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Removal of benzoylecgonine from water matrices through UV_{254}/H_2O_2 process: Reaction kinetic modeling, ecotoxicity and genotoxicity assessment

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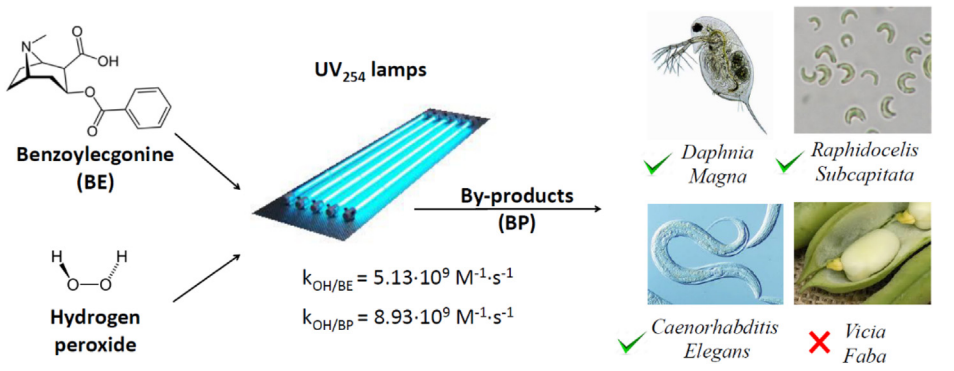
HIGHLIGHTS

- UV/H_2O_2 oxidation process is effective for BE removal from aqueous matrices.
- MCF photoreactor technology is a valid and useful tool in AOPs studies.
- The kinetic constants of HO radicals attack to BE and its by-products are estimated.
- BE removal through UV/H_2O_2 process is modeled in different aqueous matrices.
- Genotoxicity tests suggest the risk of long term effects of BE by-products.

GRAPHICAL ABSTRACT



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ABSTRACT

Benzoylecgonine (BE), the main cocaine metabolite, has been detected in numerous surface water and treatment plants effluents in Europe and there is urgent need for effective treatment methods. In this study, the removal of BE by the UV_{254}/H_2O_2 process from different water matrices was investigated. By means of competition kinetics method, the kinetic constant of reaction between BE and the photogenerated hydroxyl radicals (•OH) was estimated resulting in $k_{OH/BE} = 5.13 \times 10^9\ M^{-1}\ s^{-1}$. By-products and water matrices scavengers effects were estimated by numerical modeling of the reaction kinetics for the UV_{254}/H_2O_2 process and validated in an innovative microcapillary film (MCF) array photoreactor and in a conventional batch photoreactor. The ecotoxicity of the water before and after treatment was evaluated with four organisms *Raphidocelis subcapitata*, *Daphnia magna*, *Caenorhabditis elegans,* and *Vicia faba*. The results provided evidence that BE and its transformation by-products do not have significant adverse effects on *R. subcapitata*, while *D. magna* underwent an increase of lipid droplets. *C. elegans* was the most sensitive to BE and its by-products. Furthermore, a genotoxicity assay, using *V. faba*, showed cytogenic damages during the cell mitosis of primary roots.

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1. Introduction

BE is a contaminant of emerging concern deriving from the consumption of cocaine, one of the most widely used illicit drugs [1]. The human metabolism of cocaine is dominated by hydrolytic ester cleavage resulting in urine metabolites consisting mostly of BE (45%), ecgonine methyl ester (40%), and a residue of unchanged cocaine (1–9%) [2]. Consequently, BE represents the primary cocaine metabolite and it is detected in almost all surface water (SurW) and sewage treatment plants (STP) effluents in Europe always at levels higher than cocaine [3,4]. Although the removal of BE in conventional STP is typically 80% [5,6], the effluent concentrations is in the range 0.1–3275 ng L^{-1} [7,8]. BE in SurW ranges between 0.3–530 ng L^{-1} [9–11] and in river sediments is reported as 1.0 ng g^{-1} [12].

The exposure of freshwater mussel, *Dreissena polymorpha*, to BE contaminated water solutions (0.5 and 1.0 ppb), yielded a 3.5-fold increase in oxidative stress and increased or inhibited antioxidant and detoxifying enzymes activity depending on BE levels and exposure time [13–15]. Significant lipids peroxidation and protein carbonylation, DNA damage, and cellular apoptotic death were observed in experiments carried out up to 14 days [16]. Another study showed the negative effect of BE on fishes and plants [17].

The UV_{254}/H_2O_2 is an emerging STP tertiary treatment process, which is increasingly being used for water reuse in public works and in agriculture [18–20]. In previous studies [21,22] we have investigated the BE removal with both UV_{254} and UV_{254}/H_2O_2 using an innovative microcapillary film (MCF) array photoreactor, which allowed extremely rapid experimentation with minimal sample volumes. The feasibility of BE removal by direct photolysis (UV_{254}) in STP during a conventional water disinfection treatment is questionable due to the low molar adsorption coefficient and quantum yield [21]. However, BE removal in STP is a promising proposition using the UV_{254}/H_2O_2 process, as we determined much faster BE oxidation in different water matrices: milliQ water, synthetic wastewater (SWW), real wastewaters (RWW), and SurW [22]. Other studies have demonstrated that Fenton, Fenton-like, and potassium ferrate treatment are also effective methods for BE removal in STP effluents [23] although their practical implementation can be problematic.

