



## UV/H<sub>2</sub>O<sub>2</sub> TREATMENT AN ESSENTIAL BARRIER IN A MULTI BARRIER APPROACH FOR ORGANIC CONTAMINANT CONTROL

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### Abstract

Caused by the presence of pesticides, endocrine disruptors and pharmaceuticals, PWN has implemented multiple barriers in their surface water treatment plants (Kamp 1997). In addition to reverse osmosis (RO), a combination of UV/H<sub>2</sub>O<sub>2</sub> treatment and granular activated carbon (GAC) filtration is implemented. A research program, ranging from lab-scale and pilot research to process optimization by kinetic and CFD modeling has resulted in full-scale application of UV/H<sub>2</sub>O<sub>2</sub> technology.

During the research stage, the scope broadened from degradation of pesticides to pharmaceuticals, endocrine disrupting compounds, solvents and algae toxins. In bench scale experiments dose-response relationships were established for these organic micro-pollutants. The required degradation of 80% at process conditions 0.56 kWh/m<sup>3</sup> and 6 mg/L H<sub>2</sub>O<sub>2</sub> was confirmed at pilot scale.

At WTP Andijk (20 MGD; 3,000 m<sup>3</sup>/h), UV/H<sub>2</sub>O<sub>2</sub> is integrated in the existing process train, preceded by conventional surface water treatment and followed by GAC filtration, providing a robust barrier against reaction products from both oxidation and photolytic degradation (AOC, nitrite).

The full-scale UV/H<sub>2</sub>O<sub>2</sub> installation is operational since November 2004. Pilot results were confirmed. LC and GC-MS broad screening of the finished water confirmed the nonselectivity of the UV/H<sub>2</sub>O<sub>2</sub>-GAC process, while no harmful byproducts have been observed in finished water. All targets for organic contaminant control are achieved.

*Key words:* Ultraviolet; UV/H<sub>2</sub>O<sub>2</sub>; advanced oxidation; organic contaminant control.

### Introduction

PWN's treatment facility Andijk (20 MGD; 3,000 m<sup>3</sup>/h) treats IJssel Lake water originating from the river Rhine. In the raw water, concentrations of organic micro-pollutants such as pesticides, endocrine disruptors and pharmaceuticals as high as 1.0 µg/L have been observed. The highest concentration observed after storage in a process basin was 0.5 µg/L.

After almost 40 years of operation the water quality of WTP Andijk still complies with the EC and Dutch drinking water standards. Nevertheless an upgrade of the treatment process is introduced in view of the following aspects:

- avoidance of the use of chlorine for breakpoint chlorination thereby restricting the byproduct (THM) formation;
- multiple barriers against pathogenic micro-organisms such as Giardia and Cryptosporidium;
- a disinfection credit by multi barrier approach based on a 10<sup>-4</sup> health risk;
- a nonselective barrier against organic micro-pollutants such as pesticides, endocrine disrupting compounds, algae toxins and pharmaceuticals based on EC and Dutch standards and/or a health risk approach in order to satisfy customer confidence.

Initially PWN investigated the suitability of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment for organic contaminant control. Although the results were very promising the process was not pursued in view of the bromate formation (up to 20 µg/L) in bromide rich (300 – 500 µg/L) IJssel Lake water (Kruithof, 1995). Consequently PWN has pursued UV/H<sub>2</sub>O<sub>2</sub> treatment for both primary disinfection and organic contaminant control.

Water treatment plant Andijk has been retrofitted twice since it was built in 1968. Originally, the treatment consisted of breakpoint chlorination, coagulation, rapid sand filtration and post-chlorination. The first modifications, up to 1978, were the introduction of GAC filtration and post-disinfection with chlorine dioxide. Only recently, advanced oxidation by UV/H<sub>2</sub>O<sub>2</sub> treatment has been implemented for organic contaminant control and improved primary disinfection. Breakpoint chlorination is eliminated from the process. The UV/H<sub>2</sub>O<sub>2</sub> treatment is located just before the existing GAC filters.

## Treatment Objectives

In the Netherlands around 350 pesticides are used with a great variety in persistence, degradability and toxicity. Monitoring programs have shown the presence of many of these pesticides in drinking water sources such as the IJssel Lake. Priority pollutants such as atrazine, pyrazon, diuron, bentazone, bromacil, methabenzthiazuron, dicamba, 2,4-D, TCA and trichloropyr are found in concentrations up to 1 µg/l. After storage these concentrations were lowered to a maximum of 0.5 µg/L. For these compounds the standard of the EC and Dutch drinking water act of 0.1 µg/L must be satisfied. In view of the maximum concentrations after storage, the required degradation by treatment was set at 80%.

More recently monitoring programs have been focused on the presence of endocrine disruptors and pharmaceuticals. In the raw water sources up to several hundred nanograms per liter were found for bisphenol A, diethylphthalate, diclofenac, ibuprofen, phenazone, carbamazepine and several antibiotics and X-ray contrast media. Although no standards have been set for these compounds at this moment, PWN focused on the removal as well to satisfy customer confidence.

UV/H<sub>2</sub>O<sub>2</sub> treatment, a combination of UV photolysis and hydroxyl radical reactions (Bolton, 1994) was pursued for organic contaminant control. Some literature data for the quantum yield  $\Phi$  and  $k_{OH}$  of a number of herbicides are summarized in table 1 (Stefan, 2005).

