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Influence of process conditions and water quality on the formation of mutagenic byproducts in UV/H_2O_2 processes

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ABSTRACT

UV/H_2O_2 processes in drinking water treatment may generate byproducts which cause an increased response in Ames fluctuation assays. As this probably involves a mixture of substances in very low concentrations, it is challenging to identify the individual byproducts. Therefore it was studied under which conditions mutagenic byproducts are formed and how this can be prevented. It was found that positive Ames fluctuation test responses only are obtained when Medium Pressure UV lamps are used, and not with Low Pressure lamps. This probably is explained by the photolysis of nitrate, which plays an important role in the formation of mutagenic byproducts. The most important parameters involved in the formation of such byproducts were demonstrated to be the nitrate concentration, the natural organic matter, the UV spectrum of the lamps, and the UV dose applied. These factors explain up to 74–87% of the Ames fluctuation test responses after UV/H_2O_2 drinking water treatment. By taking this into account, drinking water utilities can estimate whether UV processes applied in their case may cause the formation of mutagenic byproducts, and how to take measures to prevent it.

1. Introduction

Disinfection based on UV irradiation is a technique commonly used for drinking water treatment. Recently, advanced oxidation processes (AOPs), such as UV/H_2O_2, O_3/UV and O_3/H_2O_2/UV processes, have become increasingly important for the conversion of organic micropollutants present in drinking water resources (Wols and Hofman-Caris, 2012). Drinking water treatment processes in general don't lead to the mineralization of the constituents. Oxidation and photolysis of natural organic matter (NOM) or organic micropollutants may result in the formation of a broad range of products. Usually these byproducts occur in very low concentrations and in complex mixtures, making health risk assessment difficult to perform. However, by applying bioanalytical assays, like the Ames fluctuation assay, information can be obtained on the potential toxicity of the treated water. Such

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assays do not give information on the exact composition of the water, but may be used as an indicator for the presence of harmful compounds Zegura et al., 2009.

For chlorine based disinfection processes the formation of toxic byproducts is well known, but alternative disinfection techniques like UV irradiation may result in the formation of toxic byproducts as well, as was shown using Ames tests (Monarca et al., 2000).

Guzella et al. (2002) reported that O_3/UV and O_3/H_2O_2/UV processes may increase the mutagenicity of treated water, although it was noticed that adsorption to granular activated carbon (GAC) may effectively remove the toxic byproducts. This is in accordance with other research (Heringa et al., 2011; Penders et al., 2012; Hughes et al., 2013; Martijn et al., 2014), which showed that treatment with UV/H_2O_2 may result in the formation of compounds which cause a positive response in the Ames fluctuation assay. GAC, applied to remove the excess of H_2O_2, was shown to effectively eliminate the mutagenic activity of drinking water treated with UV AOP.

However, other authors (Mahmoud et al., 2014) did not indicate an increase in Ames response when UV processes were applied, although QSAR (Quantitative Structure Activity Relationships) prediction (based on a statistical relation between structural features of the compounds and measured effects) had shown that mutagenic effects might be expected. This was explained from the fact that the byproducts may have been formed in too low concentrations, that antagonistic interactions of mixture components may occur, or that the positive responses would be expected in other bacterial strains than TA98 and TA100, which were used in this research.

de Veer et al. (1994), Haider et al. (2002) also did not find a positive Ames test response upon irradiation with UV doses up to 800 mJ/cm^2 (Haider et al., 2002). Heringa et al. studied the formation of mutagenic byproducts in experiments with medium (MP) and low pressure (LP) UV lamps, and their results suggest that this byproduct formation results from photolysis rather than oxidation (Heringa et al., 2011). De Veer et al. applied high pressure (HP) and LP UV lamps. HP lamps in general emit around 250 nm and in the UV-A (about 360 nm) and visible light range. Haider et al. applied only LP lamps (which emit only at 254 nm). The fact that both De Veer and Haider applied only one wavelength in the UV-C range may explain why they did not detect a positive Ames response. UV photolysis is much more important for MP UV lamps, as these emit a broad spectrum of wavelengths (200–300 nm).

Besides, the formation of toxic byproducts may also depend on the composition of the water matrix, as was shown in water containing copper (Parkinson et al., 2001). UVC and UVC/H_2O_2 treatment caused the degradation of NOM-metal binding sites, resulting in the release of the metal ions, which probably accounted for the toxicity observed.

The studies described above indicate that AOP drinking water treatment may generate potentially mutagenic byproducts, depending on the composition of the water and the process conditions. The identity of the byproducts is as yet largely unknown. Nevertheless, for drinking water utilities applying these techniques it is essential to be able to predict whether or not mutagenic byproducts may be formed, and, if so, what measures can be taken to limit or prevent this. Insight in the process parameters influencing the formation of byproducts will enable utilities to decide on appropriate measures. In this research first several full scale disinfection installations, applying various types of water sources, UV lamps and UV doses, were studied to investigate whether mutagenic byproducts can be expected during regular UV disinfection processes. Then, artificial water was prepared which was used to study which process parameters affect the formation of potentially mutagenic byproducts in AOPs. Using this approach, it becomes clear which parameters need to be adjusted in order to limit or prevent the formation of mutagenic byproducts during UV drinking water treatment.

2. Materials and methods

2.1. Full scale disinfection plants

Samples were taken in various full scale disinfection processes for drinking water treatment. UV doses were determined using sensors, flow data and software installed in the installations. Details are shown in Table 1.

The MP UV dose applied for pretreated water from the river Meuse was increased as compared to the dose usually applied at the plant for the purpose of the present study. These conditions were repeated at the laboratory in a Collimated Beam (CB) set-up. Further laboratory experiments were based on this type of water.

2.2. Laboratory experiments

For laboratory experiments, Meuse water, pretreated by means of sand filtration, was used. By means of membrane filtration (DOW Filmtec 4040 NF270) the NOM was concentrated by a factor 4–5, at the same time decreasing the natural nitrate concentration. Subsequently, the water was diluted in order to adjust the concentration of NOM. In some cases the concentrations of sodium nitrate and/or sodium hydrogen carbonate were adjusted. The effect of this procedure on the NOM composition was measured by DOC-labor Dr. Huber, and is shown in Table 2.

A Collimated beam set-up was used, which was equipped either with a low pressure lamp (LP; Philips TUV PL-L95/4P;

Table 1 – Details of sampling sites at full scale drinking water disinfection processes.

Origin and type of water	Type of lamp	Reduction equivalent UV dose (mJ/cm^2)
River bank filtrate and ground water	MP	25
Ground water	LP	70
Pretreated surface water	LP	42
Pretreated (coagulation, sedimentation, filtrations) surface (Meuse) water	MP	40 100[a] 200[a]
Surface water after pretreatment and dune infiltration	LP	40 100[a]

[a] Dose increased for research purposes.