UV/H₂O₂ treatment: an essential process in a multi barrier approach against trace chemical contaminants
Joop C. Kruithof and Bram J. Martijn

ABSTRACT
The presence of pesticides, endocrine disruptors and pharmaceuticals caused PWN to implement multiple barriers for organic contaminant control in their surface water treatment plants. A combination of advanced oxidation by UV/H₂O₂ treatment and granular activated carbon (GAC) filtration is installed. Medium pressure UV experiments in a standard pilot reactor have been carried out into the degradation of a representative selection of pesticides found in PWN’s main raw water source, the IJssel Lake. It was observed that atrazine and diuron are more sensitive to direct photodegradation while bentazone and bromacil are primarily degraded by hydroxyl radical oxidation. Addition of H₂O₂ increased the decay rate of all selected herbicides. Using computational fluid dynamics, irradiance distribution and kinetic models developed by Trojan Technologies Inc., an optimized UV-reactor was designed. In tests with a pilot reactor according to this new design, the predicted performance was confirmed, both for photodegradation and hydroxyl radical oxidation. During the research period, the scope broadened from pesticides to pharmaceuticals, endocrine disrupting compounds, solvents and algae toxins. At process conditions 0.56 kWh/m³ and 6 mg/L H₂O₂, 80–100% degradation was achieved for compounds such as mecoprop, clofibric acid and diclofenac. A somewhat lower degradation was found for dicamba, 2, 4-D, bentazone, ibuprofen, carbamazepine and sulphametoxalol. The developed modelling was used to design a full scale UV/H₂O₂ system with an electric energy of 0.56 kWh/m³ for treatment of 3,000 m³/h. In a site acceptance test, degradation of atrazine was measured at two UV-doses at a fixed H₂O₂ dose of 6 mg/L. The installation performed as predicted by the design models and design criteria were met. At wtp Andijk, UV/H₂O₂ is integrated in the existing process train, preceded by conventional surface water treatment (coagulation, sedimentation and filtration) and followed by GAC filtration providing a robust barrier against reaction products from both oxidation and photolytic degradation (assimilable organic carbon, nitrite). Replacing the conventional pretreatment by ion exchange followed by ceramic microfiltration will further improve the economics of UV/H₂O₂ treatment.

Key words | hydroxyl radical oxidation, ion exchange pre-treatment, pesticides, pharmaceuticals, photolysis, UV/H₂O₂ treatment

ABBREVIATIONS

AOC Assimilable Organic Carbon
CFD Computational Fluid Dynamics
CSF Coagulation, Sedimentation, Filtration
2,4-D 2,4-Dichlorophenoxyacetic acid
EDTA Ethylene Diamine Tetra Acetic acid
EED Electrical Energy Demand
GAC Granular Activated Carbon
GC Gas Chromatography
GC-MS Gas Chromatography combined with Mass Spectrometry
H₂O₂ Hydrogen peroxide
HPLC High Pressure Liquid Chromatography
IX Ion Exchange
kOH Hydroxyl radical reaction rate constant

INTRODUCTION

In 1919 when PWN Water Supply Company (North Holland (PWN)) was founded, the demand for drinking water was satisfied by ground water extraction. To satisfy the growing drinking water demand, in 1968 surface water treatment plant (wtp) Andijk was commissioned for direct drinking water production from IJssel Lake water. The design treatment of wtp Andijk consisted of microstraining, breakpoint chlorination, conventional treatment and post chlorination.

Shortly after 1968, a number of modifications in the treatment scheme has been introduced to suppress taste and odour and the number of higher organisms. From 1978 until 2004 the treatment shown in Figure 1 was in operation.

After about 35 years of operation the water quality of wtp Andijk still complied with the EC and Dutch drinking water standards. Nevertheless PWN decided to upgrade the treatment scheme because of the following aspects:

- Restricting byproduct (THM) formation by replacing breakpoint chlorination.
- Introducing a multi barrier approach to realize a 10⁻⁴ health risk including the removal/inactivation of Giardia and Cryptosporidium.

PWN decided to pursue a multi barrier approach for both primary disinfection and organic contaminant control with advanced oxidation as the heart of the process.

Initially PWN investigated the feasibility of O₃/H₂O₂ treatment. Primary disinfection should be achieved by ozone and organic contaminant control by both ozone and the combination of ozone and hydrogen peroxide (Kamp et al. 1991). The feasibility of O₃/H₂O₂ was shown by many authors such as Glaze et al. (1987) and Hoigné & Bader (1983). The achieved results for both primary disinfection and organic contaminant control were very promising.