**Table 1:** Literature data for  $\Phi$  and  $k_{OH}$  of herbicides

Herbicide	$\Phi$	$k_{OH}$ (M <sup>-1</sup> s <sup>-1</sup> )
Atrazine	0.05 (254 nm)	2.4 – 3.0 x 10 <sup>9</sup>
2,4-D	0.0262 (254 nm)	2.3 x 10 <sup>9</sup>
Diuron	0.022 (254 nm)	4.6 x 10 <sup>9</sup>
Isoproturon	0.045 (254 nm)	5.2 x 10 <sup>9</sup>
Simazine	0.083 (254nm)	2.9 x 10 <sup>9</sup>
TCA		0.06 x 10 <sup>9</sup>

Plotting these constants in a simplified kinetic model for herbicide decay showed that 80% degradation could be achieved under realistic conditions. After preliminary research PWN considered the perspective of UV light in combination with H<sub>2</sub>O<sub>2</sub> dosage for organic contaminant control very promising. Partly in collaboration with Trojan Technologies Inc. three major objectives were pursued:

- model degradation by UV photolysis and hydroxyl radical reaction for selected priority pollutants (pesticides, endocrine disruptors, pharmaceuticals);
- predict and determine the potential of a medium pressure UV reactor to degrade those priority pollutants;
- design a full scale UV/H<sub>2</sub>O<sub>2</sub> system for both disinfection and organic contaminant control.

This paper focuses on the degradation of organic micro-pollutants, aspects of disinfection (Kruithof, 2005) and post treatment (Kruithof, 2006) are described elsewhere.

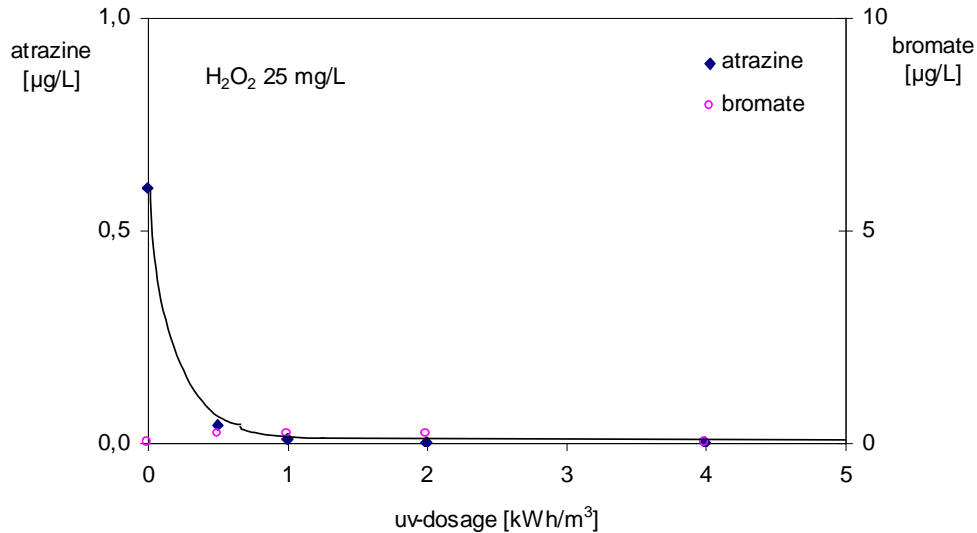
## Results and Discussion

### Bench scale research UV/H<sub>2</sub>O<sub>2</sub> phase 1

Reviewing the research experiences with the ozone peroxide oxidation process (Kruithof, 1995), PWN decided to pursue an advanced oxidation process without the formation of any bromate. UV/H<sub>2</sub>O<sub>2</sub> treatment was ideally suited for this purpose. It has been observed that bromate formation by •OH-radicals can be avoided in presence of an excess H<sub>2</sub>O<sub>2</sub> (Gunten, 1997).

UV/H<sub>2</sub>O<sub>2</sub> treatment is based on the oxidation by hydroxyl-radicals produced by photolysis of H<sub>2</sub>O<sub>2</sub>, combined with direct photolysis of organic contaminants. Dependant on the chemical characteristics of the pollutant, one of the two processes plays a pre-dominant role.

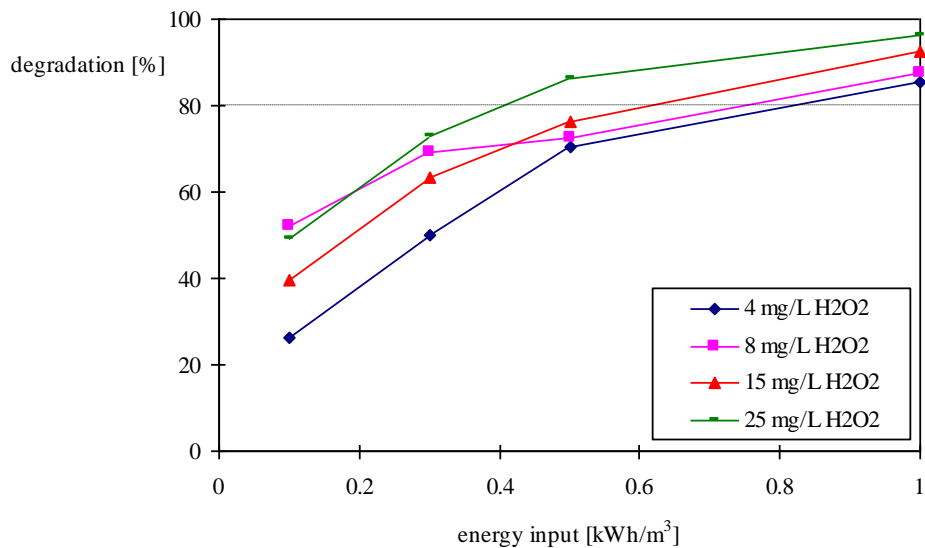
Feasibility of the UV-peroxide process has been studied on bench scale. Figure 1 shows the results of orientating tests performed on reconstituted water, with similar characteristics as the pre-treated IJssel Lake water.



