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## Radiolysis Induced Degradation of Fluoroquinolones

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#### Background of the study

The fluoroquinolones are synthetic antibiotics and inhibit very effectively gram-negative bacteria. These antibiotics do not totally degrade during the common wastewater treatments, hence, they can be released in the environment. Some compounds especially fluroquinolones can be hazardous even in small concentrations to the aquatic environments and ecosystems. The environmental exposure of the fluoroquinolones can lead to bacterial resistance. Because these compounds do not degrade during the common wastewater treatments radiolysis as an advanced oxidation process was investigated.

#### Methodology

Gamma radiation induced degradation of two frequently used fluoroquinolone antibiotics, ciprofloxacin and norfloxacin was investigated with UV-Vis spectrophotometry, with HPLC-UV and with organic sum parameter measurements (chemical oxygen demand (COD) and total organic carbon (TOC)). The samples were irradiated with doses between 0.2 and 10 kGy. The HPLC analysis was performed on a C18 column, with gradient elution and with diode array detection.

In the case of UV-Vis spectrophotometry the solutions were saturated with nitrogen, air or dinitrogen-oxide before the gamma radiation. In some cases *tert*-butanol was applied to scavenge the hydroxyl radicals. At the measurements of organic sum parameters and the HPLC analysis the fluoroquinolone solutions were saturated with air.

The degradations of ciprofloxacin and norfloxacin were also investigated with pulse radiolysis technique. Microsecond pulse radiolysis experiments were performed with 4 MeV accelerated electrons, with electron pulse length of 800 ns. The detection was kinetic spectrophotometric. An optical filter was used because of the bleaching below 400 nm in the case of fluoroquinolones. Transient absorption spectra of the intermediates produced by reactions with hydrated electrons were calculated.

#### Results

The hydroxyl radical induced degradation was the most efficient comparing to the other reactive radicals like hydrated electron and hydrogen atom formed during water radiolysis. The reaction with hydrated electrons was also effective, in this case yellow degradation products were formed. Based on literature these products were presumably isatin analogues.

The COD values decrease approximately linearly with the dose. The decrease was faster for low doses, presumably because the more easily degradable compounds degrade first. The TOC values decreased also approximately linearly with the dose and the results in case of ciprofloxacin and norfloxacin were very similar.

HPLC analysis with diode array detection showed that three intermediates were produced by gamma radiolysis. The parent compound and one of the intermediates were totally degraded, and two other intermediates were partially degraded with the increasing dose. The concentration of the parent compound decreased strongly with the absorbed dose.

Pulse radiolysis experiments showed that hydroxyl radical reacts with the parent compound and one radical intermediate was produced during 5  $\mu$ s, and then it degraded. In the case of hydrated electrons, presumably two radical intermediates were produced, and then it degraded in microsecond timescale.

#### Conclusion

The experiments showed that the degradation and mineralization of fluoroquinolones linearly depends on the absorbed dose. The removal of fluoroquinolones from water was effective in the case of gamma radiolysis and also in the case of pulse radiolysis.

### Country/Organization invited to participate

Hungary

**Primary author:** Ms TEGZE, Anna (Óbuda University, Hungary)

Co-authors: Ms ILLÉS, Erzsébet (Hungarian Academy of Sciences, Centre for Energy Research, Hungary); Ms

TAKÁCS, Erzsébet (Hungarian Academy of Sciences, Centre for Energy Research, Hungary)

**Presenter:** Ms TEGZE, Anna (Óbuda University, Hungary)

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