**Advanced oxidation and artificial recharge: a synergistic hybrid system for removal of organic micropollutants**


**ABSTRACT**

Dunea, the drinking water company for The Hague and surroundings, has as objective the production of drinking water of impeccable quality, particularly with respect to organic micropollutants. As organic micropollutants are only a minor part of the total natural organic matter, a challenge is posed in targeting the removal of a very small, specific part of the DOC, without removing all of the natural organic matter. In addition, organic micropollutants encompass a broad range of physicochemical properties, which make their removal by a single treatment step impossible. Combining AOP with artificial recharge and recovery, two complementary processes are expected to provide a hybrid system for organic micropollutant removal, according to the Dutch multiple barrier approach. Pilot-scale experiments with O3 and different advanced oxidation processes (UV/H2O2, UV/O3 and O3/H2O2) were carried out in cooperation between Dunea and ITT Wedeco. The pilot installation had a capacity of about 0.5–2.0 m³/h, with a varying LP-UV-dose, ozone dose and peroxide dose. Atrazine, isoproturon, carbamazepine, diclofenac and ibuprofen are well removed by UV/H2O2 as well as by O3/H2O2.

In general, O3/H2O2 is a more energy efficient process compared to UV/H2O2. MTBE is best removed by O3/H2O2, Amidotrizoic acid and iohexol are best removed by UV/H2O2.

**Key words** | advanced oxidation, artificial recharge, biodegradation, organic micropollutants

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**INTRODUCTION**

Priority organic substances have been found at ng/L or μg/L concentrations in surface waters throughout the world (Jurgens et al. 2002; Kolpin et al. 2002). Priority substances are also present in the Meuse River, used by Dunea as source for drinking water. Although there is still discussion about the effects of priority substances on human health, the Dutch approach is to protect the sources and, if necessary, to remove those undesired compounds.

In The Netherlands, drinking water is preferably produced from groundwater. When only surface water is available, the common approach is to apply ‘multiple barrier’ treatment. This concept has its origin in disinfection and implies a treatment train with several successive steps for disinfection. By this approach, the use of chlorine, both for primary and secondary disinfection, has been eliminated in The Netherlands (De Moel et al. 2006).

The treatment provided by the dune water company Dunea is a typical multiple barrier treatment, characterized by an extensive infrastructure and multiple treatment steps. The water is first collected in a dead end side stream of the...
Meuse River, acting as a process reservoir. In the beginning of this side stream, coagulation, flocculation and sedimentation take place through dosing of FeSO₄ in combination with aeration. At the water intake, the water is treated by microsieves and transported over 27 km to Bergambacht where the water is filtered by dual media rapid filters and transported by two, 46 and 57 km, transport pipelines to a dune area. In the dune area, artificial recharge with open infiltration takes place. After a residence time in the dunes of at least 21 days, but on average 120 days, the water is abstracted and post treated at three different locations. Post treatment consists of softening, powered activated carbon, cascade aeration, rapid sand filtration and finally slow sand filtration.

The research project described in this paper focuses on design parameters for an AOP installation and implementation of the process in the present treatment. There is special interest in the interaction between the UV/H₂O₂ and the artificial recharge and recovery. Can these two processes, oxidation and soil passage, provide a synergistic hybrid?

**Present removal of OMPs in the Dunea treatment**

Studies performed by various organizations and institutes (RIZA, RIWA and KWR) since 2000 have shown the presence of organic micropollutants (OMPs) in Dutch surface waters (Denneman et al. 2000; Barreveld et al. 2001; Mons et al. 2003; Puijker & van den Broeke 2004). Dunea considers an OMP to be a priority substance if the presence of the OMP, its toxicity and/or its low removal is a reason to take precautions to lower the concentration of this substance. A study has been performed focusing on the removal of OMPs by the Dunea treatment system. In the present treatment train, the barrier against OMPs consists mainly of soil passage during artificial recharge and recovery (ARR), and dosing of powdered activated carbon before rapid sand filtration. OMPs are not always adequately removed in the existing treatment processes.

Another study showed that ARR contributes towards the removal of OMP (Segers & Stuyfzand 2007). Removals depend on the influent concentration, the residence time, the media sorption characteristics, the temperature and the redox conditions. 61% of the OMPs measured were below the detection limit after ARR. X-ray contrast media, except iopamidol, were well removed under oxic conditions. Amiditrizionic acid and carbandazim were well removed under anoxic conditions. However, 15 substances were barely removed during ARR (Segers & Stuyfzand 2007). These substances were usually poorly biodegradable and have poor sorption characteristics, such as MTBE, diglyme, bentazon and 1,4-dioxane.

