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Formation and removal of genotoxic activity during UV/H_2O_2–GAC treatment of drinking water

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ABSTRACT

The objective of this study was to determine the genotoxic activity of water after UV/H_2O_2 oxidation and GAC filtration. Pre-treated surface water from three locations was treated with UV/H_2O_2 with medium pressure (MP) lamps and passed through granulated activated carbon (GAC). Samples taken before and after each treatment step were extracted and concentrated by solid phase extraction (SPE) and analyzed for genotoxicity using the Comet assay with HepG2 cells and the Ames II assay.

The Comet assay showed no genotoxic response in any of the samples. In the Ames II, no genotoxic response was obtained with the TAMix (a mix of six strains), but the TA98 strain showed an increase in genotoxic activity after MP-UV/H_2O_2 for all three locations. GAC post treatment effectively reduced the activities to control levels at two of the three locations and to below the level of the pre-treated water at one site. The results indicate that UV/H_2O_2 treatment may lead to the formation of genotoxic by-products, which can be removed by subsequent GAC filtration.

1. Introduction

With increasing populations and limited availability of groundwater, an increase in the use of surface waters for the preparation of drinking water may be expected. These surface waters carry a large variety of micropollutants (e.g. pesticides, pharmaceuticals and organic solvents), for which the traditional treatment technologies used in direct treatment, i.e. coagulation, rapid sand filtration and granular activated carbon (GAC) filtration, are not a robust barrier (e.g. Kruithof and Schippers, 1994). Especially the more polar emerging substances detected in sources of drinking water (Loos et al., 2009) require more rigorous treatment technologies for removal during drinking water treatment.

During the last decades, many studies have been performed on the applicability of Advanced Oxidation Processes (AOP) for the degradation of contaminants in pre-treated natural water (e.g. Beltrán et al., 1996). Although a limited number of AOP installations are in operation for drinking water production, UV/H_2O_2 treatment followed by granular activated carbon (GAC) filtration has proven to be effective in the removal of organic compounds with various chemical characteristics (Kruithof et al., 2007). Typical UV doses applied are in the order of 500–700 mJ/cm^2; H_2O_2 concentrations are typically 5–10 mg/L. In this process, the two mechanisms responsible for contaminant destruction are direct photolysis and oxidation by the in-situ produced hydroxyl radicals (•OH). The high oxidation power combined with the aselective

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character turns the hydroxyl radical into a highly effective oxidant.

It is known and expected that water treatment based on degradation processes may lead to the formation of by-products, e.g. trihalomethanes (THMs) during chlorination and bromate during ozonation of (pre-treated) natural water (e.g. Rook, 1974; Richardson et al., 2007; Von Gunten and Hoigne, 1994). Also UV/H_2O_2 treatment of water may induce the formation of by-products. It appears that practical UV/H_2O_2 process conditions do not fully mineralize contaminants to water and carbon dioxide. Indeed, formation of organic intermediates has been reported (e.g. Lau et al., 2005). By-products may result from the direct photolysis or from oxidation of compounds in the water matrix. Known by-products are nitrite (photolysis of nitrate) and assimilable organic carbon (AOC; photolysis and oxidation of dissolved organic carbon (DOC)). Most organic contaminants strongly absorb light in the UVC range (200–285 nm) of the electromagnetic spectrum and this absorbed energy may lead to changes in the molecular structure of the compounds, resulting in (by)products. Also the omni-present natural compounds in surface water, collectively grouped as natural organic matter (NOM), absorb in the UVC wavelength range and can therefore be degraded into various (by-)products. As the identity of the by-products of UV-oxidation processes is largely unknown, the formation of toxic compounds during UV/H_2O_2 treatment of natural water should be considered.

So far, only a few studies have been conducted on the toxicity of water after UV/H_2O_2 treatment, including studies on estrogenicity and acute toxicity (e.g. Linden et al., 2004). The formation of genotoxic (i.e. DNA-damaging) by-products by the oxidative reactions of ozone and chlorine is a reason to study the induction of genotoxic activity by AOPs such as UV/H_2O_2 treatment. However, although it has been shown that no bromate or THMs are formed (Kruithof et al., 2007; Kashinkunti et al., 2004), no effect-directed genotoxicity studies (detecting any possible genotoxin) have been reported for UV/H_2O_2 treatment.

