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The impact of H_2O_2 and the role of mineralization in biodegradation or ecotoxicity assessment of advanced oxidation processes

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ABSTRACT

AOP are in the focus of interest as a result of their high efficiency in persistent organic pollutant removal. In the vast majority of experiments targeting quantification of changes in biodegradability or toxicity, conclusions are drawn by a simple comparison of solutions obtained at different stages of the oxidation. These results do not express properly the toxic potential or biodegradability of distinctive product groups, due to performing investigations without taking into account the decrease of organic content caused by mineralization. Moreover, the presence of H_2O_2 is very often also neglected, although it usually exerts strong interfering effects in the analytical methods applied routinely. The aim of present study was to draw attention towards these effects. In this work, the H_2O_2 content was removed by catalytic decomposition with MnO_2, while exposure to equal pollutant concentrations was achieved by setting the solutions to equal COD or TOC values. Results obtained in such way (biological approach) have been compared to data obtained by neglecting both factors (technological approach). Biodegradation and ecotoxicity experiments were performed on the example of 0.1 mmol dm^{-3} sulfamethoxazole solutions oxidized during gamma irradiation. Significant differences were evidenced between the two approaches. Technological approach indicted only moderate transformation to bioavailable substances (BOD_5 COD^{-1} = 0.33), while the biological approach referred to ready biodegradability (0.82). Ecotoxicity assessment performed with *Vibrio fischeri* bacteria demonstrated differences not only in the extent but also in the tendency of inhibition changes. In order to make reliable ecotoxicity assays, the H_2O_2 concentrations should be reduced to at least 0.05 mmol dm^{-3} in *V. fischeri* and *P. subcapitata* experiments, while, practically complete removal is needed in case of *D. magna*. In BOD measurements performed by manometric techniques, reducing the H_2O_2 concentration to at least 0.05 mmol dm^{-3} is also recommended.

1. Introduction

Investigation of advanced oxidation processes usually focuses on quantification of hazardous pollutant removal efficiencies, but there are numerous experiments providing data on changes in toxicity or biodegradation, as well. These biological assays are performed on solutions sampled at different stages of the pollutant oxidation. In other words, toxicity or biodegradability is evaluated on solutions with continuously changing composition and continuously reducing pollutant concentration.

The questionable issue regarding such evaluation is illustrated on the example of a study conducted by Barhoumi et al. (2016). Increase of the 40% initial *Vibrio fischeri* luminescence inhibition to about 45% was reported in course of sulfamethazine degradation by electro-Fenton process. Such difference seems to be insignificant at first sight. But if we complement this data with the fact that the organic content reduced by 60% at this point, the situation becomes quite different. In spite of the high decrease in organic content, the toxicity somewhat increased. This indicates that the degradation products have notably higher toxic potential than the initial molecules, despite the negligible difference shown by the toxicity test. Authors correctly concluded higher toxicity of the resulting solution, but the extent of it is a more difficult issue. Pérez-Moya et al. (2010) prepared reference solutions that contained the initial compound (sulfamethazine) in the same TOC amounts as the solutions treated by photo-Fenton. In this way, they achieved an exposure of test organisms (*Escherichia coli* and *Staphylococcus aureus*) to

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equal pollutant loads; and therefore, direct and accurate comparison of the toxic potential was enabled.

Exposure of decomposer cultures to unequal organic content occurs in biodegradation experiments, similarly to the toxicity tests. Moreover, high degree of pollutant removal and mineralization usually results in formation of readily biodegradable substances (Byers et al., 2002; Dantas et al., 2008). In this way, microorganisms are exposed to notably higher concentrations of non-biodegradable hazardous substances when initial solution is evaluated, while low concentration of readily biodegradable substances is used for experiments following the treatment. Consequently, the results may be distorted due to such different pressure on living communities. This is well illustrated in the work of Baran et al. (2006): BOD_5 increased in course of photocatalytic degradation, but reduced towards the end of the treatment. Reduction was attributed to high degree of mineralization. This example highlights the importance of dilution in biodegradation experiments which intend to compare the post treatment characteristics to those of the initial solutions.

Application of AOP entails appearance of H_2O_2 in the treated solutions. H_2O_2 is dosed when using certain methods (e.g. O_3/H_2O_2, UV/H_2O_2 methods) or it forms in radical reactions (e.g. ionizing radiation) (von Sonntag, 2008). Presence of H_2O_2 in concentrations ranging from few tenths of mmol dm^{-3} up to few mmol dm^{-3} have been reported following various AOP treatment procedures (Lin et al., 1999; Goi and Trapido, 2002; Saritha et al., 2007; Watts et al., 2012; Barazesh et al., 2015). Such amounts may exert strong inhibitory effects on living organisms or cause interferences in analytical evaluation (Talinli and Anderson, 1992; Luukkonen et al., 2014; Wu and Englehardt, 2014). Although these factors are well-known, they are not always considered or they are handled superficially (Baran et al., 2006; Kim et al., 2015; Wang et al., 2017). We underline that experiments mentioned above are correct, but the evaluation of the results is complicated and may also be misleading.

