Electrochemical oxidation of personal care and household products in the aerobically treated grey water

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Introduction. Grey water is a part of a total sewage stream, which originates from showers, laundry, kitchen applications etc. [1]. It is considerably less loaded with organic matter and less contaminated with pathogens, than wastewater from toilets and constitute up to 80% of the total volume of wastewater, produced by households [2]. Separately collected grey water after appropriate treatment can be considered as a resource, suitable for reuse as non-potable water, e.g., as water for irrigation, car washing or toilets flushing.

Apart from the organic matter, nutrients and pathogens, grey water also contains a number of emerging micropollutants, namely constituents of personal care and household products [2]. While COD, nitrogen and phosphorous can be effectively reduced by aerobic processes, e.g., in high load aeration tanks or membrane bioreactors, micropollutants are still found in the effluent. Personal care and household products, such as fragrances, UV-filters, biocides and preservatives, mostly consist of hydrophobic compounds, which are often persistent in the environment [3]. A number of those compounds have proven environmental toxicity and/or endocrine disruptive effects. Hereby, their elimination in grey water aimed for reuse is desired.

In this study electrochemical oxidation process was applied for the post-treatment of the effluent of aerobic grey water treatment system installed at the DeSaR (Decentralized Sanitation and Reuse) pilot wastewater treatment plant in Sneek (The Netherlands). So far it is the first study on the application of electrochemical oxidation for grey water treatment. As compared with competitive processes, such as ozonation, advanced oxidation and activated carbon treatment, electrochemical oxidation has a number of advantages: no chemicals are used, the system has low footprint and can be easily automated. Moreover, further reduction of pathogens, which might be present in the effluent, occurs [4]. However, in the electrochemical oxidation process chloride is oxidised to free chlorine, which requires further processing of the effluent. Additionally, little is known on the by-products formation due to the chlorination of the parent compounds.

The aim of this study was to prove the possibility of the removal of micropollutants in grey water by electrochemical oxidation. Furthermore, possibility of by-products formation was evaluated.

Materials and methods. Effluent of aerobic process was treated in the lab-scale electrochemical cell in a batch mode. Before the experiment, effluent was spiked with a solution of micropollutants (methylparaben, ethylparaben, propylparaben, butylparaben, triclosan, galaxolide, tonalide, 4-methylbenzilidene camphor (4-MBC) and ethylhexyl methoxycinnamate (EHMC)) at 80-120 µg/l. The electrochemical cell consisted of 1 bipolar, boron doped diamond film electrode, a terminal Ru/Ir mixed metal oxide coated Ti anode, and a terminal uncoated Ti cathode. The total cell volume was 66 cm^3. With a higher overpotential for oxygen evolution and lower adsorption enthalpy for OH^- radicals BDD electrode has high oxidation potential, thus, increasing overall performance of the cell. Treated liquid (V = 2 l) was constantly pumped through the oxidation chamber during 5 h. With the current of 0.12 A applied, which correspond to the current density of 2.64 $A \cdot cm^{-2}$, total specific electrical charge (Q) was 0.6 Ah/l. Samples for micropollutants analysis were taken at time 0, 0.25, 0.5, 1, 2, 3 and 5 h, for chloride, total and free chlorine, as well as adsorbable organic halogens (AOX) – at time 0 and 5 h. Stir bar sorptive extraction followed by GC/MS-MS analysis was used for the quantitative analysis of micropollutants.

Results and discussion. Compounds, which contain a phenolic ring, namely methylated parabens and triclosan, were completely transformed at Q = 0.12 Ah/l (Figure 1). The rapid transformation was observed in spite of the low conductivity of the treated grey water (σ = 0.8 – 1.0 mS/cm). This is in line with other studies, which confirm electrochemical degradation of phenol and its derivatives. The oxidation of the phenolic ring probably occurs via aromatic ring-compounds and short chain fatty acids [5]. However, other investigated personal products, which does not contain a phenolic ring in their structure, were moderately degraded with removal efficiency of 56 to 85 % at Q = 0.6 Ah/l.