Nevertheless O₃/H₂O₂ treatment was not pursued for application because of the formation of bromate, a suspect carcinogen for humans (Kurokawa et al. 1993). In pretreated IJssel Lake water with a bromide content of 300–500 μg/L the bromate formation could not be restricted to values lower than the Dutch drinking water standard for bromate of 5 μg/L (Kruthof et al. 1995).

After rejection of O₃/H₂O₂ treatment, PWN pursued the application of advanced oxidation without any bromate formation. UV/H₂O₂ seemed a promising option. Primary disinfection should be achieved by UV, to inactivate the recently identified protozoans Giardia and Cryptosporidium (Belosevic et al. 2001).
micropolllutants should be achieved by both UV photolysis and UV/H$_2$O$_2$ oxidation.

The feasibility of UV/H$_2$O$_2$ for organic contaminant control was shown by many authors (Bolton & Cater 1994). UV light does not cause bromate formation. Bromate formation by hydroxyl radicals could be avoided by a large excess of H$_2$O$_2$ (von Gunten & Oliveras 1997).

This paper describes the feasibility of UV/H$_2$O$_2$ treatment for organic contaminant control. The application of UV/H$_2$O$_2$ treatment for primary disinfection (Kruithof & Kamp 2005) and the effect of pretreatment (Martijn et al. 2010) and post treatment (Kruithof et al. 2007) are described elsewhere.

TREATMENT OBJECTIVES ORGANIC CONTAMINANT CONTROL

At the start of this project, the focus was on pesticide degradation. In the Netherlands, around 350 pesticides were used with a large variety in persistence, degradability and toxicity. In IJssel Lake water many of these pesticides such as atrazine, pyrazon, diuron, bentazone, bromacil, methabenzthiazuron, dicamba, 2,4-D, trichlorpyr and TCA have been found in concentrations up to 1 μg/L. After storage the concentration levelled off to 0.5 μg/L. For this type of compound, the EC and Dutch drinking water standard of 0.1 μg/L must be satisfied. In view of the concentration after storage the required removal/degradation by treatment is 80%.

UV/H$_2$O$_2$ treatment has been pursued to achieve this objective. Degradation by UV/H$_2$O$_2$ treatment is based on a combination of UV photolysis and hydroxyl radical oxidation. Hardly any data for quantum yield ø and hydroxyl radical oxidation rate constant $k_{OH}$ of a number of pesticides are available in the literature. Therefore a database has been developed based on our own collimated beam experiments. Some data are presented in Table 1 (Stefan et al. 1996; Stefan & Bolton 2005).

Applying a model for UV photolysis, hydroxyl radical oxidation and scavenging, developed by Trojan Technologies Inc., it was shown that 80% pesticide degradation can be achieved under realistic process conditions.

More recently the focus was extended to the presence of endocrine disruptors, pharmaceuticals, algae toxins and solvents. In IJssel Lake water endocrine disruptors such as bisphenol A and diethylphalate, pharmaceuticals such as diclofenac, ibuprofen, phenazone, carbamazepine, antibiotics and X-ray contrast media have been found in concentrations up to several hundred ng/L. Also algae toxins such as geosmin, isoborneol and microcystine and solvents such as diglyme have been identified. Finally disinfection byproducts such as NDMA, complexing agents such as EDTA and NTA and fuel retardants such as trichloroethylphosphate, PFOA and PFOS have been found.

Partly in cooperation with UV manufacturers, the following research efforts have been carried out into:

- the degradation of pesticides with a standard pilot installation;
- the development of specialized pilot and full scale reactors for organic contaminant control and advanced models to predict the degradation by UV photolysis and hydroxyl radical oxidation and the impact of scavenging on degradation;
- the application of UV/H$_2$O$_2$ treatment for the degradation of pesticides and pharmaceuticals in an advanced pilot installation;
- the degradation of pesticides and complexing agents by full scale UV/H$_2$O$_2$ application;
- the impact of advanced pretreatment on the economics of H$_2$O$_2$ treatment.

