Optimization of UV/H$_2$O$_2$ processes for the removal of organic micropollutants from drinking water: effect of reactor geometry and water pretreatment on E$_{EO}$ values

ABSTRACT
Increasing concentrations of organic micropollutants, like pharmaceuticals, in surface water may require additional treatment for drinking water production. The UV/H$_2$O$_2$ process is very effective for this purpose, but is known for its relatively high energy demand. This energy demand may be decreased by improving the water matrix composition and/or by optimizing UV reactor geometry. Thus, operational costs of the process may be decreased. This can be visualized by calculating the Electrical Energy per Order (E$_{EO}$). By optimizing the water matrix, e.g. by pretreating the water by filtration over activated carbon or with O$_3$/H$_2$O$_2$, the energy demand decreased up to 70%. This is affected by the concentration and type of the natural organic matter present. By optimizing reactor geometry an additional decrease in energy demand, up to 40%, could be obtained. How efficient the process may become strongly depends on the characteristics of the micropollutants involved.

Key words | advanced oxidation, E$_{EO}$, process optimization, reactor geometry, UV/H$_2$O$_2$ process

INTRODUCTION
More and more organic micropollutants can be observed in sources for drinking water (Rivera-Utrilla et al. 2013; Lindberg et al. 2014; Luo et al. 2014). Recently, much attention is being paid to pharmaceuticals. These enter the water cycle via wastewater, as wastewater treatment plants in general have not been designed to deal with such compounds (Heberer 2002). Also, in the Netherlands, surface water has been shown to contain up to more than 35 μg pharmaceuticals/L (ter Laak et al. 2014). As the pharmaceutical concentration is expected to increase in near future, due to, for example, aging of the population (resulting in an increased use of pharmaceuticals) and climate change (resulting in longer periods of drought and thus lower river discharges and correspondingly higher concentrations) (Van Der Aa et al. 2011), Dutch drinking water utilities are considering possibilities for additional treatment of the water. Advanced oxidation processes (AOPs) can be very effective for the removal of such organic micropollutants, as is shown in an overview by Tijani et al. (2014). Often processes based on ozone are applied for drinking water production. However, Dutch surface water contains relatively high concentrations of bromide (on average 100 μg/L in the Rhine and 70 μg/L in the Meuse, where these rivers enter the Netherlands) (Mulder et al. 2015), which by ozone is turned into the toxic bromate. Therefore, the use of ozone is often limited in the Netherlands. However, by combining O$_3$ and H$_2$O$_2$ in a pretreatment, the bromate concentration can be decreased (Lekkerkerker-Teunissen et al. 2012). UV/H$_2$O$_2$ processes are known to be very effective for the degradation of organic micropollutants (Mariani et al. 2010; Wols et al. 2013; Velo-Gala et al. 2014), and in this case the bromide content of the water is no problem. In general, it is believed that the UV process requires a relatively large amount of energy, as high doses are required,
and therefore more effective reactor designs have been studied (Taghipour & Sozzi 2005; Chong et al. 2010).

UV irradiation for disinfection purposes has been used for several decades, and UV reactors have been optimized for this purpose. As for AOPs, a circa tenfold dose is required compared with disinfection reactors (Vilhunen & Sillanpää 2010), the water flow through these reactors in general is decreased in order to increase the UV dose. However, the reactor design has not been optimized for AOP applications (it has been optimized for disinfection purposes). In previous research (Wols et al. 2014, 2015a, 2015c) we have developed a model to describe the conversion of a broad range of organic micropollutants in a UV reactor. This model was also used to optimize the design of UV reactors (Wols et al. 2015b). These reactors were built at van Remmen UV Technology. The present research gives the results of testing of these reactors in pilot set-ups at the producer and at two Dutch drinking water utilities (Dunea and Waterleidingmaatschappij Limburg (WML)). Both utilities apply water from the river Meuse as a source for their drinking water, but with different pretreatment processes. The effect of water quality, (additional) pretreatment of water and of reactor geometry was determined by calculating Electrical Energy per Order (EEO) values (LekkerkerkerkerkerkerkerTeunissen et al. 2013). These give the amount of electrical energy required to convert 90% of a certain compound under given conditions in a certain UV reactor.

