Effect of oxidation and reduction on activated carbon adsorption of organic micropollutants

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Summary. This paper compares the effects of implementing oxidation by ozonation (being one of the state-of-the-art techniques for organic micropollutant removal) versus catalytic reduction (as a potential alternative treatment technique) prior to adsorption onto activated carbon for a set of five organic micropollutants. It can be concluded from the results that in general, reduction resulted in an enhanced affinity of the transformed micropollutants (i.e., the by-products) for activated carbon, in contrast to the by-products obtained from oxidation. It was established that next to hydrophobicity of the micropollutants (expressed as the pH-corrected octanol-water partition coefficient log D), also the polarizability and the dipole moment of the original micropollutant and the by-products formed, were the most influential factors determining adsorption behavior of these solutes.

Keywords. oxidation, reduction, adsorption

Introduction. Organic micropollutants (OMPs) are a class of emerging contaminants, and they are of increasing concern since they are often only partially removed in conventional water treatment systems (Kümmerer, 2009). Due to the ecological effects (Wilson et al., 2003) and potential health concerns, drinking water treatment plants (DWTPs) are increasingly focusing on the removal of these substances from drinking water (Kümmerer, 2009).

Oxidative processes such as ozonation or advanced oxidation processes are increasingly used in DWTPs for the removal of organic micropollutants (von Gunten, 2003). (Advanced) oxidation of organics typically results in the formation of polar by-products (i.e. assimilable organic carbon (AOC)), which are usually removed by a subsequent (biological) activated carbon (AC) filtration. This seems rather counter-intuitive, since an apolar adsorbent like activated carbon typically tends to function well for adsorption of apolar solutes, but not so much for polar solutes like AOC (Fontecha-Cámara et al., 2007).

An alternative technique to oxidation would be reduction, which results in other by-products which might be less polar and might thus be adsorbed better by AC (Li et al., 2013). Recently, several publications highlighted the potential of catalytical reduction with biologically produced bimetallic palladium-gold nanocatalysts for OMP removal (De Corte et al., 2012).

In this study, the effect of oxidation (in this case ozonation) of OMPs prior to activated carbon adsorption is investigated, and compared with the effect of reduction (i.e. catalytical reduction) prior to AC, to assess whether by-products from reduction indeed show better AC adsorption.

Materials and Methods. Stock solutions of organic micropollutants (atrazine, bromoxynil, dinoseb, carbamazepine and diatrizoic acid) were prepared separately in milli-Q water at concentrations of 5 mg C/L. Ozone was dosed to one series of these OMP solutions, at high concentrations of 18.75 mg O3/L, to ensure an as high as possible oxidation conversion, but avoid mineralization of OMPs.

Catalytical reduction was performed on a second series of these OMP solutions, using biogenic bimetallic Pd/Au nanoparticles (bio-Pd/Au). Bio-Pd/Au (with 50 mg Pd/L and 1 mg Au/L) was produced as described by De Corte et al. (2012).

Finally, activated carbon adsorption isotherm experiments (using UltraCarb® 830 (Siemens Water Technologies)) were carried out for the parent compounds, their oxidation products, and their reduction products. Total organic carbon (TOC) analysis was used to quantify the adsorbed fraction.
Results and Conclusions. Oxidation and reduction by-products were identified where possible from the U-HPLC-HRMS analysis spectra, based on known by-product structures published in literature. For OMPs for which no oxidation or reduction products were documented, an attempt was made to identify reaction products from the spectra. For dinoseb, not earlier characterized oxidation products could be identified, being 2-(2-hydroxy-3,5-dinitrophenyl)butanal and one or more of the 2,4-dinitro-6-(sec-butyl)benzene-1,3-diol, 2-(4-hydroxybutan-2-yl)-4,6-dinitrophenol and 2-(1-hydroxybutan-2-yl)-4,6-dinitrophenol isomers. Formerly unknown reduction products were identified for atrazine (4-ethylamino-6-isopropylamino-s-triazine), bromoxynil (3-bromo-4-hydroxybenzonitrile and 4-hydroxybenzonitrile), dinoseb (one or both of the 4-amino-2-nitro-6-(sec-butyl)phenol and 2-amino-4-nitro-6-(sec-butyl)phenol isomers) and carbamazepine (10,11-dihydrocarbamazepine).

After the oxidation and reduction runs, the adsorption efficiency of reduction and oxidation products and the parent compounds was compared (see Figure 1 for diatrizoic acid as an example, and Table 1 for a summary of qualitative comparisons). For atrazine, diatrizoic acid and dinoseb, reduction prior to adsorption resulted in a better adsorptive removal than oxidation, while for bromoxynil and carbamazepine reduction products and oxidation products showed a comparable activated carbon adsorption removal. Thus in all cases, reduction products adsorbed better or equal than oxidation products. When comparing reduction to the parent compound, in three cases (bromoxynil, diatrizoic acid and dinoseb) the reduction pretreatment resulted in an improved removal by activated carbon adsorption; in one case, there was no change (atrazine); and in one case reduction resulted in a worse activated carbon removal (bromoxynil).

Table 1 Adsorption efficiency of reduction products, oxidation products and parent compounds

<table>
<thead>
<tr>
<th>Parent/Reduction</th>
<th>Oxidation/Reduction</th>
<th>Parent</th>
<th>Reduction</th>
<th>Reduction</th>
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<tbody>
<tr>
<td>atrazine</td>
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<td>bromoxynil</td>
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<td>carbamazepine</td>
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<td>diatrizoic acid</td>
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<td>dinoseb</td>
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Adsorption could not be related well to the log D values of the solutes, it was shown that other factors such as polarizability and dipole moment play a role as well in adsorption behavior.

References.