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# Electron beam accelerator for detoxification of effluents. When radiation processing can enhance the acute toxicity?

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**Abstract**

Several studies concerning electron beam accelerator and gamma radiation have been developed for treating hazardous contaminants from different matrices. For wastewater improvement, hundreds of papers showed the organics degradation schemes as a function of radiation doses. Nevertheless, few studies included the whole toxicity evaluation. This paper will show the total acute toxicity reduction for several hard toxic effluents treated by electron beam radiation (EBR), using bench scale. Once this kind of studies assess the negative effect of effluent in aquatic organisms, it can be possible that radiation process can enhance the toxicity even due to the presence of hydrogen peroxide. For two hundred real samples submitted to EB radiation treatment, the whole acute toxicity has been substantially reduced for more than 75% of them. The negative effect of hydrogen peroxide for toxicity will be presented and discussed.


*Keywords:* Ionizing radiation; Toxicity; Wastewater; Daphnids and *Vibrio fischeri*

## 1. Introduction

Ionizing radiation has been considered for treating effluents since the 1970s. Nevertheless, few real treatment systems exist around the word using this technology. Considering the costs of such technology it seems to be important in very particular situation, i.e. when biological process are not enough. Although the environmental regulations are getting restrictive by time, it is easy to find untreated or not efficiently treated industrial effluents discharges. Evidence exists of bad management of industrial effluents at hundreds of contaminated sites around the world. This situation will cost considerable amount to clean up.

Using a mobile Electron Beam Treatment System, Nickelsen et al. (1998) have shown the performance of the system with destruction removal efficiency higher than 99% for phenol from chemical industry and refinery process wastewater and other contaminants (BTXE, anthracene, fluorene and naphthalene from refinery wastewater; hexachlorohexane) from commercial pesticides and insecticides manufacture. Nevertheless, when Environmental Protection Agency (EPA) evaluated the process for groundwater decontamination they indicated that EB technology increased groundwater toxicity for *Fathead minnows* but not for water fleas, and removal efficiencies observed for tri and perchloroetilene were 98%; for other chlorinated compounds RE ranged from 68% to >97%; BTEX > 96% (EPA/540/R-96/504, 1997).

When gamma radiation was tested for real sewage disinfection (500 and 700 Gy), chronic toxicity was also

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measured (*Ceriodaphnia dubia*), using samples from six wastewater treatment plants. The authors suggested that $\gamma$ -irradiated effluents either decreased or was unchanged as compared to an undisinfected sample. The effluent samples subjected to chlorination/dechlorination often showed a statistically significant increase in toxicity as compared to the undisinfected and irradiated samples (Thompson and Blatchley, 1999). The study included 30 samples which presented a biological chemical demand between 1 to 15 ppm. None of these samples got higher toxicity after being treated by $\gamma$-radiation.

In Brazil, more than 10 years of study with Electron Beam Accelerator (E-beam) applied to real samples, demonstrated more than 80% acute toxicity reduction for many effluents. An important fact is the very high original toxicity of samples, before treatment. Industrial wastewater and sewage mixture were subjected to radiation (41 raw samples—bench scale) resulting in a statistically significant reduction, after the ideal radiation dose was selected. Part of the samples required radiation doses higher than 20 kGy during the experiments and less than 10% presented higher toxicity. It must be taken into account that for toxicity evaluation, more than one biological species should be used to confirm the treatment requirements.

## 2. Methodology

Table 1 summarizes all the ecotoxicological aspects presented for the irradiated and non-irradiated effluents that were based on two Biological Assays performed with *Daphinia similis* and *Vibrio fischeri* (Borrely, 2001). The toxic response or result means a negative impact of effluent for 50% to the exposed organisms (EC50), in a given standardized condition (CETESB L5.227, 1987 and L5.018, 1986).

The same assay technique was performed for treated effluents from two wastewater treatment plants (WWTP) and for natural water. This water is the same used for the maintenance of aquatic organisms (daphnids) and used for studying water radiolysis product effects and $H_2O_2$.

The radiation was performed with the Dynamitron Electron Beam Accelerator, energy 1.5 MeV, power 37.5 KW (batch—500 ml sample). The samples were collected in two different Wastewater Treatment Plant from São Paulo (WWTP). Composite samples were prepared (for 24 h with 4 subsamples).