MATERIALS AND METHODS

Modeling

The model used consists of two parts:

1. A kinetic model, describing the conversion of pharmaceuticals as a function of the UV dose applied. This model takes into account photolysis and oxidation by hydroxyl radicals, and the effect of matrix compounds like the presence of carbonate, nitrate and natural organic matter.

2. Computational fluid dynamics modeling, calculating the UV dose throughout the reactor.

By combining both models, a model is obtained which can predict the conversion of several compounds throughout the UV reactor. This model has been validated and described in detail in previous research (Wols & Hofman-Caris 2012a, 2012b; Wols et al. 2015a, 2015b, 2015c).

Reactor design

Most commercial UV reactors have been optimized for disinfection purposes, where a log degradation > 5 (>99.999% inactivation) is required. Then it is crucial to minimize short-circuit flows. For AOP, a log degradation of 1.5–3 (96.8–99.9% conversion) in general will be sufficient. Here, the best performance can be obtained when the velocity profile is similar to the fluence rate profile. The original UV disinfection reactor used in these experiments was a D130 reactor, equipped with 1 monochromatic (low pressure) UV lamp (Hereaus NNI 125-84-XL) with an electrical power output of 120 W. The flow through the reactor is 1–2.5 m³/hour. An optimized version of this reactor (D200) was built according to a design optimized based on our models. This reactor also had one LP-UV lamp, and was equipped with either one or two flow plates, as shown in Figure 1. However, at high UV-T values the mean UV fluence will be lower as radiation will be lost to the outer wall. Therefore, the ‘NEW’ reactor was designed for such applications (UV-T > 85%), in order to improve the mean fluence. It contained four 300 W LP lamps, and was applied with a flow of 10 m³/hour. These reactors were described in more detail in Wols et al. (2015b). Finally, an additional type of reactor (‘CHAOS’) was constructed, which has a volume of 1,000 L, contains ten 120 W LP lamps, and is applied with a flow of 10 m³/hour (Figure 1). At van Remmen UV Technology, experiments were carried out with D130 and D200. At Dunea, the D200 with two flow plates, NEW and CHAOS were applied, at WML, the D200 with two flow plates was also used.

Water used

Part of the experiments were carried out at Van Remmen UV Technology, using the drinking water of the village of Wijhe. This is groundwater, treated by drinking water utility Vitens by means of anaerobic nanofiltration, rapid sand filtration, activated carbon filtration (ACF) and aeration. At WML, located in the south of the country, at the production site of Heel Meuse water is taken from a connected channel...
the ‘Lateral Channel’), and then collected in a basin. From there it is extracted by means of bank filtration. Further pretreatment consists of aeration and rapid sand filtration. Drinking water utility Dunea is located downstream of WML in the western part of the Netherlands, and takes its water from a dead end side stream of the Meuse. This water is pretreated by means of coagulation, sedimentation, micro sieves and sand filtration. For some experiments an additional pretreatment step was applied, consisting of ACF, or an O₃/H₂O₂ process (1.5 mg O₃/L in combination with 6 ppm H₂O₂) (Lekkerkerker-Teunissen et al. 2015).

Organic micropollutants

A mixture of over 40 organic compounds, mostly pharmaceuticals, was applied, which had been used for modeling experiments before (Wols et al. 2013, 2015c). These compounds were spiked from a stock solution upstream of the reactor. The targeted concentration of pharmaceuticals in the main stream ranged from 1 to 5 μg/L. H₂O₂ from a stock solution of 5 g/L that was added to the main stream to a resulting concentration of 5 or 10 mg/L. Experiments in Wijhe took place in October/November 2013, experiments at Dunea during summer 2014, and the pilot at WML ran from September 2014 until March 2015, during which period (in September, November and March) three series of dosing experiments were carried out. Every experiment was repeated at least once or twice; detailed information on all EEO calculations and standard deviations is shown in the supplementary information (available with the online version of this paper). Further details can be found in Wols et al. (2015b, 2015c). Pharmaceutical concentrations were determined using ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). The excess of H₂O₂ was not quenched by addition of Na₂SO₃, as this appeared to interfere with the analytical results. (Wols et al. 2013).

