{HP'} \varepsilon_i}{(\varepsilon_i R_{OPT} + 1)^2} = k \sum_i \frac{p_i \Phi_{HP'} \varepsilon_i^2 R_{OPT}^2}{(\varepsilon_i R_{OPT} + 1)^2} \quad (14)$$

Eqn. (14) cannot be rearranged to obtain R_{OPT} since it is an implicit equation (in R_{OPT}). However, it can be reordered to give eqn. (15)

$$R_{OPT} = \sqrt{\frac{k_S}{k_{HP}} \frac{\sum_i \frac{p_i \Phi_{HP'} \varepsilon_i}{(\varepsilon_i R_{OPT} + 1)^2}}{\sum_i \frac{p_i \Phi_{HP'} \varepsilon_i^2}{(\varepsilon_i R_{OPT} + 1)^2}}} \quad (15)$$

and if we define the quantity $f(i)$ as

$$f(i) = \frac{p_i \Phi_{HP'} \varepsilon_i}{(\varepsilon_i R_{OPT} + 1)^2} \quad (16)$$

we obtain

$$R_{OPT} = \sqrt{\frac{k_S}{k_{HP}} \frac{\sum_i f(i)}{\sum_i f(i) \varepsilon_i}} \quad (17)$$

where $f(i)$ is a function of the spectral and kinetic properties of the system.

The quantity $f(i)$ may be considered as a probability distribution function and by definition

$$\frac{\sum_i f(i) \varepsilon_i}{\sum_i f(i)} = \langle \varepsilon \rangle \quad (18)$$

where $\langle \varepsilon \rangle$ is the statistical expected value of $\varepsilon = \varepsilon_{HP}/\varepsilon_S$. The expression for R_{OPT} then becomes

$$R_{OPT} = \sqrt{\frac{k_S}{k_{HP}} \left\langle \frac{\varepsilon_S}{\varepsilon_{HP}} \right\rangle} \quad (19)$$

Although eqn. (19) does not allow the calculation of R_{OPT}, it is interesting to note its similarity with eqn. (7) derived for monochromatic irradiation.

Evaluation of rate constants for the reaction of hydroxyl radicals with substrates from the UV–H₂O₂ experiments

The results of the UV–H₂O₂ experiments under polychromatic irradiation may be used to determine rate constants for the reactions of hydroxyl radicals with the substrates (k_S). Two different mathematical approaches were applied.

Method I involves eqn. (20) [obtained by reordering eqn. (14)] and the determination of R_{OPT} from the experimental plots of r_S as a function of R (*vide supra*, Fig. 3). In eqn. (20) all the wavelengths of emission of a polychromatic lamp are included.[30] In the case of a monochromatic radiation source, eqn. (20) reduces to eqn. (7).

$$k_S = k_{HP} \left[\frac{\sum_i \frac{p_i \Phi_{HP'} \varepsilon_i^2}{(\varepsilon_i R_{OPT} + 1)^2}}{\sum_i \frac{p_i \Phi_{HP'} \varepsilon_i}{(\varepsilon_i R_{OPT} + 1)^2}} \right] R_{OPT}^2 \quad (20)$$

Method II involves a standard non-linear regression analysis of the experimental degradation rates using eqn. (12). The curves in Fig. 3 were obtained using this procedure and show a good correlation between experimental results and calculated profiles.

Knowledge of the spectral distribution of the lamp emission, of Φ_{HP}, of k_{HP} and of the relative molar absorption coefficients ($\varepsilon_{HP}/\varepsilon_{S'}$), in the wavelength range of interest, is required for proceeding with either of the methods. As reported in the literature,[6] Φ_{HP} is about 0.5 due to recombination reactions of HO• radicals in the solvent cage. The relative absorption coefficients for H₂O₂ and the nitroaromatic derivatives investigated (ε_i) are shown in Fig. 4.

The values of the rate constants, k_S, for the different substrates obtained using Methods I and II are listed in Table 2.
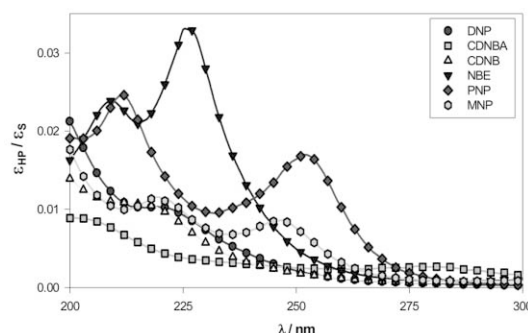

Fig. 4 Molar absorption coefficients of H₂O₂ relative to those of CDNB, DNP, NBE, PNP, MNP and CDNBA in aqueous solution.

Table 2 Rate constant values at 25 °C for the investigated nitroaromatic derivatives with HO$^{\bullet}$ radicals[a]

Compound	k_S/mol L^{-1} s^{-1} Method I	Method II
DNP	$(2.1 \pm 0.4) \times 10^9$	$(2.4 \pm 0.2) \times 10^9$
CDNBA	$(2.9 \pm 1.1) \times 10^8$	$(3.2 \pm 0.2) \times 10^8$
CDNB	$(1.0 \pm 0.4) \times 10^9$	$(8.7 \pm 0.5) \times 10^8$
NBE	$(4.4 \pm 1.3) \times 10^9$	$(4.3 \pm 0.4) \times 10^9$
PNP	$(6.5 \pm 1.1) \times 10^9$	$(5.8 \pm 0.5) \times 10^9$
MNP	$(5.4 \pm 1.5) \times 10^9$	$(5.0 \pm 0.4) \times 10^9$

[a] The indicated error values correspond to one standard deviation.

The results indicate that very similar k_S values are obtained with both methods. Nevertheless, by application of Method II, in addition to the calculation of the rate constant k_S, the normalized experimental profiles for r_S can be compared with the values predicted by the kinetic model [eqn. (12)].

Analysis of the values in Table 2 shows that the reactivity order as given by k_S coincides with the trend observed in our previous studies.[13]

Conclusions

Degradation of nitroaromatic compounds in aqueous solution by photolysis is a slow process. Considerably faster degradation rates could be achieved adding H$_2$O$_2$ before irradiation. The optimal concentration of hydrogen peroxide ([H$_2$O$_2$]$_{OPT}$) leading to the fastest degradation rate[2,12–13] may be calculated using a simplified kinetic model. Under polychromatic irradiation, the optimal ratio R_{OPT} (= [H$_2$O$_2$]$_{OPT}$/[S]$_0$) depends on the ratio k_S/k_{HP}, the spectral distribution of the lamp emission, and the absorption spectra of H$_2$O$_2$ and of the substrate.

If R_{OPT} is determined experimentally, the bimolecular rate constant for the reaction of hydroxyl radicals with the substrate (k_S) may be evaluated from readily available data [eqn. (20)]. The methods proposed in this work offer a double advantage: i) a standard AOP may be used to evaluate rate constants for the reactions of substrates with hydroxyl radicals under polychromatic as well as under monochromatic irradiation, and ii) optimal amounts of additive may be estimated using only a few parameters as predictive tools.

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