*Hydrogen peroxide studies ($H_2O_2$) and organic carbon content (TOC)*: For natural water hydrogen peroxide measurements a 100 ml sample was processed (doses: 0.5, 1.0, 1.5, 2.0, 3.0, 5.0, 10 and 20 kGy) and immediately frozen with dry ice to avoid further $H_2O_2$ loses.

(a) Amperometric hydrogen peroxide determination - Hg Electrode and Polarecord Polarograf with VA stand 663 eletrochemical cell, Metrohnm (−0.07 V vs. Ag/AgCl).
(b) Vanadate reaction and spectrophotometry was also used for $H_2O_2$.
(c) Dissolved total organic carbon was measured, Shimadzu, 5000A.

*Radiation performance*: The benefits of radiation for toxicity removal was analyzed for (a) natural water and (b) wastewater. The toxic effect was demonstrated by the effective concentration that reduces 50% of biological response (bacterial luminescence, immobility and death of fish) expressed as effective concentration (%, v/v—EC50). Transforming this parameter to a proportional number, EC50 can be used as toxic unit (UT). UT values were compared and plotted for most of the studies mentioned in Table 1.

## 3. Results and discussion

Table 1 summarizes the improvement of effluents when treated with irradiation. Partial data concern two different WWT Station from São Paulo. One site required a dose 10 times lower than the second (10–20 kGy). The occurrence of industrial effluents at the WWTP 2/SP made the difference. On the other hand, raw and very toxic industrial effluents (EC50 $<10\%$) required doses between 20 and 50 kGy, sometimes higher.

In general, radiation was very effective for acute toxicity removal for the two biological systems considered in this study. The data suggest that 87% of the total sample was reduced for toxicity (RE $>95\%$).

Nevertheless for less aggressive ambient, contaminated groundwater, for instance, the irradiation introduced toxicity to aquatic organisms (EPA, 1997). This negative radiation effect has been reported as a consequence of hydrogen peroxide as a radiolysis byproduct.

Part of the job was dedicated to natural water irradiation in order to confirm the biological effect and the hydrogen peroxide content. Results are presented in Figs. 1 and 2. Radiation doses from 0.5 to 30 kGy resulted in $H_2O_2$ residual (23.77 up to 64.71 μM), for initial total dissolved organic carbon (TOC) 18ppm. Organic matter as TOC decreased substantially when irradiated (see Fig. 1). The hydrogen peroxide could not be detected in irradiated effluents. There is a possibility of residual $H_2O_2$ being consumed by organic matter.

Table 1
Radiation applied to several sources of effluents and evaluated as a detoxification technique

| Source of wastewater | Level of treatment | Radiation dose (kGy) | Radiation improvement (Toxicity removal) | Observation | References |
|---|---|---|---|---|---|
| WWTP 1/SP[a] | Secondary | 0.25 up to 1.0(EBT) | Complete acute detoxification | Undisinfected final effluent. | |
| WWTP 2/SP[b] | Primary | 10 up to 20.0(EBT) | Higher than 85% for 93% of tested samples | Very important detoxification for *V. Fischeri* and for *D. Similis*. | Borrely, 2001 |
| | Secondary | 5.0 up to 10.0 | 47% and 36% for *V. Fischeri* and for *D. Similis*, respectively | | |
| Chemical ind. 1/SP | Neutralization | > 50.0(EBT) | Higher than 77% for 90% of tested samples; | Received by the municipal WWTP 2 | Borrely et al. (2000) |
| Chemical ind. 2/SP | Several AOP | > 20.0(EBT) | Unchanged (hard original toxicity: < 0.03% for *V.fischeri* ) | Not allowed to discharge | Duarte et al. (2000) |
| Petrol extraction/SP | Untreated | 20 up to 200.0(EBT) | 63% (average for water flea and for *V. fischeri* ) | Several AOPs are being tested | Petrobras Technical Report (2002) |
| Petrol extraction/RJ | Untreated | 20(EBT) | 95% (average for water flea and for *V. fischeri* ) | Several AOPs are being tested | Petrobras Technical Report (2002) |
| Groundwater containing VOCs[c] | Untreated | — | Increased toxicity for fish (*Pimephales promelas*) and not for water fleas | EBT—as a Superfund Innovative Technology Evaluation | EPA/540/R-96/504 (August/1997) |
| Six WWTP(only domestic; domestic + petrochem/ and pharmaceuticals | Primary + chlorination/ dechlorinat. Or ozone | 0.5 and 0.7 Gamma Technology | Less toxic when compared to chlorination/ dechlorination and unchanged as compared to undisinfected samples. | $\gamma$ -irradiation as a disinfectant. *C. dubia* for chronic toxicity | Thompson, Blatchley III (1999) |