Electrical Energy per Order (EEO)

The EEO value gives the amount of electrical energy required to obtain 90% conversion for a certain compound in a
certain reactor under specified conditions, and is calculated according to Equation (1):

$$E_{EO} = \frac{P}{F \times \log \left( \frac{C_i}{C_e} \right)}$$ (1)

In this formula, $P$ is the electrical power, $F$ is the flow through the reactor, $C_i$ is the concentration in the influent and $C_e$ is the concentration in the effluent.

RESULTS AND DISCUSSION

The $E_{EO}$ value strongly depends on the properties of the compound concerned, water matrix composition and reactor geometry. All factors were studied in this research.

Effect of reactor geometry

At van Remmen UV Technology, the D200 reactors were built and tested. Detailed results for all the conversion of all pharmaceuticals investigated is presented in the supplementary information (available with the online version of this paper). In Figure 2, a selection of the $E_{EO}$ values is shown, covering a range of organic micropollutants with various characteristics. Some compounds, like pCBA, are not very sensitive towards UV but react very fast with hydroxyl radicals generated by, for example, H$_2$O$_2$ photolysis (Katsoyiannis et al. 2011). Other compounds, such as ketoprofen, are already very sensitive towards UV photolysis, and do not really require radicals for degradation. Other compounds can be very well degraded by a combination of UV and hydroxyl radicals, whereas metformin, for example, is very difficult to decompose in this way.

In Figure 2, it can be observed that for compounds like ketoprofen and diclofenac, which can easily be degraded by means of UV photolysis, the differences in $E_{EO}$ values for different reactor types are negligible. However, in general the disinfection reactor D130 requires significantly (20–30%) more energy for the degradation than the optimized reactor D200. The difference between both D200 reactors, with one or two flow plates, appears to be very small. Metformin in all cases shows a very high $E_{EO}$ value, as had been expected (Wols et al. 2013).

A similar experiment was carried out at the drinking water production site of Dunea at Bergambacht, The
The performance of D200, equipped with two flow plates, was compared with the performance of the NEW and the CHAOS reactors. These results are shown in Figure 3.

The ‘NEW’ reactor design was optimized for water with a high UV-T value (>85%). Model predictions showed that at lower UV-T values this reactor would not perform better than the D200 version, but at higher UV-T values it would perform better (Wols et al. 2015c). Figure 3 shows that indeed the NEW reactor requires about 5–15% less energy for the same degree of conversion for a broad range of compounds, compared with the D200 reactor (at a UV-T ≥ 85%). Again, for compounds which can easily be converted by means of photolysis, the differences are smaller. The ‘CHAOS’ reactor is characterized by a relatively long residence time of the water inside the reactor, a higher mean UV dose and a broader UV dose distribution. This is beneficial for compounds with a relatively low removal rate, which are less sensitive towards the UV dose distribution, resulting in an increase in degree of conversion (or a lower energy demand to obtain the same conversion). However, for compounds with a high removal rate, the UV dose distribution is more critical. For example: if a UV reactor has a short-circuit (with no UV dose) of 1% of the total water flow, the total removal will be limited to 99%. For compounds with high degradation rates, this will become a limitation for their degradation. This is also shown in Figure 3: for some compounds the EEO value decreases, whereas for others it increases. This especially becomes clear for metformin, which can be better degraded in the CHAOS reactor, with its relatively long residence time, than in the other reactors.

In general from Figures 2 and 3 it can be concluded that optimization of reactor geometry results in a decrease in energy demand of the UV/H₂O₂ process of up to 40% for some compounds (i.e. in EEO value), depending on water quality (UV-T) and the type of compounds involved. In the supplementary information, more data are shown on the improvements obtained at Dunea, first by applying D200 instead of D130, and later by applying NEW instead of D200.

**Effect of water matrix**

The composition of the water matrix can strongly affect the performance of a UV/H₂O₂ process. The role of dissolved organic matter (DOM) both as a photosensitizer and as an inhibitor for the transformation of aquatic contaminants...
was shown, for example, by Wenk et al. (2011). The effect of the water matrix was clearly shown at the pilot set-up at Dunea, where part of the water underwent additional pretreatment by either ACF or by an O\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} process. The composition of the water matrices used, and the effect of additional pretreatment, is shown in Table 1, the effect of additional pretreatment at Dunea is shown in Figure 4. A comparison of the effect of different water matrices at the different pilot sites is shown in Figure 5.

