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Feed-back action of nitrite in the oxidation of nitrophenols by bicarbonate-activated peroxide system

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ABSTRACT

In this study it was found that the nitrite anion greatly increases the oxidation rate of the substituted phenols by the bicarbonate-activated peroxide (BAP) system at ambient temperature. This feed-back effect was investigated in the BAP oxidation of 2-amino-4-nitrophenol and 4-nitrophenol, where the kinetic analysis showed that the rate determining step was the elimination of a nitro group as nitrite. Complementary oxidation experiments with 2-aminophenol in BAP system, performed in the presence/absence of sodium nitrite confirmed the catalytic role of this anion. High concentrations of nitrite/BAP prevented formation of polymeric species and favoured the degradation to aliphatic fragments such as 3-oxobutanoic and acetic acid. Indirect evidence suggested in-situ generation of reactive oxygen species (ROS), other than hydroxyl, peroxyl and carbonate radicals, during the nitrite/BAP oxidation. Formation of additional ROS – peroxynitrite and nitrosoperoxycarbonate – may account the synergistic action of nitrite/BAP system. The estimated value of the apparent rate constant of the autocatalytic step for 2-amino-4-nitrophenol ($k_{app} = (4.97 \pm 0.19) \times 10^3\ M^{-3}\ s^{-1}$) demonstrates that fast degradation of this oxidation-resistant phenolic dye is feasible even in ambient conditions. These findings can be exploited for developing clean, cost-effective methods for the removal of phenolic dyes as alternative to current advanced oxidation processes.

1. Introduction

The efficient degradation of contaminants from natural waters such as pharmaceuticals, dyes and detergents is still one of the targets in water- or waste treatment strategies. These xenobiotics, mostly containing phenolic rings, pose major ecological threats due to their long biological half-life and accumulation in water, soil and living organisms [1–3]. The treatment of contaminated water before discharging into the aquatic environment demands additional non-biological technologies as advanced oxidation processes (AOPs) [4–8]. (AOPs) are considered the most important technologies for environmental remediation of natural and wastewaters containing recalcitrant compounds, through the production of reactive oxygen species (ROS) [9,10]. AOPs are based on the in-situ generation of highly reactive hydroxyl radicals (•OH) in mild conditions [11–14]. The hydroxyl radicals can oxidize any compound present in the water matrix, frequently at diffusion controlled rates [5]. Once formed, •OH reacts unselectively and degrades efficiently the water contaminants to non-toxic, low molecular weight (LMW) compounds [15]. The use of primary oxidants (e.g. ozone, hydrogen peroxide, dioxygen) [16], energy sources (ultraviolet light) [17–19] or catalysts (titanium dioxide, iron(III), cobalt(II), potassium permanganate) [20–26] are the current pathways of generating hydroxyl radicals and other ROS such as superoxide radical ($O_2^{-\bullet}$), peroxyl radical and singlet oxygen [9]. Despite the advantage of removing organic compounds in aqueous phase AOPs hold several drawbacks which prevent their full-scale implementation; most prominently, AOPs costs are very high, requiring continuous inputs of expensive chemicals in order to maintain the operability of the oxidative system [16]. Another issue is the need of pre-treatment procedures, which are costly and technically demanding. The presence of bicarbonate anion (HCO_3^-) can significantly reduce the concentration of •OH due to scavenging processes that lead to H_2O and to a much less reactive ROS, the carbonate radical $^{\bullet}CO_3^-$ [27]. Consequently, HCO_3^- must be removed from the contaminated samples before starting the generation of ROS in

Abbreviations: AOP, advanced oxidation processes; BAP, bicarbonate activated peroxide; ROS, reactive oxygen species; AP, 2-aminophenol; NAP, 2-amino-4-nitrophenol; NP, 4-nitrophenol; APX, 2amino-3H-phenoxazin-3-one; OQI, *o*-quinoneimine.