[a] WWTP 1/SP—Wastewater treatment plant—São Paulo (domestic influent prevalence).
[b] WWTP 2/SP—Wastewater treatment plant—São Paulo (industrial influent prevalence).
[c] Trichloroethene and tetrachloroethene; 1,2 dichloroethene, 1,1,1,-trichloroethane, BTEX, chloroform and carbon tetrachloride. EBT—Electron beam technology.

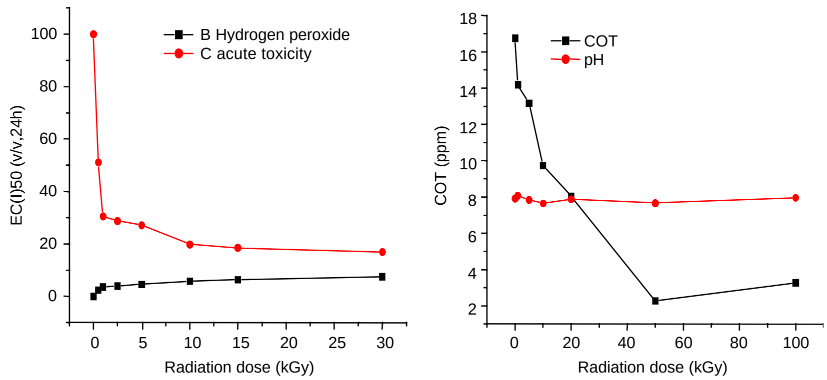


Fig. 1. Radiation-inducing toxicity to natural waters (TOC $<18$ ppm) and increased hydrogen peroxide (from 23.77 up to 64.71 μM).

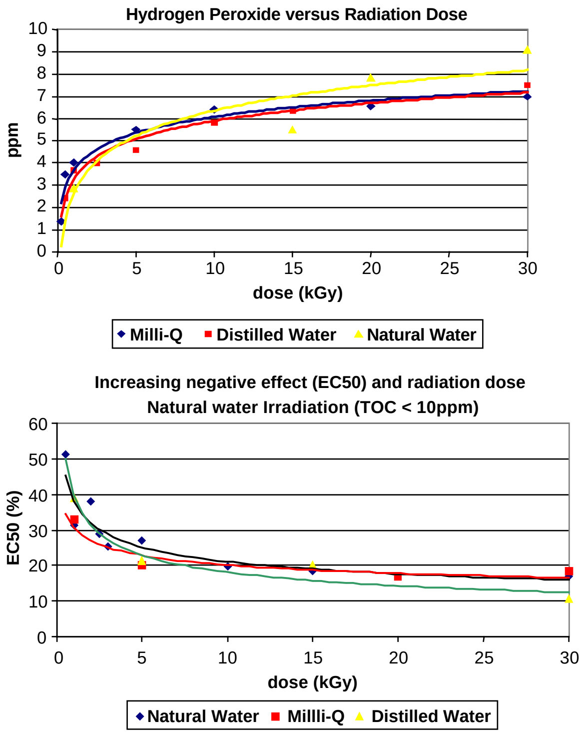


Fig. 2. Hydrogen peroxide formation and its toxicity effects.

## 4. Conclusion

The electron beam irradiation has proved to be an efficient technique for the detoxification of wastewater and must be thinking as a real possibility for complex effluents. For natural water some residual hydrogen peroxide in fact may represent a negative biological effect, which is minimized if little amount of organic matter is present in the wastewater.

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