**Figure 1:** Atrazine degradation and bromate formation by UV/H<sub>2</sub>O<sub>2</sub> treatment

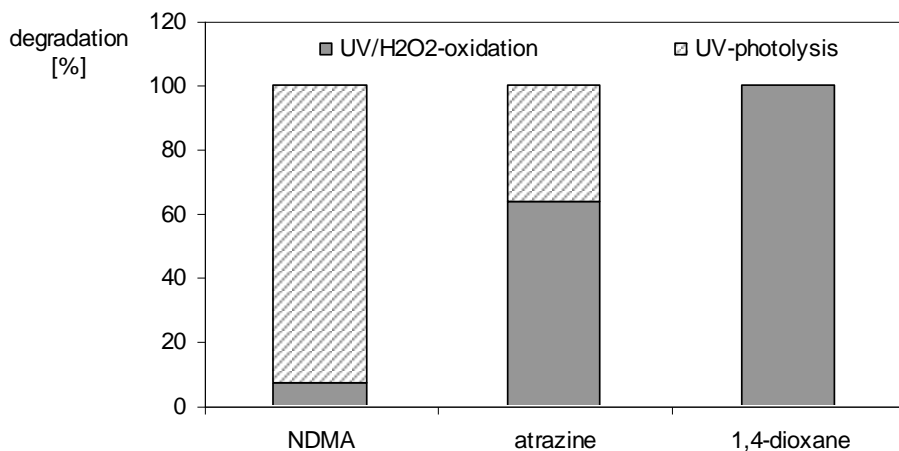
Atrazine was removed to values lower than 0.1 µg/L at an UV-dose of 0.5 kWh/m<sup>3</sup>, while no bromate formation could be observed at an energy input as high as 4 kWh/m<sup>3</sup>. Formation of metabolites was insignificant. No concentrations > 0.1 µg/L were observed.

In additional bench scale experiments (figure 2), dose-response relationships for atrazine degradation were established in pre-treated IJssel Lake water. For a range of combinations of UV-dose and H<sub>2</sub>O<sub>2</sub> dosage, the desired 80% degradation of atrazine was achieved.



**Figure 2:** Atrazine degradation for several process conditions, bench scale experiments in pre-treated IJssel Lake water

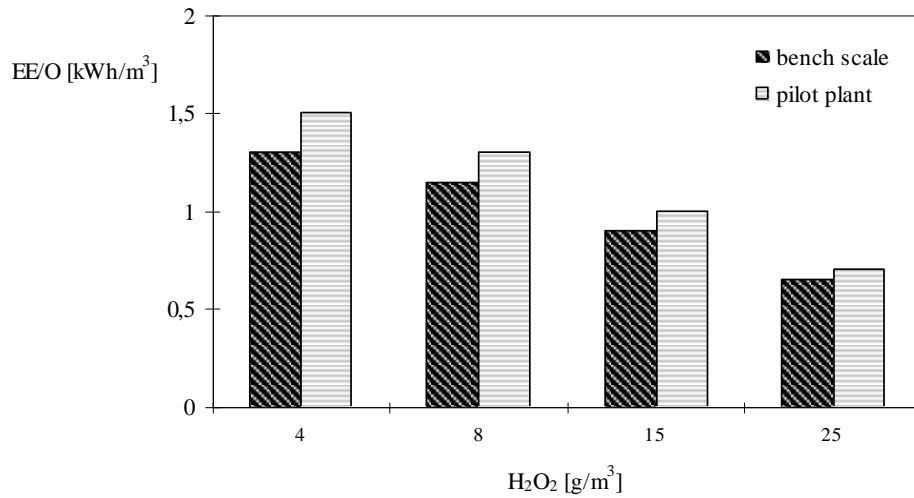
Dependant on the chemical characteristics of the pollutant, either photolysis or hydroxyl radical oxidation plays a pre-dominant role. Figure 3 illustrates this for the degradation of NDMA, primarily due to photolysis, 1,4-dioxane, completely based on hydroxyl radical oxidation and atrazine degradation, based on a combination of both.