MATERIALS AND METHODS

Standard UV equipment consisted of three Berson InLine250 reactors in series. Each reactor was equipped with two medium pressure UV lamps of 2 kW. The power level of the

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>ø</th>
<th>$k_{OH} \times 10^9$ (M$^{-1}$s$^{-1}$)</th>
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<tbody>
<tr>
<td>Atrazine</td>
<td>0.005 (254 nm)</td>
<td>2.4–3.0</td>
</tr>
<tr>
<td>2,4-D</td>
<td>0.0262 (254 nm)</td>
<td>2.3</td>
</tr>
<tr>
<td>Diuron</td>
<td>0.22 (254 nm)</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>0.014 (296 nm)</td>
<td></td>
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<tr>
<td>Isoproturon</td>
<td>0.045 (254 nm)</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>0.0045 (275 nm)</td>
<td></td>
</tr>
<tr>
<td>Simazine</td>
<td>0.083 (254 nm)</td>
<td>2.9</td>
</tr>
<tr>
<td>TCA</td>
<td>-</td>
<td>0.06</td>
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</tbody>
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UV lamps could be set at 60, 80 and 100% of their maximum power. Individual reactors could be switched off. The flow in the standard UV equipment could be varied between 5 and 12 m³/h. For photolysis experiments, no hydrogen peroxide was dosed. The hydrogen peroxide dosage could be varied between 0 and 15 mg/L.

The advanced UV pilot reactor, designed for AOP, was a Trojan SWIFT4L12 UV reactor. The reactor was equipped with four medium pressure UV lamps of 2.8 kW. The output of the UV lamps could be controlled continuously between 30 and 100% of the maximum output. The flow could be varied between 10 and 40 m³/h. The hydrogen peroxide dosage could be varied between 0 and 15 mg/L.

The full scale UV/H₂O₂ installation of wtp Andijk consists of 12 Trojan SWIFT16L30 UV reactors, arranged in three trains of four reactors each. Each UV reactor is equipped with 16 medium pressure UV lamps of 12 kW. The output of the UV lamps could be controlled continuously between 30 and 100% of the maximum output. The design capacity of the system is 0.56 kWh/m³ to treat 3,200 m³/h. The hydrogen peroxide dosage could be varied between 0 and 15 mg/L.

For the pilot experiments, pesticides and pharmaceuticals were added to the feed water of the UV reactor to such level that the residual after treatment was well above the detection limit of the analytical method of 0.02 μg/L. Chemical analyses were performed using gas chromatography (GC) and high pressure liquid chromatography (HPLC). The performance of the full scale installation was monitored by using gas chromatography-mass spectrometry (GC-MS).

RESULTS AND DISCUSSION

UV/H₂O₂ research in standard pilot equipment

The degradation of 10 emerging pesticides: atrazine, pyrazon, diuron, bentazon, bromacil, methabenzthiaxon, dicamba, 2,4-D, trichlorpyr and TCA has been studied in three Berson Inline 250 reactors in series.

In the first place, the degradation by UV photolysis was investigated for an electric energy ranging from 0.25 to 2.0 kWh/m³. All investigated pesticides showed a significant degradation by UV photolysis. The conversion for an electric energy input of 1.0 kWh/m³, (a UV dose of ~1,000 mJ/cm²) is presented in Figure 2.

For an electric energy input of 1.0 kWh/m³, degradation by UV photolysis ranged from 18% for TCA to 70% for atrazine showing that TCA is least susceptible and atrazine most susceptible for UV photolysis. A higher conversion should be realized by adding H₂O₂ to initiate an additional oxidation by hydroxyl radicals.

The degradation of the same 10 pesticides by combined UV photolysis and OH radical oxidation was studied for a range of electric energy consumptions (0.33–2.2 kWh/m³) and H₂O₂ dosages (0–15 mg/L). The degradation for a compound with a high susceptibility for UV photolysis (atrazine) and OH radical oxidation (pyrazon) in the same standard Berson reactor configuration is presented in Figure 3.

As already mentioned atrazine was photolized by an electric energy of 1 kWh/m³ for 70%. To increase the degradation to the target conversion of 80% a dosage of 13 mg/L H₂O₂ was needed.

Pyrazon was photolized by an electric energy of 1.0 kWh/m³ for 54%. To increase this conversion to 80% a dosage of 8 mg/L H₂O₂ was needed.

These results established the feasibility of UV/H₂O₂ treatment, although the energy consumption was rather high. Therefore a reduction of the required energy consumption was pursued by developing a new reactor design.