In the post treatment powdered activated carbon is dosed on the top layer of the rapid sand filtration step. In a pilot installation, the present removal of OMP by powered activated carbon and rapid sand filtration was investigated. Polar substances, like MTBE, ETBE, 1,4-dioxane, PFOS, PFOA and NDMA were not or poorly removed after 1 day. After a complete filter run of 7 days, 14 compounds were removed by less than 14%.

Especially polar compounds with a low molecular weight are not adequately removed by the present treatment. This is confirmed by low concentrations of MTBE, iopamidol, ibuprofen and diglyme in the drinking water.

Therefore Dunea is performing research to extend the present treatment with an advanced oxidation process (AOP) with UV radiation and hydrogen peroxide. The pretreatment location Bergambacht is seen as the most appropriate location to install the UV/H₂O₂, after the dual media rapid filters (Teunissen et al. 2006; Knol et al. 2007).

**Removal of OMPs by AOPs**

Many AOP processes exist, such as UV/H₂O₂, H₂O₂/O₃, UV/O₃, UV/H₂O₂/O₃ or UV/TiO₂. In order to prevent the formation of bromate from bromide, Dunea is mainly interested in AOPs without the use of ozone such as UV/H₂O₂ which avoid bromate formation.

Pilot trials were carried out by Ried et al. (2008) to treat groundwater at an industrial site contaminated with 1.4 dioxane and chlorinated compounds like tetrachlorethene (PCE) and trichlorethene (TCE). Different AOPs (UV/O₃−H₂O₂/O₃−UV/H₂O₂) were tested and compared in terms of reduction rate. All tested options fulfilled the requirements, but economical aspects also have to be taken into consideration. The evaluation of the power consumption is a vital point in selecting a competitive treatment
process using advanced oxidation. It appears that \( \text{H}_2\text{O}_2/\text{O}_3 \) in this case was the most efficient process regarding the energy consumption.

**The removal of OMPs by soil passage**

Soil passage is also able to remove OMPs. Few studies exist about this subject, and most of them deal with bank filtration (Grüneheid et al. 2005) and not dune infiltration. The removal depends on the contaminant itself, but also on the hydraulic and chemical characteristics of the sediment and aquifer, the local recharge/discharge conditions, and biochemical processes.

Artificial recharge and recovery can eliminate up to 100 percent of the hydrophobic OMPs with high sorption tendencies, such as DDT and heptachlor. Infiltration is found to be accompanied by leveling of or a reduction of the pesticide peak concentrations found in the influent water. The fate of triazine and acetamide herbicides and their degradation products at the Lincoln RBF site in Nebraska USA was studied (Verstraeten et al. 2002). Concentrations of herbicides and degradation products in the collector wells were generally one-half to one-fifth the concentrations of herbicides in the river for atrazine, alachlor, alachlor ESA, metolachlor, cyanazine, and acetochlor. It was found that the quality of drinking water can be improved by encouraging longer subsurface travel times.

Grüneheid et al. (2005), compared a lake bank filtration (LBF) site and an ARR site, at Lake Tegel near Berlin. Both sites near Lake Tegel differ in retention times and in the predominant redox status (ARR: aerobic, 50 days; LBF: short oxic conditions followed by prolonged anoxic conditions). In both cases the concentration of pollutants was measured via a series of monitoring wells. The monitored compounds included: iopromide, sulfamethoxazole and three isomers of the naphthalenedisulfonates. This monitoring program showed that these trace organic compounds, which are representative of different groups of persistent pollutants, behaved differently between BF and ARR. For some compounds an influence of redox conditions on the degradability was observed.

**METHODS**

**Removal by AOP**

Pilot-scale experiments with AOP (UV/H\(_2\)O\(_2\), UV/O\(_3\) and O\(_3)/H\(_2\)O\(_2\)) were carried out in cooperation between Dunea and ITT Wedeco. The pilot installation from ITT was shipped to the treatment plant of Dunea and the installation was fed with pretreated river water which was spiked with different OMPs. The UV-T (UV transmission by 254 nm) of this water was about 78–80%, the average DOC concentration was 5 mg/L.