**Figure 3:** Ratio of degradation by oxidation and photolysis for NDMA, atrazine and 1,4-dioxane

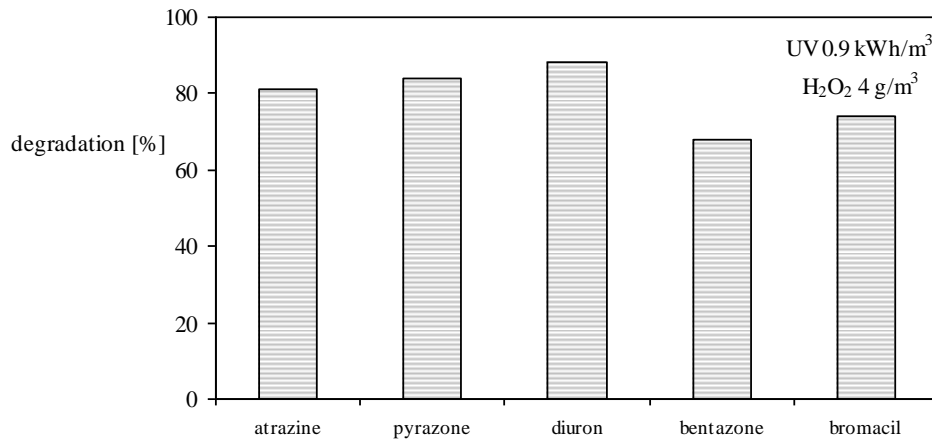
### Pilot scale research UV/H<sub>2</sub>O<sub>2</sub> phase 1

Research was extended to pilot scale. Figure 4 presents the atrazine degradation for several hydrogen peroxide dosages for both the bench scale and the pilot scale installation. A slight decrease in efficiency can be observed, moving from bench scale to pilot scale.



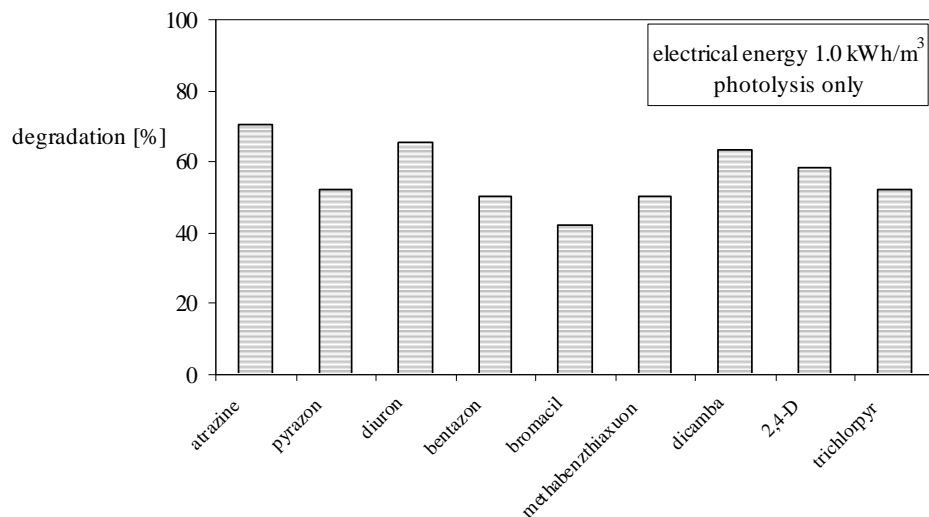
**Figure 4:** Required electrical energy per order for atrazine degradation in pre-treated IJssel Lake water in bench scale experiments and pilot scale experiments for four H<sub>2</sub>O<sub>2</sub> concentrations

Based on the established dose-response relationship for reference pollutant atrazine in the bench scale experiments phase 1, the desired 80% degradation and the good agreement between bench scale experiments and pilot scale experiments, degradation of pesticides atrazine, pyrazone, diuron, bentazone and bromacil was determined in pilot experiments at an UV-dose of 0.9 kWh/m<sup>3</sup> and a H<sub>2</sub>O<sub>2</sub> dosage of 4 g/m<sup>3</sup> (figure 5).



**Figure 5:** Degradation of pesticides at process conditions for 80% degradation of atrazine

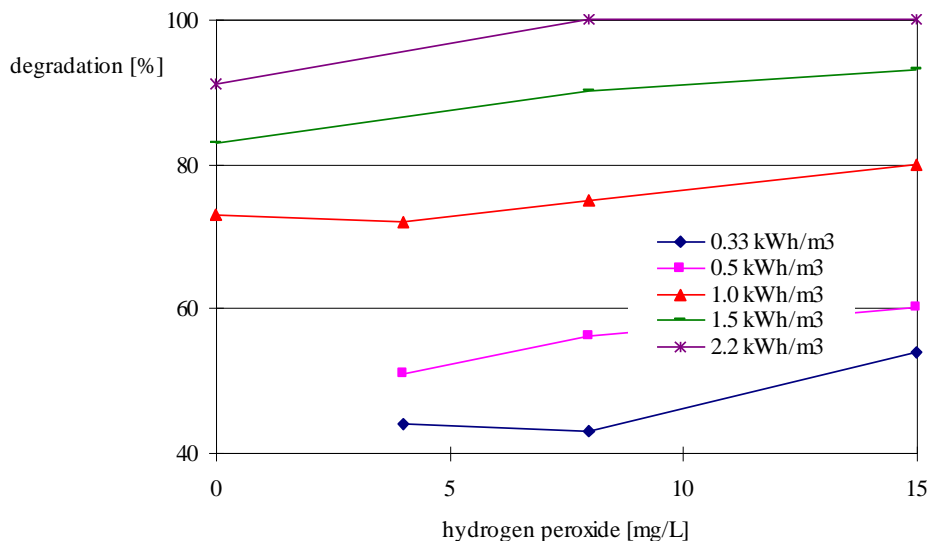
Figure 5 shows that at the selected process conditions, a pesticide degradation varying from 68% for bentazone to 88% for diuron was achieved. Pilot research was extended. For a selection of ten pesticides and one atrazine metabolite, the degradation by UV-photolysis as a function of UV-dose has been studied in an in line Berson pilot. The electric energy was ranging from 0.25 – 2.0 kWh/m<sup>3</sup>. All priority pollutants showed a significant degradation by UV-photolysis. The conversion for an electric energy of 1 kWh/m<sup>3</sup> (~ 1000 mJ/cm<sup>2</sup>) is summarized in figure 6.



