

## Identification of ecotoxicity caused by O<sub>3</sub> and ClO<sub>2</sub> treatment of wastewater

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**Keywords:** Pharmaceuticals, chlorine dioxide, ozone, wastewater

### Introduction

Chemical treatment with ozone (O<sub>3</sub>) is one of the most promising technologies for removal of organic micro-pollutants<sup>1</sup> from wastewater effluents. Another capable treatment is chlorine dioxide (ClO<sub>2</sub>)<sup>2</sup> which may be implemented in our wastewater treatment plants (WWTPs) in order to increase the removal of micro-pollutants from the effluent. By decreasing the content of micro-pollutants e.g. pharmaceuticals etc. the risk of causing biological damage in the receiving waters will be reduced. By oxidation the micro-pollutants will be either completely mineralized, or transformed into structures that hopefully are easier to degrade biologically. Though, there is also a risk that they are transformed into structures that are similar to the parent compound and still biologically active or that they gain a new toxic potential. This risk increases with lowering the doses of oxidants. It has been shown that transformation products generated from Carbamazepine during chemical treatment with oxidation was more harmful to aquatic organisms compared to the parent compound<sup>3</sup>. To aim at complete mineralization by implementing chemical treatment with oxidation will increase the costs and is therefore not justified. Thus transformation products will most likely be formed. Another risk is formation of by-products e.g. bromate<sup>4</sup>. The aim with this work is to evaluate the risk for increasing the environmental hazard by formation of transformation products and by-products with unwanted biological effects during chemical polishing of wastewater. Presented here is the design and procedure of the tests which will elucidate the hazardous effects caused by chemical treatment of pharmaceuticals and wastewater.

### Material and Method

In order to evaluate the risk of formation of hazardous compounds when water spiked with pharmaceuticals and wastewater is treated with chemical oxidation, ecotoxicological evaluation is required. The ecotoxicological tests employed were an acute toxicity test with *Daphnia magna* (24 h exposure; OECD TG 210) and a growth inhibition test with microalgae (72 h exposure; OECD TG 201).

**Experimental set-up:** Purified organic free water spiked with a mixture containing 114 pharmaceuticals and wastewater effluent collected from a wastewater treatment plant in Stockholm, Sweden was treated with oxidants. The starting concentration of the pharmaceutical mix was set to 96µg/L in order to fit the chosen ecotoxicological test. The samples were prepared in blue cap bottles to which different volumes of ClO<sub>2</sub> or O<sub>3</sub> was added according to Table 1. The ClO<sub>2</sub> stock solution was prepared by mixing solutions of chlorite (ClO<sub>2</sub><sup>-</sup>) with hydrochloric acid. The ozone stock solution was created by passing ozone gas from an oxygen feed reactor through demineralised water placed in an ice bath. The experimental set-up for the ozonation includes an ozone generator from ADD that operates with max 1.5 bar O<sub>2</sub> (g). The addition of either ClO<sub>2</sub> or O<sub>3</sub> to the spiked water was performed in mole ratios to the sum of mole of pharmaceuticals (Tab. 1). Expert judgment was used to determine the amount of the oxidants that would be added to the wastewater for removing pharmaceuticals from effluents. After addition of the oxidant the bottles were left to react for 1 h before residual oxidants was destroyed with Na<sub>2</sub>SO<sub>3</sub> (50 mg/L) thereafter

were the ecotoxicological tests started. Furthermore were the oxidations of wastewater repeated without termination with Na<sub>2</sub>SO<sub>3</sub> before the ecotoxicological tests (Tab. 1). This was done in order to elucidate at which concentration the oxidant residual becomes toxic in wastewater.

Table 1. Samples performed with the presented mole of the oxidant in relation to 1 mole of the sum of pharmaceutical.

|                                   | ClO <sub>2</sub> or O <sub>3</sub><br>with<br>Na <sub>2</sub> SO <sub>3</sub> (50 mg/L) | ClO <sub>2</sub> or O <sub>3</sub><br>without<br>Na <sub>2</sub> SO <sub>3</sub> |
|-----------------------------------|---|--|
| <b>Spiked water</b><br>Mole ratio | 0, 0.5, 1, 2, 5   | -  |
| <b>Wastewater</b><br>Conc. (mg/L) | 0, 2, 4, 6, 15  | 2,4,6  |

**Analysis:** TOC, COD and pH was measured employing standard methods in the effluent. The concentration of the stock solution of ClO<sub>2</sub> was analyzed by oxidation of DPD (N, N-diethyl-p-phenylenediamine) using an Allcon spectrophotometer (Alldos, GmbH). The delivered ozone doses are measured with the indigo method<sup>5</sup>, by preparing bottles with indigo trisulfonate solution in demineralised water in parallel with the treatment samples. The ozone was measured by the unimolecular reaction between ozone and indigo which removes the strong blue colour at 600 nm. The pharmaceuticals were quantified by solid phase extraction (SPE) followed by liquid chromatography-mass spectrometry (LC-MS) with limit of detection in the order 1-10 ng/L.

### Results and Discussion

The experiment will be carried out during November and December 2010. The outcome of these experiments will give valuable information regarding the formation of transformation products and by-products hazardous effect as a consequence of chemical treatment. Whether there is a difference in toxicity between treatment with ClO<sub>2</sub> and O<sub>3</sub> might be answered though this study. Furthermore as the oxidants is added in mole ratios of the mole sum of pharmaceuticals in purified organic water it will be possible to identify at which level of oxidant the most hazardous effects are generated.

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