The pilot plant is equipped with a WEDECO ozone generator with a capacity of 8 g/h and a special designed UV LP reactor with a rated power of 330 Wh. For the H\(_2\)O\(_2)/\text{O}_3\) trials, the water was enriched with hydrogen peroxide and the ozone was introduced into the water by a venturi injector. The applied ozone dosages were regulated by the rated power of the ozone generator. For the H\(_2\)O\(_2)/\text{UV LP}\) trials, the water was enriched with H\(_2\)O\(_2\) and then irradiated with UV light. The UV dosage was regulated by the flow through the UV reactor. The samples for the analysis were taken and residual ozone or H\(_2\)O\(_2\) were not quenched.

The experiments were carried out in two phases, the first in July and the second phase in September (see Table 1). Applied settings are given by the results, as shown in Figures 1–8.

**The removal of OMPs by ARR, with BIOWIN**

As shown in AOPs performance, it is not effective for all selected compounds removal (Figures 1–6). For those compounds showing low removal efficiencies in AOPs, such as atrazine, MTBE and ibuprofen, there is a need of further treatment to improve their removal efficiencies. Natural treatment processes such as ARR or riverbank filtration (RBF) based on soil passage could be an alternative process before or after AOPs to enhance its performance on persistent compounds. The field investigation done by Schmidt et al. (2007) showed that ibuprofen was removed more than 80% at four different bank filtration sites under different redox conditions (aerobic, suboxic, anoxic and strictly anaerobic). The degradation of selected organic micropollutants may not
be strictly by biodegradation, however biodegradation in the natural system play an important role in removal mechanisms of organic compounds. EPI Suite v.3.20 BIOWIN model (US EPA, http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm) predicts biodegradation potential using group contribution approach. A compound is divided into different fragments and each fragment has biodegradation weight. BIOWIN model 3 and 4 predict primary degradation and ultimate biodegradation in a time frame, respectively. Persistent compounds observed during AOP's were tested using these models, and these compounds can be degraded within long weeks to months (Table 2). Thus, traveling time during ARR will be an important factor to eliminate atrazine, MTBE and ibuprofen. Combining AOP's and natural system processes could be one of combined system in a multi barrier approach to enhance removal of organic micropollutants.

RESULTS

Removal by AOP

A significant removal of the investigated OMPs (atrazine, isoproturon, diclofenac, carbamazepin, ibuprofen, MTBE, amidotrizoic acid and iohexol) were possible with all of the tested processes. The degradation of the pharmaceuticals diclofenac and carbamazepine and the pesticide isoproturon can be very easily done by an ozone treatment step with low ozone dosages (<2 mg/L) (Figure 1). These low dosages even do not result in a detectable bromate formation (Figure 7). Based on the fact that other pesticides like atrazine or chemicals like MTBE do not react efficiently with ozone alone (Figure 2), more powerful full radical producing processes are needed. The tested AOP processes (O3/UV, O3/H2O2 and H2O2/UV) fulfill these requirements.

Table 1 | Field tests—concentration of spiking compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (µg/L) phase 1</th>
<th>Concentration (µg/L) phase 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazin</td>
<td>5.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>5.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>5.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Carbazemepin</td>
<td>4.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>3.0</td>
<td>0.6</td>
</tr>
<tr>
<td>MTBE</td>
<td>4.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Amidotrizoic acid</td>
<td>–</td>
<td>1.1</td>
</tr>
<tr>
<td>Iohexol</td>
<td>–</td>
<td>1.4</td>
</tr>
<tr>
<td>Bromide</td>
<td>110 (measured concentration)</td>
<td>110 (measured concentration)</td>
</tr>
<tr>
<td>Bromate</td>
<td>&lt;1.0 (measured concentration)</td>
<td>&lt;1.0 (measured concentration)</td>
</tr>
</tbody>
</table>

Figure 1 | Results from the first phase—Ozone.
With the H\textsubscript{2}O\textsubscript{2}/UV process, all OMPs except MTBE could be removed by over 90\% or, like atrazine, close to 90\%. Especially the X-ray contrast agents showed a very good degradation by UV/H\textsubscript{2}O\textsubscript{2} (Figures 3 and 4) because both compounds (amidotrizoic acid and iohexol) contain chemical (double, aromatic) bonds which have a good absorption of UV light at a wavelength of 254 nm.