**Figure 6:** Pesticide degradation by UV-photolysis with 1 kWh/m<sup>3</sup>

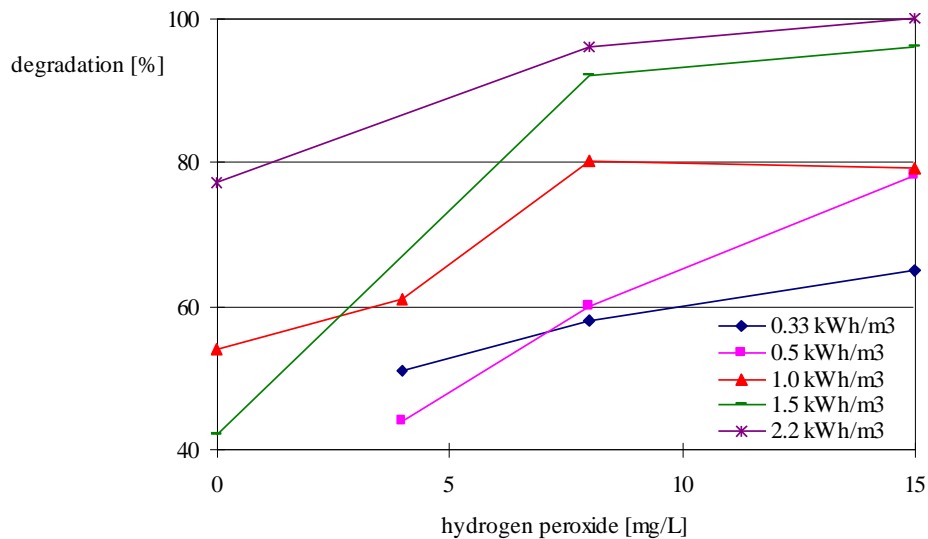
By UV-photolysis with 1 kWh/m<sup>3</sup>, degradation ranged from 18 % for trichloroacetic acid (TCA) to 70 % for atrazine. The criterion of 80 % conversion had to be achieved by an additional H<sub>2</sub>O<sub>2</sub>-dosage to initiate a supplementary conversion by hydroxyl radicals.

The degradation of emerging pesticides by combined UV-photolysis and hydroxyl radical oxidation, for several peroxide-electrical energy combinations was studied. Examples for a compound with a high and a low UV-photolysis susceptibility are shown in figure 7 and 8.



**Figure 7:** Atrazine degradation by combined UV-photolysis and hydroxyl radical oxidation

Degradation of atrazine by an electric energy of 1 kWh/m<sup>3</sup> amounted 70 %. This degradation was increased to the required 80 % by adding 13 g/m<sup>3</sup> H<sub>2</sub>O<sub>2</sub>.



**Figure 8:** Pyrazon degradation by combined UV-photolysis and hydroxyl radical oxidation

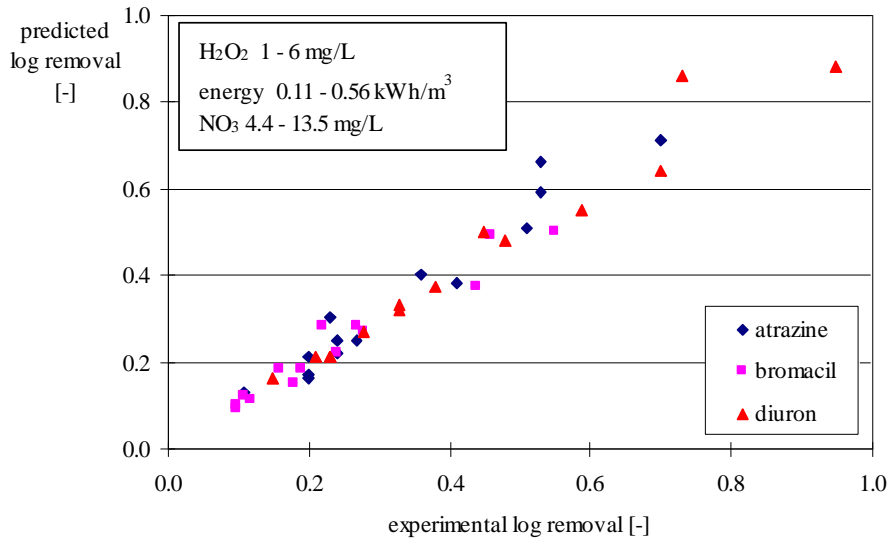
Degradation of pyrazon by an electric energy of 1 kWh/m<sup>3</sup> amounted 54 %. This degradation was increased to the required 80 % by adding 8 g/m<sup>3</sup> H<sub>2</sub>O<sub>2</sub>.

