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Type I vs Type II photodegradation of pollutants

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ABSTRACT

Rose Bengal (RB) is a widely used photocatalyst due to its high quantum yield of singlet oxygen ($^1O_2$) formation. Hence, when RB has been employed for wastewater remediation, the observed photodegradation has been attributed to reaction between the pollutants and the $^1O_2$ formed (Type II mechanism). However, RB could also react, in principle, via electron transfer (Type I mechanism). Herein, competition between Type I vs Type II oxidation has been investigated for RB in the photodegradation of emerging pollutants such as diclofenac (DCF) and acetaminophen (ACP). In parallel, the photocatalyst perinaphthenone (PN) has also been evaluated for comparison. The degree of removal achieved for both pollutants in aerated/deaerated aqueous solutions irrespective of the employed photocatalyst does not support the involvement of $^1O_2$ as the main species responsible for removal of the pollutants. Photophysical experiments showed that the triplet excited states of RB and PN are efficiently quenched by both DCF and ACP. Moreover, $^1O_2$ emission was also quenched by DCF and ACP. Thus the contribution of Type I versus Type II in the photodegradation has been evaluated from the experimentally determined rate constants. Nevertheless, at the upper limit for the typical concentration of emerging pollutants (10^{-5} M) photodegradation proceeds mainly via Type I mechanism.

1. Introduction

Rose Bengal (RB) (Fig. 1) is a well-known photocatalyst that has been widely used due to its high quantum yield of singlet oxygen ($^1O_2$) formation (Φ_Δ = 0.76-0.83) [1–5]. For this reason, when it has been employed for wastewater remediation for the study of photochemical behavior of natural waters, the observed photodegradation has been, in general, attributed to reaction between the pollutants and the $^1O_2$ formed (Type II mechanism) [6–9]. However, RB with a redox potential of $E_{RB/RB^{\cdot-}} = -0.95$ V vs SCE, could also react, in principle, *via* electron transfer (Type I mechanism) [10–12]. In the context of water remediation, Type I reactions would be more favored than Type II, due to: i) the higher relative permittivity value of water compared to polar organic solvents, such as acetonitrile, ($\varepsilon_{H2O} = 80.16$ vs $\varepsilon_{ACN} = 35.94$); ii) the lower concentration of O_2 (0.29 mM in water vs 1.9 mM in acetonitrile); and iii) the lower lifetime of $^1O_2$ (2 μs in water vs 68 μs in acetonitrile) [13,14]. Furthermore, RB has a high Φ_{ISC} (Fig. 1), and Type I photodegradation processes happen mainly from the triplet excited states, due to the longer lifetime of the triplets compared to that of the singlets [15]. Therefore, competition between Type I vs Type II oxidation deserves further investigation to establish the real mechanism involved in the photodegradation processes that often take place in aqueous solutions.

Herein, RB has been employed to investigate the photodegradation of two representative commonly used drugs, such as diclofenac (DCF) and acetaminophen (ACP) found in real wastewaters at low concentrations (see Fig. 2). For a deeper understanding of the Type I/Type II competition, a second photocatalyst, perinaphtenone (PN), less widely employed but with a higher $^1O_2$ quantum yield formation (Φ_Δ *ca* 1) and a $E_{PN/PN^{\cdot-}} = -0.62$ V vs SCE, has also been evaluated using the same representative pollutants [16,17]. Laser flash photolysis and transient emission spectroscopy experiments of RB/PN in the presence of the contaminants provided valuable fast-kinetic data. From the determined quenching rate constants, the contribution of Type I/Type II mechanisms in the photodegradation of the selected contaminants has been evaluated and a general conclusion has been drawn.

2. Experimental

2.1. Reagents

Diclofenac (DCF), acetaminophen (ACP), 4-nitrobenzoic acid, Rose Bengal disodium salt (RB) and perinaphthenone (PN) were obtained from Aldrich. Water was Milli-Q grade and acetonitrile (ACN) was of HPLC quality from Scharlau.

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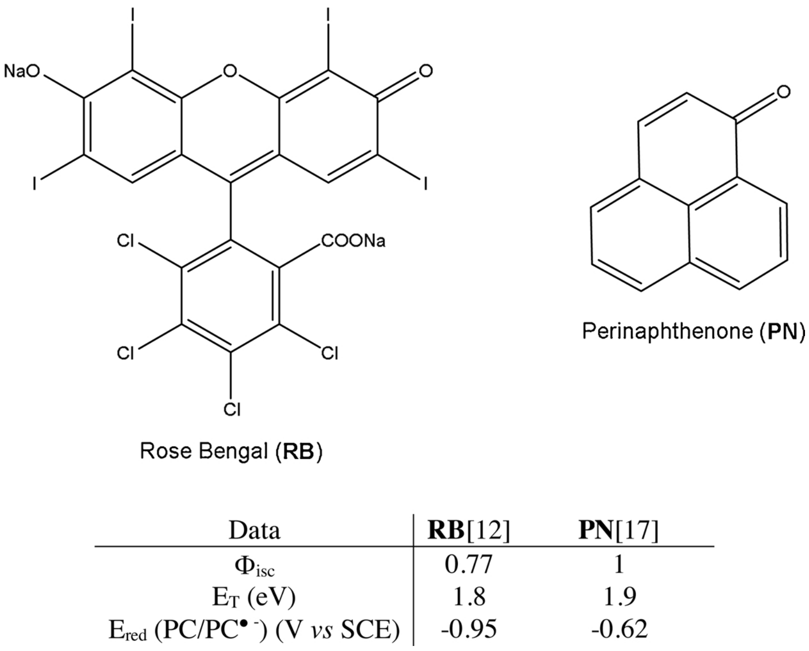