Figure 2 | Pesticide degradation by UV photolysis for an electric energy input of 1.0 kWh/m³.
Development of a specialized reactor for organic contaminant control

To improve the required process conditions for 80% atrazine degradation (1.0 kWh/m³ and 13 mg/L H₂O₂), Trojan Technologies Inc. developed an advanced pilot and full scale reactor for organic contaminant control.

The full scale SWIFT 30 reactor without baffling showed some short circuiting at the top and bottom of the reactor. This short circuiting is shown by the yellow spots in the reactor area (see Figure 4(a)). Therefore this reactor was equipped with baffles at the top and bottom to decrease short circuiting with a minimal impact on head loss. The baffled reactor showed an excellent residence time distribution as shown by a strong decrease of the yellow spots in the reactor area (see Figure 4(b)).

The baffled reactor had an excellent calculated efficiency and is implemented in the full scale WTP Andijk plant. For the pilot plant research, a SWIFT 4L12 reactor is developed with the same calculated efficiency.

In collaboration with Trojan Technologies Inc. advanced kinetic models were developed to predict the degradation of organic micropollutants by UV/H₂O₂ treatment (Stefan et al. 2005). In collimated beam research kinetic parameters (quantum yield, OH⁻ radical rate constant) were determined. Combined CFD and kinetic modelling was used to show the efficiency of the developed reactors.

For the newly designed 4L12 pilot reactor, the relationship between the realized degradation and the degradation predicted by the advanced modelling was investigated (see Figure 5).

For several process conditions (0.11–0.56 kWh/m³ and 1–6 mg/L H₂O₂), an excellent relation was found between the predicted and experimental degradation of atrazine, bromacil and diuron.

Figure 6 shows the atrazine degradation as a function of the energy consumption.

In the standard Berson in line reactors, to satisfy PWN’s degradation target for atrazine degradation of 80% an energy consumption of 1.0 kWh/m³ together with a H₂O₂ dose of 13 mg/L was needed. In the newly designed Trojan SWIFT 4L12 reactor only 0.56 kWh/m³ and 6 mg/L...
H₂O₂ were needed, lowering the electric energy consumption by 44% and the H₂O₂ dose by 54% respectively. So the new reactor design strongly increased the economic feasibility of UV/H₂O₂ treatment.

UV/H₂O₂ research in advanced pilot equipment

In this phase of the study, the focus was extended from pesticides to endocrine disruptors, pharmaceuticals, algae toxins and solvents. Degradation of endocrine disruptor bisphenol A, pharmaceutical carbamazepine, algae toxin microcystin and solvent diglyme has been investigated in collimated beam experiments (see Supplementary material Figure S1–S4, available online at http://www.iwaponline.com/ws/013/091.pdf). Additional pilot scale experiments have been carried out in the advanced pilot reactor.

Under standard UV/H₂O₂ conditions, electric energy demand (EED) 0.56 kWh/m³ (UV dose 540 mJ/cm²), H₂O₂ dose 6 mg/L the degradation in the advanced pilot reactor for a set of pesticides and pharmaceuticals are presented in Figures 7 and 8.
With the SWIFT 4L12 reactor a degradation >60% could be achieved for all pollutants under standard conditions. Therefore PWN decided to implement UV/H₂O₂ treatment at their surface wtp Andijk.

Full scale UV/H₂O₂ application

PWN decided to implement UV/H₂O₂ treatment at wtp Andijk after conventional treatment (coagulation sedimentation and filtration) prior to granular activated carbon (GAC) filtration. At the same time breakpoint chlorination was stopped (Figure 9).

PWN has installed a Trojan Technologies Inc. UV/H₂O₂ system consisting of 12 SWIFT 16L30 reactors in three rows of four reactors each. The installation is equipped with a control unit calculating the atrazine degradation capacity under actual process conditions.

Before start up of the retrofit plant, a site acceptance test has been performed. The actual atrazine degradation, the degradation calculated by the control unit and the degradation predicted by the kinetic model is presented in Figure 10.

Good agreement was found between the measured degradation, the model calculation and the prediction by the installation software. At a UVT₂₅₄ of 87%, the realized degradation of 77 ± 9% satisfied the target conversion of 80%.

In IJssel Lake water 25 priority pollutants have been identified in 2004. Most compounds are removed below a concentration of 0.1 μg/L by GAC filtration only. The removal of EDTA by GAC filtration only is poor. The removal of EDTA before and after the installation of UV/H₂O₂ treatment is presented in Figure 11.