Depending on the UV molar absorption coefficients and quantum yields on the one hand and the chemical structure (double bonds, aromaticity, H-atoms) on the other hand either direct photolysis or hydroxyl radical reactions play a predominant role.

## Research UV/H<sub>2</sub>O<sub>2</sub> phase 2

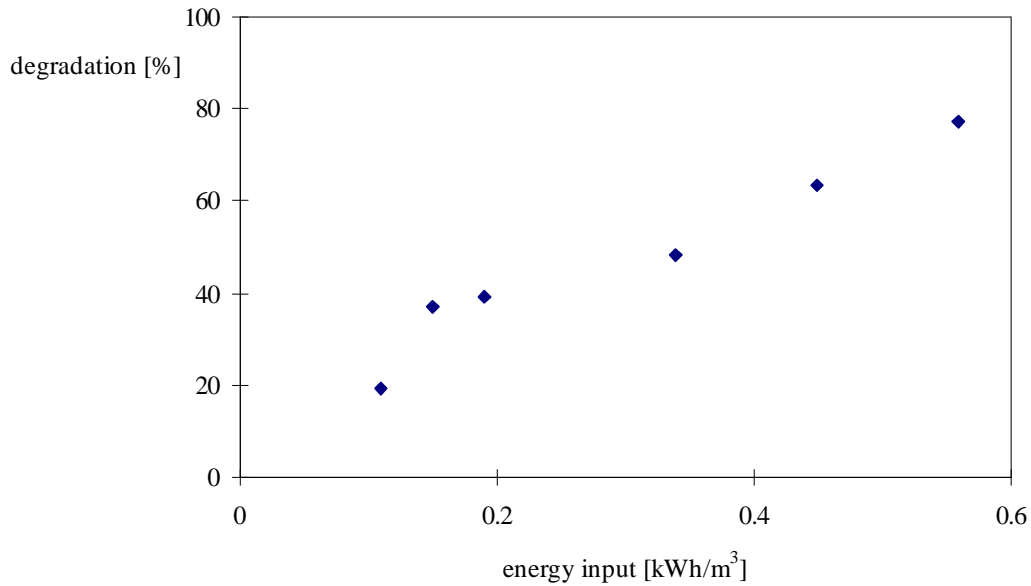
In collaboration with UV-equipment supplier Trojan Technologies Inc., kinetic models for the dominant oxidation processes by UV/H<sub>2</sub>O<sub>2</sub> treatment, OH-radical oxidation and photolysis have been developed. Extensive research on bench scale provided the kinetic parameters (quantum yield, rate constants) (Stefan, 2005). Based on CFD-modeling in combination with the established kinetic models, an UV-pilot reactor was designed and optimized for organic contaminant control.

Predicted organic micro-pollutant degradation at several process conditions was confirmed and refined by experimental work with the newly designed pilot reactor (figure 9).



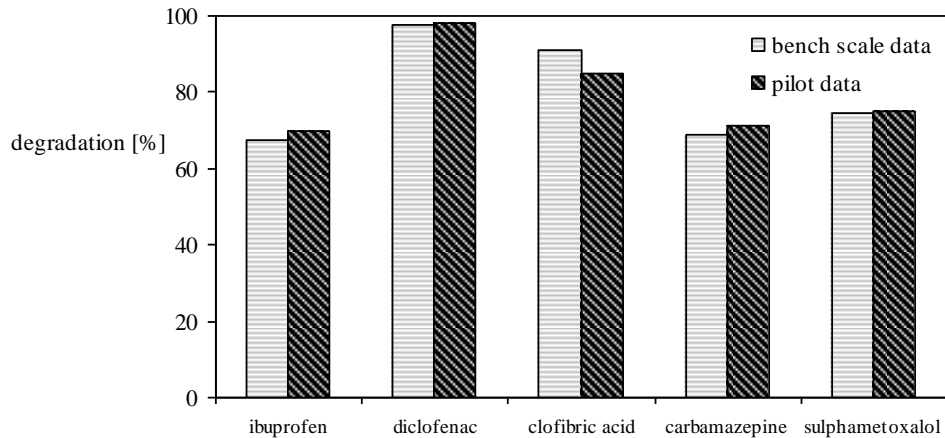
**Figure 9:** Experimental log removal versus predicted log removal for diuron, atrazine and bromacil at several process conditions and nitrate levels (pilot experiments in pre-treated IJssel Lake water)

Figure 10 presents the dose-response relationship for atrazine degradation by UV/H<sub>2</sub>O<sub>2</sub> treatment. In the newly designed pilot UV-reactor (20 m<sup>3</sup>/h), under UV/H<sub>2</sub>O<sub>2</sub> process conditions of 0.56 kWh/m<sup>3</sup> and 6 mg/L H<sub>2</sub>O<sub>2</sub>, PWN's atrazine degradation target of 80% is achieved. Compared to results in a reactor designed for disinfection purposes the electric energy consumption and H<sub>2</sub>O<sub>2</sub> dose were lowered by 44 and 54% respectively.



**Figure 10:** Degradation of atrazine as a function of the UV-dose in combination with 6 g/m<sup>3</sup> H<sub>2</sub>O<sub>2</sub> (pilot data)

Research into degradation characteristics of organic micro-pollutants, observed in IJssel Lake water, is ongoing. For several pharmaceuticals, the degradation under standard process conditions was studied (figure 11). The observed degradations in bench scale experiments and pilot plant experiments match well.