For the Dunea water, it can be concluded that additional pretreatment results in a lower E\textsubscript{EO} value for the UV reactor (in fact the energy use related to ACF or ozone generation should also be taken into account in order to obtain a good idea about the energy use of the total process). The ‘original’ pretreated water here shows the highest E\textsubscript{EO} value for the majority of the compounds tested. In general, ACF seems to give a lower E\textsubscript{EO} value than pretreatment by O\textsubscript{2}/H\textsubscript{2}O\textsubscript{2}. In Figures 4 and 5, the effect of pretreatment on the efficiency of the UV reactors is shown. However, for the total energy consumption of the process, the energy requirement of the pretreatment should also be taken into account. For the O\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} pretreatment at Dunea for a set of compounds overlapping the present mix, this is about 0.027 kWh/m\textsuperscript{3} of water (Lekkerkerker-Teunissen et al. 2012), so for the total process this should be added to the E\textsubscript{EO} value of the UV reactor. Naturally, for other compounds and under different circumstances, this figure can be different.

Obviously, the WML water by far shows the lowest energy demand for the same order of conversion of micropollutants. Even metformin can now be degraded to about 20% (16–28%, depending on the H\textsubscript{2}O\textsubscript{2} concentration, varying from 4.5 to 10.0 mg/L)). The UV-T value at WML is very high: in modeling, UV-T > 85% was already considered to be high, but here it was ≥ 94%. In general, for water treatment (disinfection), lower values and higher flow rates are applied and then reflection does not have to be considered. Because of the high UV-T of WML water, it was found that reflection of the UV irradiation at the outer reactor wall had to be taken into account: the actual UV dose appeared to be over 20% higher than had been calculated without taking this effect into account. Thus the conversion of compounds will be relatively high. Other factors that are involved are the high UV-T value and the DOC concentration/composition. This explains the low E\textsubscript{EO} values calculated. Chu et al. (2016) determined E\textsubscript{EO} value for diclofenac in water with a UV-T of 94% of about 0.1–0.2. This is higher than was found in this case, which is due to the fact that LP lamps are more energy efficient than the MP lamps these authors used.

Although very important, UV-T appears not to be the only important parameter in this respect. Although ACF pretreatment results in a slightly lower UV-T than O\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} pretreatment, the E\textsubscript{EO} for the former process is (significantly) lower. This is probably due to the fact that ACF removes more TOC than O\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} (see Table 1). The TOC composition also plays an important role, as the TOC contents in the water of Wijhe and WML are identical, whereas the UV-T and E\textsubscript{EO} are not. As LP lamps were used, the difference in nitrate content is not expected to significantly affect the UV/H\textsubscript{2}O\textsubscript{2} process (the absorption spectrum of nitrate shows a maximum between 200–240 nm); the effect of the presence of nitrate is accounted for in the models used (Wols et al. 2014). The effect of the TOC composition is probably even larger than is shown in Figure 5, as in this case for Wijhe water a higher H\textsubscript{2}O\textsubscript{2} dose was applied, which lowers the E\textsubscript{EO} value for most compounds. In general, improving the water quality can result in a 30–70% decrease in energy demand of the process, depending on the type of compound involved.

The effect of the H\textsubscript{2}O\textsubscript{2} dose was separately tested at WML, by varying the H\textsubscript{2}O\textsubscript{2} dose at a UV-dose of 365 mJ/cm\textsuperscript{2} (Figure 6). Obviously, the E\textsubscript{EO} for most components strongly increases with decreasing H\textsubscript{2}O\textsubscript{2} content (i.e. when the contribution of oxidation is reduced because of the lower hydroxyl radical concentrations). This is in accordance with the findings of Chu et al. (2016). It also explains why for e.g. diclofenac and ketoprofen this