After the installation of UV/H₂O₂ treatment, no EDTA was detected in the finished water, even when the raw water concentration was as high as 6 μg/L.

Amongst the micropollutants found in raw IJssel Lake water was anti-epileptic carbamazepine, flame retardant trichloropropylphosphate, detergent Surfynol 104 and melanine. After installation of UV/H₂O₂ treatment, these compounds were removed to below the detection limit of 0.02 μg/L by combination of UV photolysis and hydroxyl radical oxidation. The solvent diglyme does not absorb UV

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**Figure 9** | Treatment scheme wtp Andijk since 2004.

**Figure 10** | Atrazine degradation for an electric energy of 0.42 and 0.56 kWh/m³ with 6 mg/L H₂O₂ (full scale data).

**Figure 11** | EDTA concentration in raw and finished water before and after installation of UV/H₂O₂ treatment (full scale data, 2008).
light. Therefore 50% degradation is achieved completely by hydroxyl radical oxidation. Additional collimated beam research showed that almost all priority pollutants are degraded to a certain extent by UV/H₂O₂ treatment. The contribution of UV photolysis is determined by the UV absorbance and quantum yield. The contribution of hydroxyl radical oxidation is determined by the hydroxyl radical reaction rate constant, depending on the unsaturated sites and/or H-atoms present in the compound. Perfluorinated flame retardants PFOA and PFOS do not absorb UV light and contain neither unsaturated sites nor H-atoms. Therefore these compounds were not degraded at all. Fortunately for treatment perspectives, these compounds are strongly adsorbed by GAC.

The full scale installation is in operation since October 2004. The process has proven to be a very robust and reliable barrier against organic micropollutants. In addition it is a strong and robust barrier against pathogenic micro-organisms (Belosevic et al. 2003). Although improved significantly the electric energy consumption still deserves further attention.

**PERSPECTIVE**

UV/H₂O₂ treatment has shown to be a robust, non-selective barrier against most organic micropollutants. Its application in standard UV equipment, developed for disinfection purposes, was economically feasible, although rather expensive. Development of an advanced reactor for organic contaminant control has improved the economics of the process strongly. A decrease in operational costs of about 50% was achieved.

With the currently available medium pressure UV technology, a further cost reduction by reactor optimization may not be expected. Nevertheless a further cost reduction should be pursued to make UV/H₂O₂ treatment even more attractive.

An option to decrease the operational costs of UV/H₂O₂ treatment even further is to increase the UV transmission (UVT) of the water. The UVT of the water is predominantly determined by the natural organic matter (NOM) and nitrate content, which should be lowered by pretreatment as much as possible.

At this moment pretreatment by (enhanced) coagulation and dual media filtration are applied at wtp Andijk before UV/H₂O₂ treatment (see Figure 1). By this process UVT₂₅₄ is increased from around 60 to 85% by NOM removal. Nitrate is not removed.

In the short term, PWN will replace the current pretreatment. One of the objectives of the new treatment is the increase of UVT by both NOM and nitrate removal. After extensive pilot research, PWN has decided to implement a combination of ion exchange (IX) and ceramic microfiltration. The total treatment scheme after the implementation of the new process is presented in Figure 12.

The new pretreatment has a significant impact on both NOM and nitrate content, caused by the removal with ion exchange. The realized removal depends on the ion exchange process conditions. Under the conditions PWN will install, the UVT₂₅₄ will be increased to 93%.

As already mentioned, the UVT has a strong impact on the electric energy consumption. The relation between the EED for 80% atrazine degradation by UV/H₂O₂ treatment and the UVT₂₅₄ is presented in Figure 13 applying the reactor sizing model provided by Trojan Technologies Inc.

By conventional treatment (CSF), a UVT₂₅₄ of about 85% is realized. Under these conditions, the EED for 80% atrazine degradation by UV/H₂O₂ treatment is 0.56 kWh/m³. By ion exchange (IX), the UVT₂₅₄ is increased to 93% thereby lowering the EED for 80% atrazine degradation to 0.34 kWh/m³, a decrease of 40%. This new pretreatment enables to increase the plant capacity by 40%, from 3,000 m³/h to 4,200 m³/h or to increase the maximum UV
dose by 40% at the original capacity of 3,000 m$^3$/h. Under these conditions, UV/H$_2$O$_2$ treatment is a very robust barrier against organic micropollutant with attractive economics.

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