The purpose of the present work was to draw attention towards effects often neglected in toxicity or biodegradability evaluation of AOP. To illustrate the impact of mineralization and H_2O_2, two different sample application approaches were performed in biodegradation and ecotoxicity experiments. The biological approach involved exposure of activated sludge, *Daphnia magna*, *Vibrio fischeri* or *Pseudokirchneriella subcapitata* to equal loads of contaminants and H_2O_2 was removed from the samples (biological approach). In contrast, technological approach was implemented regardless of residual H_2O_2 and pollutant dilution caused by mineralization. The previously mentioned approaches were illustrated and compared on the example of emerging antibiotic pollutant sulfamethoxazole (SMX). The advanced oxidation of solutions containing SMX was carried out using ionizing radiation.

2. Experimental

2.1. Chemicals and materials

All chemicals were purchased from VWR International Ltd. Hungary, except sulfamethoxazole (SMX, 4-amino-N-(5-methyl-1,2-oxazol-3-yl)benzenesulfonamide) that was obtained from Sigma-Aldrich Ltd., Hungary. Activated sludge was taken from the aeration basin of the South-Pest municipal wastewater treatment plant (Budapest Sewage Works, Hungary). The liquid-dried *Vibrio fischeri* Beijerinck (Vibrionales: Vibrionaceae) (ATCC 49387) was supplied by Hach Lange GmbH, Germany, while the standard laboratory colony of *Pseudokirchneriella subcapitata* (Korshikov) (Chlorophyta: Selenastraceae) (ATCC 22662) was supplied by the Agro-Environmental Research Institute, National Research and Innovation (Budapest, Hungary). *Daphnia magna* Straus (Crustacea: Cladocera) originated from LAB Research Ltd. (Hungary).

2.2. Irradiation procedure and sample preparation

Aqueous solution of SMX was prepared in 0.1 mmol dm^{-3} concentrations to ensure results in the well measurable range of the available devices. The initial concentration was checked by liquid chromatography tandem mass spectrometry (LC-MS/MS). Gradient type elution and positive ionization mode was applied with electrospray ionization (ESI), using Agilent 1200 LC and Agilent 6410 MS devices. Further details are described in our previous study (Sági et al., 2015). Advanced oxidation was carried out at room temperature by a ^{60}Co panoramic type γ-irradiation facility (dose rate = 7.6 kGy h^{-1}). The unbuffered samples (1 dm^3, in amber glass bottles) were air saturated prior to irradiation and they were constantly aerated during the procedure.

The solutes decompose indirectly in ionizing radiation treatment, through the reactions of reactive intermediates formed in water radiolysis (von Sonntag, 2008). The major reactant under the experimental conditions used is the hydroxyl radical (˙OH) (Wojnárovits and Takács, 2017). The solutions irradiated with 1 kGy absorbed dose contain hydroxylated products overwhelmingly, but initial molecules are also present in low amounts (Guo et al., 2012; Sági et al., 2015). Prolonged irradiation with 2.5 kGy leads to decomposition of all these molecules and entails appearance of low molecular mass acids (Liu and Wang, 2013; Sági et al., 2015). As these two product groups (hydroxylated products and low molecular mass acids) separate distinctively, 1 kGy and 2.5 kGy doses were used for the sample treatment. In course of irradiation, H_2O_2 forms in radical reactions and it proved to be persistent in purified water matrix. The absorbed doses were measured by ethanol chlorobenzene dosimetry with oscillometric detection (ISO/ASTM 51538, 2009). The standard deviation of the absorbed doses was less than 5%.

In experiments performed with the technological approach, the samples were used as received, without dilution and H_2O_2 removal. In contrast, setting the pollutant concentration to equal values was conducted and the H_2O_2 was removed in experiments executed by the biological approach. H_2O_2 was eliminated by heterogeneous catalysis using 5 g dm^{-3} MnO_2 (overnight stirred at 20 °C, pH = 10). The catalyst was removed by regenerated cellulose membrane filter (RC 0.2 μm). Although results obtained by LC–MS/MS showed that MnO_2 contributes to oxidation of some degradation products, H_2O_2 elimination by this method still represents a good compromise (Kovács et al., 2017). To achieve exposure of test organisms to same pollutant concentrations in the biological approach, samples were adjusted to chemical oxygen demand (COD) or total organic carbon (TOC) values measured at 2.5 kGy. The pollutant load was set by dilution with purified water. This is the most convenient method, as the samples irradiated with 1 kGy and the initial solutions have higher COD or TOC values. Terms biological or technological approach were chosen since all major factors influencing biological evaluation were considered in the biological approach, while in technological approach unaltered solutions were measured as in case of any wastewater treatment plant.

2.3. Biodegradability evaluation

Biodegradability was specified by the ratio of biological and chemical oxygen demand (BOD_5 COD^{-1}). BOD_5 experiments were performed by using OxiTop® Control BOD Respirometer System according to DIN EN 1899-1 (1998). Evaluation of O_2 consumed by the inoculum community was calculated from the pressure drop due to absorption of evolving CO_2. Dilution water was prepared and conditioned as described in the OECD Test No. 301 (1992). 20 cm^3 supernatant of sedimented activated sludge was added to 1 dm^3 of this dilution water. Inoculated dilution water obtained in such way was used to seed the samples (pH set to 7–8 by NaOH or HCl) by a dilution factor of 2. Test mixtures contained allylthiourea nitrification inhibitor to ensure that oxygen consumption derives solely from utilization of the carbon

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