Chlorinated parabens formation was assessed semi-quantitatively, thus, only the peak areas over specific electrical charge are presented (Figure 2). These results prove that parabens transformation occurs via chlorination pathway and starts with displacement of two hydrogen atoms with chlorine. Yet with increase of specific electrical charge applied those intermediate products are subjected to further degradation. At Q = 0.6 Ah/l chlorinated parabens are completely eliminated.

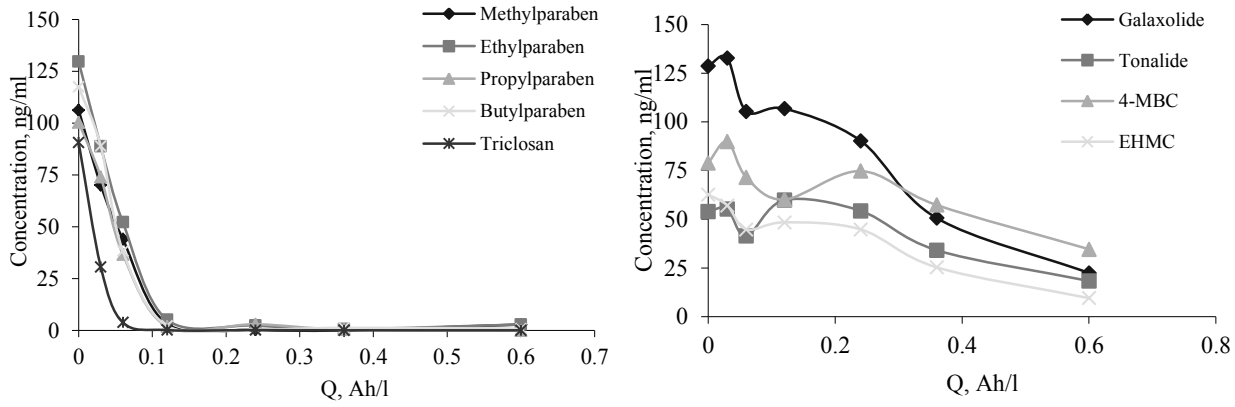

Figure 1. Electrochemical degradation of the personal care and household products which contain (left) and do not contain (right) phenolic ring.

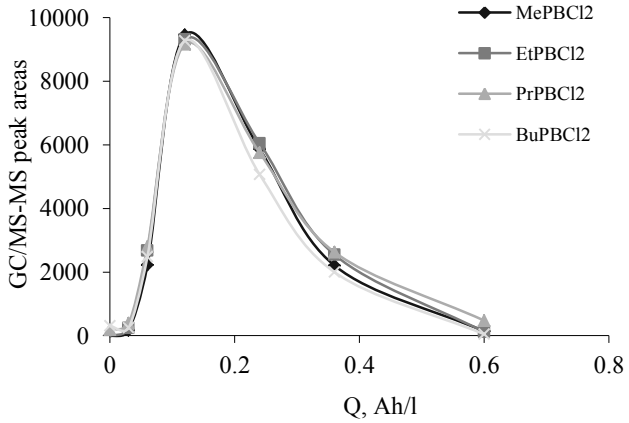

Figure 2. Formation of chlorinated parabens with increased specific electrical charge.

AOX concentration in the effluent increased from 0.2 to 1.3 mg/l, free chlorine – from 0.1 to 13.4 mg/l, while total chlorine – from 0.13 to 13.9 mg/l. The difference between total and free chlorine, which also increases from 0.03 to 0.5 mg/l, is possibly attributed to the chlorinated organics and chloramines. Chlorinated organic species are generally recognized as toxic substances with a potential for bioaccumulation [6]. Even so the toxicity of those oxidation products is under question, e.g., Wang and Farrell (2004) showed that the products of electrochemical oxidation of triclosan are considerably less toxic, than the parent compound [7].

Conclusions. The results of this study proved the possibility for electrochemical oxidation of personal care and household products in treated grey water with low chloride content, though undesirable chlorinated organic compounds are also produced. Electrochemical oxidation also proved to be less effective for the personal care products, which have polycyclic structure. Whether the toxicity is reduced or increased is questionable and requires further evaluation with bioassays. Selection of cathode with catalytic properties for reductive dechlorination may be a possible solution to minimize the concentrations of undesired by-products in the electrochemical grey water treatment.

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