Effect of Electron Beam Irradiation on mineralization and toxicity of aspirin

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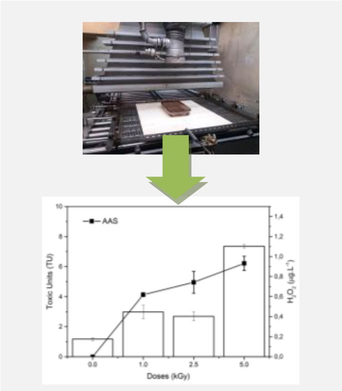

Electron Beam Irradiation (EBI) is an important technology for degradation, mineralization and detoxification of pollutants. In this work, total organic carbon (TOC) and toxicity was evaluated for aspirin after Electron Beam Irradiation at doses of 1.0, 2.5 and 5.0 kGy. Low mineralization was achieved at all applied doses. Toxicity increase and hydrogen peroxide formation was observed with the increase of absorbed dose. EBI can be an interesting alternative process applied as a pre-treatment for alternatives AOPs.

Introduction

Electron beam irradiation (EBI) is a process based on chemical transformation of pollutants induced by ionizing radiation. The degradation of pollutants occurs through reactions with highly reactive species such as hydrated electron, radicals $OH^{\cdot}$ and $H^{\cdot}$, formed by water radiolysis [1]. Several works present EBI as an important technology for degradation, mineralization and detoxification of pollutants. [2, 3].

Pharmaceutical and their metabolites play an important role in the degradation of environment. These contaminants are not completely removed from wastewater treatment plants (WWTPs), reaching water bodies [4].

Non-steroidal anti-inflammatory drugs (NSAIDs) are widely prescribed classes for pain and inflammation. Acetylsalicylic acid (ASA) is widely used in human medicine as an analgesic and antipyretic drug, being also active in preventing platelet aggregation [5].

Previous works have reported complete degradation of anti-inflammatory diclofenac by EBI in presence of fluoxetine at doses of 5 kGy, presenting 65% of toxicity removal for *Aliivibrio fischeri* [3]. The present work focuses on assement of the effect of EBI on mineralization and toxicity of ASA.

Material and Methods

Acetylsalicylic acid ($C_9H_8O_4$), 180.16 g.mol^{-1}; CAS 50-78-2) was obtained from Labsynth, (99.5%). Sulfuric acid was obtained from Neon. Ammonium metavanadate was purchased from Carlo Erba. All the solutions used in EBI experiments were prepared using ultra-pure water (Millipore Milli-Q).

Electron beam irradiation (EBI) was performed using a Dynamitron® Electron Beam Accelerator at 37.5 kW and 1.4 MeV. Samples containing 100 mg.L^{-1} of pharmaceuticals were placed in rectangular glass recipients (Pyrex®) and irradiated in batch at doses of 1.0, 2.5, and 5.0 kGy. The recipients passed twice under the electron beam on an automated conveyor at 6.72 m.min^{-1}.

UV–vis spectra was obtained using a Shimadzu UV Spectrophotometer (UV-1800). Conductivity and pH were measured by an HQ40D Portable Multi Meter (Hach). The total organic carbon (TOC) of the samples was measured using a Shimadzu TOC-5000 A equipment.

Acute toxicity assays were performed with the microcrustacean *Daphnia similis*, according to ABNT Brazilian Standard NBR-12713 [6]. The organisms were exposed during 48h to the toxic agents. The evaluated parameters were immobility/mortality. From obtained results, it was estimated the EC50 (Effective Concentration 50), which calculated by the Trimmed Spearman-Karber method. Tukey's multiple comparison significance test (at p = 0.05) was applied to assess the existence of significant differences between toxicity results. Concentration of H_2O_2 was determined thought spectrophotometer measurement with

Ammonium metavanadate in acid medium [7]. The absorbance was measured at 450 nm.

Results and Discussion

The UV absorption spectrum of ASA shows the characteristic aromatic π-π* excitation band centered at 295.0 nm [8]. The intensities of bands increase after irradiation process, showing changes in the aromatic structure (fig 1A).

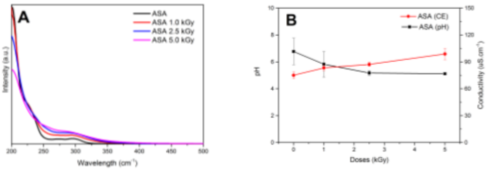

Figure 1. (A) Absorption spectra and (B) pH solutions and conductivity of non-irradiated and irradiated samples of NSAIDs at doses of 1.0, 2.5 and 5.0 kGy.

Figure 1B shows the effect of the absorbed dose on pH and conductivity. A decrease in the solution pH for aspirin was observed with the increase of the absorbed dose. Solution pH ranged from 6.8 ± 0.1 to 5.1 ± 0.0 for ASA. These trends are related with the oxidation of the aromatic ring, ring opening and transformation to carboxylic acids, resulting in decrease of pH [2,9].

Solution conductivity showed an increase, after irradiation process. ASA solution conductivity showed an increase from 77.8 μScm^{-1} to 98.8 μScm^{-1}, which are related to increased concentration of dissolved ions [2].

During the irradiation process, the transformation of organic molecules is a multistep process, which may be detected in carbon content (TOC) [11]. Table 1 represent TOC values from ASA. Low TOC removal was achieved. About 3% of mineralization was reached at all applied doses.

Table 1. TOC concentrations of non-irradiated and irradiated samples of ASA at doses of 2.5 and 5.0 kGy.

Doses (kGy)	TOC (mg. L^{-1})	TOC Removal (%)
0	69.47 ± 0.31	-
1.0	67.37 ± 0.31	3.03 ± 0.65
2.5	66.91 ± 0.47	3.69 ± 0.89
5.0	67.25 ± 0.24	3.19 ± 0.67

Toxicity for ASA was assessed with *D. smilis* (Graphical abstract). EC50 values of 85.14 ± 6.18 mg. L^{-1} was determined for aspirin. For irradiation process, acute toxicity measurements were evaluated in Toxic Units (TU = 100/EC50%). After irradiation process, formation of by-products more toxic may occur. It was verified an increase of toxic according to applied dose. Irradiated ASA at 5.0 kGy presented a higher toxicity, when compared to 1.0 and 2.5 kGy. SZABÓ et al. (2014) demonstrated in increased of toxicity for the luminescent *Aliivibrio fischeri* bacteria test up to 10 kGy of gamma irradiated samples of ASA.

During irradiation, it may occur formation of toxic H_2O_2 always forms, especially in the presence of dissolved O_2 [8]. An increase of peroxide was observed according to the absorbed dose (Graphical abstract). It was verified an increase of H_2O_2 concentration, which varied according to toxicity. These results demonstrated that toxicity may be related to H_2O_2 formation.

Conclusions

In this study, low mineralization was achieved for the anti-inflammatory aspirin at low doses, under the experimental conditions. Increase of toxicity and formation of hydrogen peroxide was observed with increase of dose. In conclusion, EBI can be an interesting alternative process applied as a pre-treatment for alternatives AOPs, technology able to start degradation of many pharmaceuticals.

Acknowledgments

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