For this degradation rate a UVC-Dosage of 2,050 mJ/cm\textsuperscript{2} which requires a specific energy input of 660 Wh/m\textsuperscript{3} and a H\textsubscript{2}O\textsubscript{2} dosage of 12 mg/L is needed.
The H$_2$O$_2$/Ozone AOP showed a similar performance to the H$_2$O$_2$/UV AOP. Except for the X-ray contrast agent amidotrizoic acid all compounds could be degraded similar or better (like MTBE) compared to the H$_2$O$_2$/UV AOP (Figures 5 and 6).

Bromate formation during the application of this AOP was in the range of $<1-3\, \mu$g/L (Figures 7 and 8). This is relatively low in comparison to the WHO limit of 10 $\mu$g/L but still a measurable concentration. The optimization of the H$_2$O$_2$/ozone process may further minimize the formation of bromate.
The Ozone/UV AOP also showed good performance, but the efficiency regarding the energy consumption and the bromate formation did not show any advantages for this process compared to the others (Figure 2).

DISCUSSION

There are several AOP techniques available. Compounds react different with different AOP techniques. To compare AOPs in a water quality sense, a QSAR (quantitative structure activity relationship) approach is recommended. If the AOP techniques are compared on efficiency, energy consumption can best be expressed in Electrical energy per order (Eeo).

It would appear that the hydroxyl radical should be the clear choice for most oxidation needs. However, practically speaking, one must first consider several factors before selecting an AOP for a particular application. Since it usually takes a combination of two technologies to create the hydroxyl radical, each individual technology has its pros and cons based on the specific application, water quality, and constituents to be treated. System sizing should always be based on pilot trials and bench scale studies to show whether there really is any advantage in using a specific technology over another. The following factors are important when considering AOP:

- water quality
- the potential yield of hydroxyl radicals with a given AOP
- the presence & amount of radical scavengers (which negatively impact the available radicals)
- the required energy input of the AOP system
- the hydrogen peroxide residual (if used) and impact on downstream processes
† plant design
† investment and operational cost

AOP and ARR show complementary behavior concerning residence time (short vs long), process fundamentals (chemical vs biological), hydraulics (short circuiting vs smoothing). By this complementary behavior they are expected to be a synergistic hybrid against organic micro-pollutants. In addition a lack of BDOC is often found to be the limiting factor for biological processes. AOP produces BDOC which can enhance the biological processes during ARR when AOP is installed before ARR. Their synergy will be optimal if compounds leaving AOP are or more easily breakdown by biology or less toxic. This phenomenon will be investigated in the near future.

CONCLUSIONS

In this study the removal of the OMPs atrazine, isoproturon, diclofenac, carbamazepin, ibuprofen, MTBE, amidotrizoic acid and iohexol was investigated for several AOP techniques. On a pilot scale O₃, UV/H₂O₂, UV/O₃ and O₃/H₂O₂ were applied on pretreated river water. The degradation of the pharmaceuticals diclofenac and carbamazepine and the pesticide isoproturon can be very easily done by an ozone treatment step with low ozone dosages (<2 mg/L). With the H₂O₂/UV process, all OMPs except MTBE could be removed by over 90% or, like atrazine, close to 90%. Especially the X-ray contrast agents showed a very good degradation by UV/H₂O₂. The H₂O₂/Ozone AOP showed a similar performance to the H₂O₂/UV AOP. Except for the X-ray contrast agent amidotrizoic acid all compounds could be degraded similar or better (like MTBE) compared to the H₂O₂/UV AOP. Bromate formation during the application of this AOP was in the range of 1–3 μg/L and low in comparison to the WHO limit. The optimization of the H₂O₂/Ozone process may further minimize the formation of bromate. The Ozone/UV AOP also showed good performance, but the efficiency regarding the energy consumption and the bromate formation did not show any advantages for this process compared to the others.

As the concern over emerging contaminants grows, it is only a matter of time until more and more of these contaminants are regulated. More than looking for a specific technology, end users should focus on selecting a cost-effective advanced solution to meet their treatment needs. Beside the cost effectiveness of the oxidation step or an adsorption step on its own the possible synergistic effects with other treatment steps in a treatment train is important. To meet future regulations and producing safe drinking water it is essential to understand the effects of the single treatment steps e.g. ARR and AOP better and find out the best synergistic effects in a treatment train.

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REFERENCES

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