Quite a few studies have been conducted on the effects of UV-disinfection (without H_2O_2) on the formation of genotoxicity. Conflicting results have been reported, with some finding an increase in genotoxicity after UV-disinfection and others that do not. These differences might be attributed to the use of different water qualities, applied UV-lamps (medium pressure (MP) vs. low pressure (LP)), UV dose and genotoxicity tests (e.g. Helma et al., 1994; Carnimeo et al., 1995; Haider et al., 2001, 2002).

The present study therefore had the following objective: to study the genotoxic activity of surface water before and after treatment with UV/H_2O_2 AOP and after subsequent GAC. To our knowledge, this is the first submitted study on the formation of genotoxic by-products during UV/H_2O_2 AOP.

Several assays are available for evaluating the genotoxic potential of water extracts. To detect gene mutations, we chose to use the Ames II assay (Gee et al., 1998; Fluckiger-Isler et al., 2004). This is a modified version of the well-known classic Ames test, which demands less sample volume. As complementary assay, detecting chromosomal damage, we chose the Comet assay in HepG2 liver cells. The Comet assay is a sensitive test that can be performed with any cell type and allows rapid detection of chromosomal damage such as single and double DNA strand breaks (Tice et al., 2000). The human HepG2 liver cell line has the advantage of having endogenous metabolic capacity and liver cells are one of the first cell types chemicals encounter after intestinal absorption.

2. Materials and methods

Three studies were performed: one in October 2007 with pre-treated Meuse water from Bergambacht (The Netherlands) in a pilot reactor, one in September 2008 with pre-treated Ohio river water, directly upstream of the Cincinnati metropolitan area (OH, USA), in a pilot reactor, and one in February 2009 with samples taken from the full scale plant of PWN at Andijk (the Netherlands), which treats IJssel Lake water. Experimental details (e.g. materials) can be found in the Supplementary Information.

2.1. Water treatment and sampling

Fig. 1 shows the general scheme of the three treatment setups and shows at which points samples were taken. Table 1 gives the most important details of the different treatment steps. Further details can be found in the Supplementary Information.

Table 2 shows the water quality parameters of the sand filtrate prior to the oxidation step. To all samples of the Meuse and IJssel Lake study, 300 mg Na_2SO_3/L was added to quench residual H_2O_2. To all samples of the Ohio River study, 500 mg Na_2SO_3/L was added, whereafter the samples were frozen and shipped to the Netherlands for analysis. At the full scale plant treating IJssel Lake water, duplicate samples were taken.

2.2. Sample extraction and concentration

The detailed extraction procedure can be found in the Supplementary Information. In brief, within 24 h after collection or thawing, three replicates of 1 L of every sample were extracted by solid phase extraction (SPE) with 200 mg Oasis® HLB cartridges (Waters Corporation, Milford, USA) at pH 2.3. In the studies with Ohio River water and IJssel Lake water, mineral water samples (Evian from glass bottles) were included as procedure controls. Elution was performed with 3 serial additions of 2.5 mL of 20% methanol in acetonitrile. The 7.5 mL eluates were evaporated and taken up in 50 μL of DMSO yielding 20,000-fold concentrated extracts. All extracts were stored at −18 °C until analysis.

2.3. Ames II tests

The Ames II test strains (TA98 and TAMix) and media were purchased from Xenometrix (Basel, Switserland). The test procedure provided by Xenometrix, also described by Fluckiger-Isler et al. (2004), was followed, with minor modifications as described in the Supplementary Information. In brief, the water extracts were diluted to 100 μL (1:1) with DMSO to obtain a sufficient amount of sample for all tests and the bacteria were finally exposed to a 200-fold concentration of the water samples in culture medium. Water extracts were