<table>
<thead>
<tr>
<th>Type of water</th>
<th>Additional pretreatment</th>
<th>pH</th>
<th>UV-T (%)</th>
<th>TOC (mg C/L)</th>
<th>NO\textsubscript{3} (mg/L)</th>
<th>HCO\textsubscript{3} (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wijhe</td>
<td>–</td>
<td>8.0</td>
<td>86</td>
<td>1.4</td>
<td>2.8</td>
<td>155</td>
</tr>
<tr>
<td>Dunea</td>
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<td>82</td>
<td>3.3</td>
<td>9.0</td>
<td>166</td>
</tr>
<tr>
<td>Dunea ACF</td>
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<td>2.4</td>
<td>155</td>
<td>168</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dunea O\textsubscript{2}/H\textsubscript{2}O\textsubscript{2}</td>
<td>8.0 87</td>
<td>3.4</td>
<td>8.6</td>
<td>160</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WML</td>
<td>–</td>
<td>7.5</td>
<td>94</td>
<td>1.4</td>
<td>0.5</td>
<td>167</td>
</tr>
</tbody>
</table>
Figure 4 | Effect of composition water matrix on E<sub>EQ</sub> values in the NEW reactor at Dunea. Gray bars show standard pretreated water, black bars after ACF, dark gray bars additionally pretreated with O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>. 
difference cannot be observed, as these compounds mainly react via photolysis, and are sensitive to that wavelength. Especially as in this case an LP-UV lamp was used, which emits only at a wavelength of 25.7 nm, pure photolysis for most compounds is less effective than in case a broader spectrum, as for a MP-UV lamp, would have been used.
Effect of target choice

Apart from the reactor design and process conditions also the structure of the organic micropollutants plays an important role in the efficiency of the UV/H₂O₂ process. This is related to the sensitivity of the compound towards photolysis and oxidation by hydroxyl radicals. This is shown in Figure 7, which shows the E<sub>E</sub> values for several compounds under different circumstances. The choice of the pharmaceuticals studied here was based on their presence and persistence in the environment, and their toxicity (Ter Laak et al. 2011). Other criteria were their availability and analyzability (Wols et al. 2013). The selected compounds cover a broad range in reactivity towards photolysis and oxidation. Metformin is known to be very difficult to remove by most water treatment techniques, as it is a small, hydrophilic compound that is not very sensitive towards oxidation. However, together with its metabolite guanylurea, it occurs in relatively high concentrations in surface waters.

In Figure 8, a box plot for these compounds is shown. It appears that for most compounds a kind of ‘average’ E<sub>E</sub> value can be calculated, which strongly depends on the compound characteristics but in general varies between 0.1 and 0.5 kWh/m³, depending on water quality, reactor geometry and H₂O₂ concentration. This clearly shows the enormous influence of reaction conditions and reactor geometry on the efficiency of the process. Metformin, and its metabolite guanylurea, are very difficult to oxidize, which is reflected in their very high E<sub>E</sub> values when compared to the other pharmaceuticals. Diclofenac and ketoprofen, which are very sensitive towards photolysis, have a low E<sub>E</sub> value, which is hardly affected by conditions. For paracetamol, on the other hand,
process conditions can play a very important role, and optimization may significantly improve the process efficiency.

The concept of EEO can be used to compare the effectiveness and energy requirement of UV/H2O2 treatment under different circumstances. Parameters affecting EEO are the type of contaminants present, the water matrix, and reactor conditions. By changing one of these parameters, keeping the others constant, the influence of this particular parameter can be calculated. This can be used to optimize the energy requirement of the process. As energy costs contribute largely to the operating costs of the process, EEO can be used to reduce these costs.

CONCLUSIONS

UV/H2O2 processes can be very effective for the degradation of organic micropollutants like pharmaceuticals. Only for metformin (and its metabolite guanylurea), the conversion is significantly lower than for the majority of other pharmaceuticals. Process efficiency, which is directly related to the EEO value (which gives an indication of the energy efficiency of the process), can be strongly increased by optimization of reactor geometry (30–40% energy savings) and/or by improving the water matrix composition and, for example, UV-T (50–70% energy savings). We applied a model based on a kinetic model to describe the UV/H2O2 process and CFD of the flow through the UV reactor; this modeling can be applied to predict the effects of additional treatment on the process efficiency, expressed as EEO values. Furthermore, it can be used to optimize reactor geometry, which also can be expressed in the EEO development. However, the efficiency of the process and the effects of an optimization of either reactor geometry and/or water quality also strongly depend on the molecular structure of the pollutants involved.

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