In this study, we therefore focused on the UV_{254}/H_2O_2 process as a potential tertiary treatment of STP effluents [24–31] since it appears of more feasible implementation.

In the UV_{254}/H_2O_2 process the homolytic cleavage of H_2O_2 leads to the formation of •OH radicals (1) that unselectively attack dissolved organic substances such as BE (2) [32]:

$$H_2O_2 \xrightarrow{hv} 2^{\bullet}OH \quad (1)$$

$$^{\bullet}OH + BE \xrightarrow{k_{OH/S}} By - products \quad (2)$$

However, the second-order rate constant ($k_{OH/BE}$) for the reaction of BE with •OH is unknown. Furthermore, the ecotoxicity and genotoxicity of the BE transformation by-products generated through the UV_{254}/H_2O_2 process have not been reported.

In this study, competition kinetics in the presence of benzoic acid (BA) [33,34], was used to determine the second-order rate constant ($k_{OH/BE}$) for the reaction of BE with •OH, which was evaluated in the MCF array photoreactor and validated in a batch photoreactor. The effect of by-products and water matrices scavengers was estimated by numerical modeling of the reaction kinetics for the UV_{254}/H_2O_2 process in the MCF array photoreactor dissolving BE in milli-Q water, SWW, RWW, and SurW. Ecotoxicological bioassays with *R. subcapitata*, *D. magna* and *C. elegans* were further used to provide information for environmental health and to investigate the effects of BE before and after the proposed treatment. Several endpoints were monitored on terrestrial and aquatic organisms to expand the range of effect expression due to differences in species sensitivity and exposure. Furthermore, the potential genotoxicity of BE and its by-products was investigated by means of the count of micronuclei observed in *V. faba* roots.

This study was based on the "effect-driven approach" [35] in which a parent compound is undergoing degradation and is analyzed with eco-bioassays to follow the toxicity evolution during a transformation process.

Indeed, it was chosen an initial concentration of BE higher than usually found in effluents or SurW [7–12] to better assess ecotoxicological effects of by-products solutions, as reported in previous studies [36–38]. Furthermore, such high concentrations are not of limited relevance because they are suitable to determine the median effective concentration (EC50), an indicator of by-products toxicity and the time onset of the effects.

The investigation on the relative toxicities of BE and its by-products is relevant to future discussions regarding the treatment, control and fate of BE and BE-derivatives in the environment.

2. Materials and methods

2.1. Materials

Hydrogen peroxide (30% v/v), benzoylecgonine (≥99% w/w), acetonitrile (≥99.9% v/v), formic acid (≥95% v/v), benzoic acid (≥99.5% w/w), catalase from Micrococcus lysodeikticus were purchased from Sigma-Aldrich. Milli-Q water (18 MΩ resistivity) was prepared with a Millipore Elix water purification system.

In agreement with the OECD guidelines [36], SWW was prepared with peptone (32 ppm), meat extract (22 ppm), urea (6 ppm), K_2HPO_4 (28 ppm), $CaCl_2{\cdot}H_2O$ (4 ppm), NaCl (7 ppm) and Mg_2SO_4 (0.6 ppm) in milli-Q water. These substances were from Sigma-Aldrich and were used as received. RWW was sampled from the Severn Trent Sewage Water Treatment Plant of Festival Drive, Loughborough, Leicestershire (UK). SurW was collected from the Grand Union Canal in the same area. RWW and SurW samples were filtered through Whatman nylon filters (0.45 μm) to avoid clogging of the MCF and of the high performance liquid chromatography (HPLC).

For toxicity assessment, reference toxicants (potassium dichromate, cupric chloride, maleic hydrazide) and salts for the preparation of artificial freshwater ($CaCl_2{\cdot}2H_2O$, $MgSO_4{\cdot}7\,H_2O$, KCl, $NaHCO_3$, $NaNO_3$, NH_4Cl, $MgCl_2{\cdot}6(H_2O)$, K_2HPO_4, KH_2PO_4, $FeCl_3{\cdot}6(H_2O)$, $Na_2EDTA{\cdot}2(H_2O)$ H_3BO_3, $MnCl_2{\cdot}4(H_2O)$ $ZnCl_2$, $CoCl_2{\cdot}6(H_2O)$, $Na_2MoO_4{\cdot}2(H_2O)$, $CuCl_2{\cdot}2(H_2O)$, NaCl) were used. All chemicals were analytical grade supplied by Sigma Aldrich. Double distilled water (Microtech) was used to prepare dilution water and treatments.

2.2. Analytical methods

Hydrogen peroxide, BE, and benzoic acid were assayed by HPLC (1100 Agilent) equipped with a Gemini C18 (Phenomenex) reverse phase column and a diode array detector (λ = 232 nm). The mobile phase was a mixture of formic acid aqueous solution (25 mM) (A) and acetonitrile (B) flowing at 0.6 mL min^{-1} with a gradient 7% B to 28% B in 9 min, then 50% B in 5 min, constant for 2 min, and then to 7% B in 3 min. The retention times for H_2O_2, BE, and BA were 4.9, 13.8 and 17.1 min, respectively. Moreover, H_2O_2, BE, and BA concentrations down to 0.01 mM, 1.2×10^{-4} mM and 2.08×10^{-3} mM were successfully measured. The pH of the reacting solutions and the total organic carbon (TOC) of water samples were measured with an Accumet Basic AB-10 pH-meter and a TOC-5000A TOC analyzer (Shimadzu), respectively.