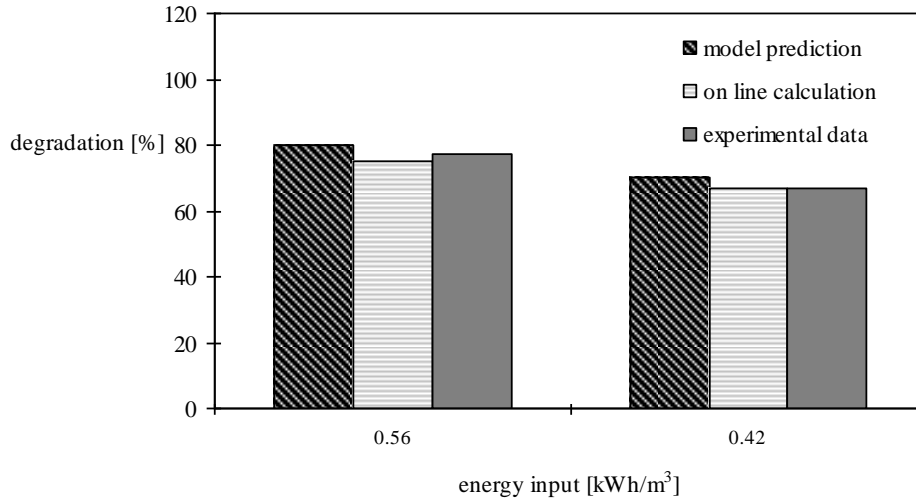
**Figure 11:** Observed correspondence between degradation results for pharmaceuticals, obtained in both bench scale experiments and pilot plant research

Based on the results, a full scale UV-reactor was designed by Trojan and a reactor configuration consisting of three lines of four 30 inch SWIFT reactors, each with sixteen 12 kW MP UV-lamps was installed at WTP Andijk.

## Full Scale UV/H<sub>2</sub>O<sub>2</sub> Installation

Upon start up of the retrofitted plant Andijk, a site acceptance test was performed. For operating purposes, the UV/H<sub>2</sub>O<sub>2</sub> installation is equipped with a control-unit, calculating the atrazine degradation capacity under actual process conditions. Both for the 'installation software' as for the 'kinetic model prediction', the presented predictions were based on the actual water characteristics.

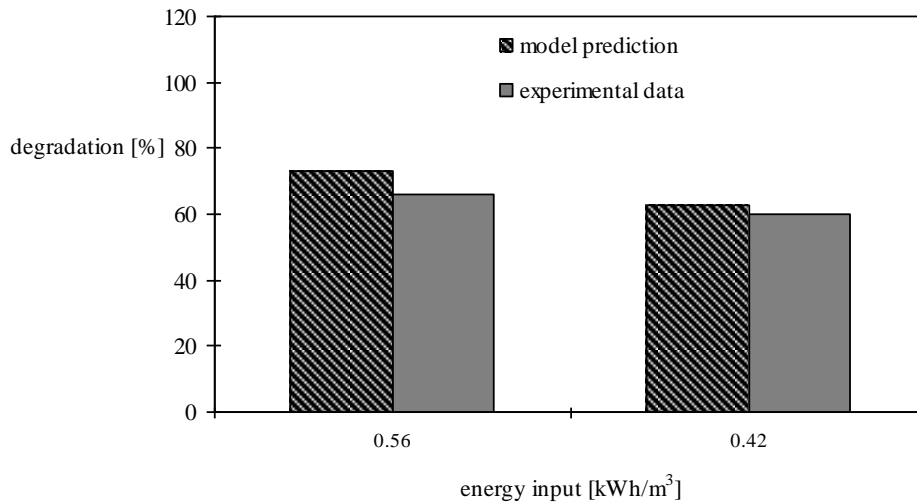
For testing purposes, one of the three full scale UV/H<sub>2</sub>O<sub>2</sub> production lines was isolated and spiked with atrazine and bromacil (~3 µg/L). Figure 12 presents the measured atrazine degradation (experimental data) together with the predicted degradation (kinetic model prediction and the on line atrazine destruction calculation).



**Figure 12:** Degradation of atrazine for two electrical energies and 6 mg/L H<sub>2</sub>O<sub>2</sub> (full scale data)

Process parameter electrical energy was set at two levels, 0.42 kWh/m<sup>3</sup> and standard process condition 0.56 kWh/m<sup>3</sup>. It was found that within acceptance limits the measured degradation of atrazine was predicted by the installation software. Furthermore, good agreement was found between the model calculations and the measured atrazine degradation in the full scale installation.

Collimated beam and pilot work showed that atrazine is degraded predominantly by photolysis while bromacil is more susceptible to hydroxyl radical oxidation. These characteristics have been taken into account in the developed kinetic models. Figure 13 presents the agreement between the predicted degradation of bromacil in the full scale UV/H<sub>2</sub>O<sub>2</sub> installation and the measured degradation during the site acceptance test.



**Figure 13:** Degradation of bromacil for two electrical energies and 6 mg/L H<sub>2</sub>O<sub>2</sub> (full scale data)

Based upon the results of the site acceptance test, it was concluded that the full scale UV/H<sub>2</sub>O<sub>2</sub> equipment met the design criteria.