Data	**RB**[12]	**PN**[17]
Φ_{isc}	0.77	1
E_T (eV)	1.8	1.9
E_{red} (PC/PC$^{\bullet -}$) (V *vs* SCE)	-0.95	-0.62

Fig. 1. Chemical structures, photophysical properties such as intersystem crossing quantum yield (Φ_{isc}) or energy of the triplet excited state (E_T) together with electrochemical details, such as redox potentials (E_{red} (PC/PC$^{\bullet -}$) of the selected photocatalysts.

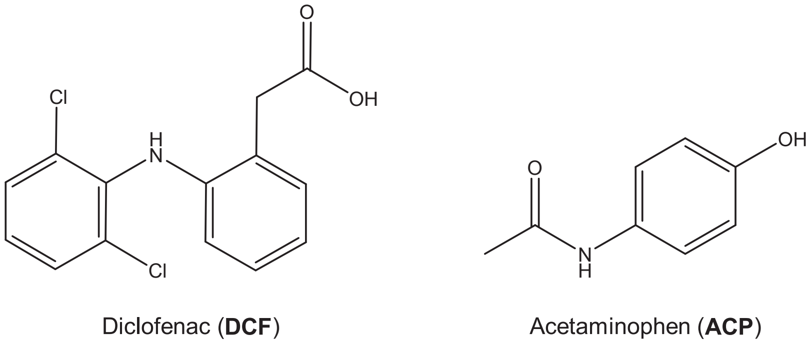

Fig. 2. Chemical structures of the selected contaminants.

2.2. Photochemistry

Photochemical reactions were performed in Pyrex glass tubes with magnetic stirring. For the reactions photocatalyzed by RB, a home-made photoreactor built with a spiral set-up of 2.5 m strip green LEDs (λ_{em} centered at 515 nm), Samsung SMD5630IP20 of 40 W was employed; whereas for the reactions photocatalyzed by PN, a Luzchem photoreactor (model LZC–4 V) with 14 bulbs emitting at 420 nm was used. Aqueous solutions (16 mL) containing a mixture of the two pollutants (5×10^{-5} M each) and either RB or PN (10 mg L^{-1}) were irradiated under air or N_2 atmosphere. To monitor the removal of the pollutants, aliquots of 90 μL were taken at different irradiation times, and were analyzed by HPLC, using 4-nitrobenzoic acid (10 μL of a 0.1 mM solution) as internal standard. The equipment was an Agilent 1220 Infinity LC model with a quaternary pump G4290B, photodiode detector G4290 B and wavelength detection from 200 to 360 nm equipped with a Mediterranea Sea 18 column (25 cm × 0.46 cm, 5 μm particle size). The mobile phase was a gradient mixture of water (pH 3):ACN (70:30-30:70) at a flow rate of 1.5 mL min^{-1}; the detection wavelength was fixed at 250 nm.

2.3. Photophysical instrumentation

Absorption spectra (UV/Vis) were recorded on a Cary 50 (Varian) spectrophotometer. A pulsed Nd: YAG SL404G-10 Spectron Laser Systems at the excitation wavelength of 355 nm or 532 nm in the case of PN or RB, respectively, was employed to carry out the laser flash photolysis (LFP) experiments. The energy of the single pulses (~10 ns duration) was lower than 30 mJ $pulse^{-1}$. The laser flash photolysis system is formed by the pulsed laser, a pulsed Lo255 Oriel Xenon lamp, a 77200 Oriel monochromator, an Oriel photomultiplier tube (PMT) housing, a 70705 PMT power supply and a TDS-640A Tektronix oscilloscope. Lifetime of singlet oxygen was recorded at 1270 nm with a Hamamatsu NIR detector (peltier cooled at −62.8 °C operating at 800 V, coupled to a grating monochromator) upon excitation with a 355 nm Nd:YAG laser. A customized Luzchem Research LFP-111 system was employed to collect and process the data.

2.4. Photophysical experiments

Quartz cells of 1 cm optical path length were employed for all photophysical measurements, which were run at room temperature. For the laser flash photolysis experiments, increasing amounts of pollutants (up to 3 mM) were added to ACN:H_2O (4:1) solutions of RB or PN (absorbance *ca.* 0.3 at 355 or 532 nm for PN or RB, respectively), under N_2 atmosphere. Lifetime of singlet oxygen was determined from phosphorescence decay curves at 1270 nm upon increasing amounts of pollutant (up to 3 mM) in aerobic ACN:H_2O (4:1) solutions.

2.5. Electrochemical measurements

Electrochemical measurements were carried out using a computer-controlled potentiostat Autolab PGSTAT302N Metrohm. A three-electrode electrochemical cell was employed for the electrochemical