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typical AOPs. The HCO_3^-/CO_2 buffer is ubiquitous in natural waters and stimulate the oxidation, peroxidation and nitration of several biological targets [28]. In addition Richardson et al. [27] used HCO_3^- as activator H_2O_2 in sulphide oxidation in alcohol/water mixtures. The bicarbonate-activated peroxide (BAP) system has been highly efficient in the epoxidation of alkenes [29] through generation of $^\bullet CO_3^-$ and $O_2^{-\bullet}$. Although less oxidizing than $^\bullet OH$ ($E^\circ = 2.3$ V vs. NHE, pH 7.0), $^\bullet CO_3^-$ ($E^\circ = 1.78$ V, pH 7.0) is a very strong one-electron oxidant that acts by both electron transfer and hydrogen abstraction mechanisms to produce radicals from the reducing substrates [30]. ROS generation from BAP system occurs according to the sequence (1)–(4):

$$H_2O_2 + HCO_3^- \rightleftarrows HCO_4^- + H_2O \quad (1)$$

$$HCO_4^- \rightarrow {}^\bullet CO_3^- + {}^\bullet OH \quad (2)$$

$$CO_3^- + H_2O_2 \rightarrow HOO^\bullet - HCO_3^- \quad (3)$$

$$HOO^\bullet \rightarrow H^+ + O_2^{-\bullet} \quad (4)$$

$^\bullet CO_3^-$ is a selective ROS, attacking preferentially phenolic residues from tyrosine, indolic moieties from tryptophan and sulphides from methionine [31] especially when acting in tandem with $^\bullet NO_2$ [32–34].

$$ArH + {}^\bullet CO_3^- \rightarrow Ar^\bullet + CO_3^{2-} + H^+ \quad (5)$$

$$Ar^\bullet + {}^\bullet NO_2 \rightarrow ArNO_2 \quad (6)$$

The BAP system can be used to build-up environmental-friendly oxidizing technologies as alternatives to current AOPs. However, the BAP system become efficient in the degradation of phenol-based compounds only when is taken in a large excess (10^2–10^4 fold) with respect to the target concentration [35]. The issue is to ensure steady concentrations of ROS, enough to prevent polymeric by-products formation. Since both H_2O_2 and HCO_3^- are relatively inexpensive and non-polluting reagents, the required high BAP/target concentration ratios could successfully be ensured either in batch or continuously-stirred reactors. In the case of nitroaromatics (e.g. nitrophenols), the elimination of nitro groups may provide supplementary ROS such as peroxynitrite ($ONOO^-$), nitrosoperoxycarbonate ($ONOOCO_2^-$) and NO_2 [30,31,36,37], all of them potential oxidizing agents. In this work we attempted to exploit the positive feed-back action of the nitro group (consistent with an autocatalytic degradation path) on the BAP oxidation of three phenol-based dyes: 2-aminophenol (AP), 2-amino-4-nitrophenol, (NAP) and 4-nitrophenol (NP). NAP and NP are particularly resistant to chemical/biological oxidation due to the electron-withdrawing nitro group which deactivates the aromatic ring towards the electrophilic/radical attacks [38]. AP undergoes (bio)-catalysed oxidation to its stable condensation product 2-amino-3*H*-phenoxazin-3-one (APX), which is also recalcitrant to conventional oxidative treatments [39,40]. The oxidative degradation of NAP is by far the less studied compared to AP and NP; therefore, we focused our kinetic study on NAP oxidation. We proposed first a simplified kinetic model which highlighted the autocatalytic effect of the nitro group during the BAP oxidation and the time-evolution of NAP, H_2O_2, HCO_3^- and NO_2^- concentrations; an extended kinetic model including the time-evolution of the reaction intermediates was further developed, because their toxicity can sometimes be even higher than the toxicity of the initial pollutants [5]. The degradation pathways of AP and NP were depicted elsewhere [9,11,39]. For these substrates we developed only simplified kinetic models describing the time-evolution of spectrophotometrically detectable intermediates.