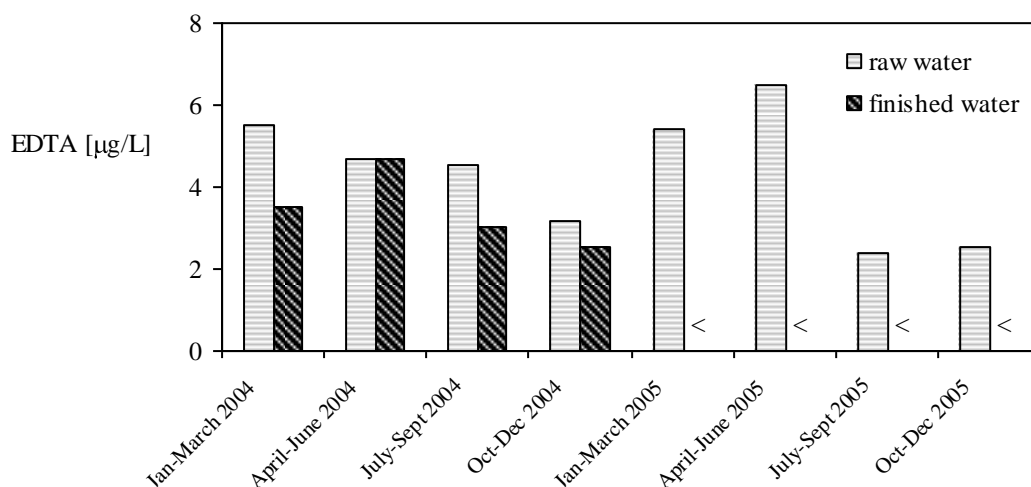
After introduction of UV/H<sub>2</sub>O<sub>2</sub>, raw water and finished water have been monitored on the presence of organic compounds by LC and GC-MS broad screening. These methods are suited for identification of organic compounds but have restricted value for quantification.

In IJssel Lake water, 25 organic compounds have been identified (107 observations), after storage 22 organic compounds were found (84 observations). In finished water, this number was reduced to 9 organic compounds (14 observations).

In raw water flame retardant trichloropropylphosphate was identified 5 times. Detergent Surfynol 104 and melamine were detected 11 and 7 times respectively while anti-epileptic carbamazepine was detected 4 times. All compounds were not detected in the finished water.

Solvent diglyme was detected 8 times in raw water and 5 times in finished water. The observed degradation was approximately 50%.

Figure 14 presents the EDTA content in raw and finished water before and after introduction of UV/H<sub>2</sub>O<sub>2</sub> treatment. After the introduction of UV/H<sub>2</sub>O<sub>2</sub> per 2005, no EDTA is detected in finished water even with the high EDTA levels in raw water in the first half of 2005.



**Figure 14:** EDTA in raw and finished water before and after introduction of UV/H<sub>2</sub>O<sub>2</sub> (full scale data)

### Evaluation

This paper describes the research and full scale application of the UV/H<sub>2</sub>O<sub>2</sub> process as nonselective barrier for organic contaminant control at PWN's water treatment facility Andijk (20 MGD; 3000 m<sup>3</sup>/h).

Bench scale research on UV/H<sub>2</sub>O<sub>2</sub> proved that 80% degradation of reference pollutant atrazine to achieve the set standard of 0.1 µg/L was feasible without any bromate formation.

From additional pilot work, it was concluded that UV/H<sub>2</sub>O<sub>2</sub> treatment is a nonselective barrier for a broad selection of emerging organic micro-pollutants.

Degradation target of selected reference pollutant atrazine (80% degradation) was reached in an optimized pilot UV-reactor at an UV-input of 0.56 kWh/m<sup>3</sup> (~540 mJ/cm<sup>2</sup>) in combination with 6 g/m<sup>3</sup> H<sub>2</sub>O<sub>2</sub>. This has resulted in a 40% reduction in energy consumption and a 50% reduction of H<sub>2</sub>O<sub>2</sub> dosage compared to the degradation achieved in a reactor designed for disinfection purposes only.

Full scale testing showed that the UV/H<sub>2</sub>O<sub>2</sub> installation meets the design criteria. Model calculations are confirmed by the performance of the full scale installation. Collimated beam experiments with solvent diglyme resulted in 60% degradation under standard process conditions. In the full scale installation 50% degradation was observed, confirming the predicted performance of the full scale UV/H<sub>2</sub>O<sub>2</sub> installation.

By LC and GC-MS screening of the raw water 22 organic compounds (84 observations) were detected. After UV/H<sub>2</sub>O<sub>2</sub> treatment, only 9 different organic compounds were found (14 observations). Complexing agent EDTA, present in the raw water in relatively high concentrations (2.5 – 6.5 µg/L), was completely degraded by UV/H<sub>2</sub>O<sub>2</sub> treatment.

Despite the limited full scale data of WTP Andijk until now, from the observed complete degradation of compounds such as EDTA, significant degradation of diglyme and the results of the LC and GC-MS screening, it is concluded that photolysis and oxidation processes are a robust nonselective barrier for organic contaminant control.

In the near future UV/H<sub>2</sub>O<sub>2</sub> treatment will be implemented at WTP Heemskerk, PWN's UF/RO plant, as well.

### Acknowledgements

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