2. Materials and methods

2.1. Reagents

AP, NAP and NP (99%), 4-nitrocatechol (97%), methanol (HPLC grade), acetonitrile (ACN) (HPLC grade) formic acid (LC–MS grade), sodium bicarbonate (99.5%), sodium hydroxide (purity ≥97%), sodium nitrite (purity ≥97%), sodium nitrate (purity ≥99) and acetic acid (purity ≥99%) were acquired from Sigma-Aldrich (Germany). H_2O_2 obtained as a 30% solution from Merck was diluted and the concentration was determined spectrophotometrically, using $\varepsilon_{240\,nm} = 43.6\,M^{-1}\,cm^{-1}$. APX (m.p. = 249 °C) was synthesized upon the oxidation of 2-aminophenol with mercury oxide followed by recrystallization from ethanol. Ultrapure water from a Millipore Simplicity 185 (conductivity $<6 \times 10^{-8}\,S\,cm^{-1}$, max. 5 ppb total organic compounds, TOC) system was used in the chromatographic experiments. Gaseous dioxygen was purchased from Linde (99.6% purity). *Trametes versicolor* laccase was purchased from Fluka (26U/mg specific activity) and was used to prepare 2-amino-8-nitro-3*H*-phenoxazin-3-one and 3-amino-8-nitro-1*H*-phenoxazin-2(10*H*)-one from oxidation of NAP with dioxygen. Other chemicals used were of analytical reagent grade.

2.2. Analytical methods

2.2.1. Spectrophotometric assays

The ultraviolet–visible (UV–VIS) measurements during the BAP oxidation of AP, NAP and NP were made on a Lambda 25 PerkinElmer spectrophotometer with a Peltier cell for temperature and stirring control. For IR analysis of the reaction products of AP and NAP oxidation, the collected solution after 240 min was adjusted to a pH of 2.5 with HCl to completely decompose HCO_3^-, then dried at 30 °C. The resulted solid sample was recorded in KBr pellets on a BrukerTensor 37 spectrophotometer.

2.2.2. Differential scanning calorimetry (DSC) analysis

The DSC analysis of the reaction products of NAP oxidation was performed with DSC-2 PerkinElmer apparatus connected to a Tektronix TX3 multimeter and optically coupled to the interface RS 232. The scan heating rate employed was $10\,K\,min^{-1}$ in the range 300–650 K under an argon atmosphere; the apparatus sensitivity was $5\,mcal\,s^{-1}$ and the multimeter had a maximum display at 50 000 with a 0.03% error on the work domain.

2.2.3. Liquid chromatography–mass spectrometry (LC–MS) analysis

Experiments were conducted in an Agilent 1260 series LC system (Agilent, Waldbronn, Germany) consisting of: a binary pump, a thermostated autosampler, a thermostated column coupled with an Agilent 6410B triple-quadrupole mass analyzer with electrospray ionization (ESI) source. Data acquisition was performed using Mass Hunter software. All chromatographic runs were carried out on a Zorbax SB-C18 (50 × 2.1 mm, 1.8 μm) column from Agilent at 35 °C. Isocratic elution was performed with a mobile phase composition of aq. 0.1% formic acid and acetonitrile in the volumetric ratio 90/10. A mobile phase flow-rate of 0.15 mL/min was chosen to enhance ESI ionization and sensitivity. Injection volume was 10 μL. MS detection of the substrates and their oxidation products was done in Single Ion Monitoring (SIM) and full scan mode. Both positive and negative spectra were acquired in full scan mode using the range 50–500 Da. ESI source parameters were: drying gas temperature 300 °C, drying gas flow-rate 9 L/min, nebulizer pressure 50 psi. Sampling capillary voltage was set to 2500 V for negative mode and 4000 V for positive mode. Skimmer (fragmentor) voltage was set to 90 V. First quadrupole (Q1) resolution was set to *Unit* when SIM mode was used. Cell accelerator voltage of second quadrupole (Q2)