

IMPLEMENTATION OF UV/H₂O₂ TREATMENT FOR INACTIVATION OF MICRO-ORGANISMS AND PESTICIDE CONTROL

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ABSTRACT

N.V. PWN Water Supply Company North Holland will replace breakpoint chlorination at their Andijk drinking water treatment plant. Major objectives are restriction of disinfection by-product formation, increased pathogen inactivation and multiple barriers for organic contaminant control. The aim of this study was to show the feasibility of UV/H₂O₂ treatment for primary disinfection and pesticide control in direct surface water treatment.

For 12 priority pesticides conversion by UV photolysis and hydroxyl radical reactions were studied. UV photolysis gives a selective degradation, hydroxyl radical reactions were more aselective. These findings were confirmed in pilot plant studies. For an electric energy of 1 kWh/m³ conversion varied from 18 % for trichloroacetic acid to 70 % for atrazine. For a combination of ≤ 1 kWh/m³ and ≤ 15 g/m³ H₂O₂ all pesticides could be degraded for more than 80 %. At this conversion of 80 % metabolite formation was insignificant, while no bromate formation was found.

A 2 – 3 log inactivation of *Giardia muris* and *Cryptosporidium parvum* was achieved by an UV dose of 20 mJ/cm². For a complete inactivation of all micro-organisms an UV dose up to 105 mJ/cm² was required.

Reactivation of protozoa was established for an UV dose up to 25 mJ/cm². For doses higher than 60 mJ/cm² no reactivation was observed.

Based on quantum yields, reaction rate constants, CFD modelling and pilot plant experiments it was shown that 80 % pesticide degradation can be achieved with a proper combination of electric energy and hydrogen peroxide. The electric energy for pesticide degradation is much higher than required for disinfection. Residual H₂O₂ removal and AOC control are achieved by GAC filtration.

In view of the very promising results PWN will install UV/H₂O₂ at their Andijk plant. Three streets of 4 Trojan Swift 16L30 reactors will be installed before the middle of 2004.

INTRODUCTION

In 1920, when N.V. PWN Water Supply Company North Holland (PWN) was founded, the demand for drinking water was satisfied by ground water extraction. However by the growing drinking water demand PWN was compelled to utilize surface water as an additional source.

Therefore in the 1960's water treatment plant Andijk was constructed for the direct production of drinking water from IJssel Lake (River Rhine) water. Originally the plant consisted of microstraining, breakpoint

chlorination, coagulation, sedimentation, rapid filtration and post disinfection. In 1978 the plant was upgraded with a pseudo moving bed GAC filtration.

After about 40 years of operation, wtp Andijk still complies with all Dutch drinking water standards. Nevertheless an upgrade is desired in view of by-product (THM) formation and the barriers against pathogenic micro-organisms such as protozoa and organic micropollutants such as pesticides.

PWN has pursued the application of advanced oxidation for both primary disinfection and organic contaminant control followed by the already present GAC filtration for removal of residual H_2O_2 and AOC with very promising results. UV/ H_2O_2 will be installed and become operational mid 2004.

PROCESS SELECTION

PWN's aim was to select an oxidative process able to inactivate pathogenic micro-organisms and to degrade pesticides aselectively with a restricted by-product formation compared to breakpoint chlorination.

Initially the focus was on ozone based technologies. (1) Ozone was able to achieve the required disinfection capacity. However ozone proved to be a selective barrier against pesticides.

In advanced oxidation technologies hydroxyl radicals react 10^6 to 10^9 times faster than ozone, causing a much more aselective pesticide degradation.

O_3/H_2O_2 treatment proved to be a sound barrier against pesticides. In pretreated IJssel Lake water 80 % pesticide degradation could be achieved by an O_3 dose of 2.8 g/m^3 and a H_2O_2/O_3 ratio of 2 g/g. (2)

However bromate was found at high levels especially at low water temperature. (3) Feasible treatment options (increase H_2O_2/O_3 ratio, increase pH) could not control bromate formation completely caused by mass transfer limitations. (see figure 1) (3)

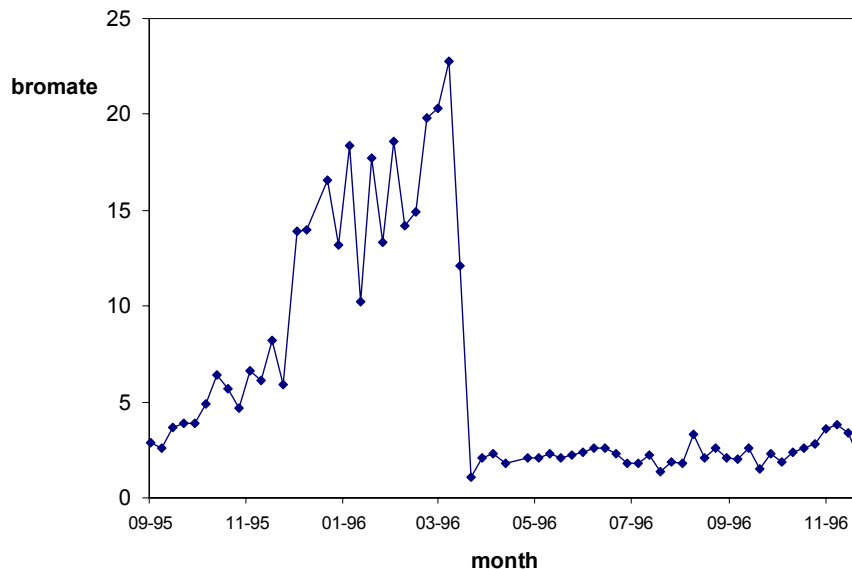


Figure 1 Bromate Formation by O_3/H_2O_2 treatment ($O_3/DOC = 1.13 \text{ g/g}$) before April '96 $H_2O_2/O_3 = 2 \text{ g/g}$, pH = 7.5 after April '96 $H_2O_2/O_3 = 4 \text{ g/g}$, pH = 7.8

Under optimal conditions for pesticide and bromate control disinfecting properties of the O₃/H₂O₂ process were very poor. Corresponding with high H₂O₂/O₃ ratios and very low c.t. values for ozone, inactivation of spores of sulphite reducing clostridia was insignificant. (4)

In view of these findings PWN rejected O₃/H₂O₂ treatment for primary disinfection and pesticide control at wtp Andijk and decided to pursue alternative strategies with the focus on UV technologies.

PHOTOLYSIS AND ADVANCED OXIDATION BY UV/H₂O₂ TREATMENT

UV photolysis is based on the absorption of UV photons by contaminants to cause their degradation into smaller products. The absorbed energy must be higher than the energy of the band to be broken to cause photolysis.

In addition to the absorption of UV photons the quantum yield of the degradation is an important parameter. Compounds with a high UV absorbance and a high quantum yield are very susceptible to photodegradation. (5)

However not all substances absorb UV light significantly or have a high quantum yield. In order to promote a more aselective degradation H₂O₂ may be added to produce hydroxyl radicals.

The general expression for the degradation rate of a contaminant is a combination of direct UV photolysis and hydroxyl radical reactions:

$$-\frac{d c}{d t} = \emptyset_C \varepsilon_{\text{abs,C}}^{\circ} + k_{\text{C,OH}} [C] [\text{OH}^{\cdot}]$$

where \emptyset_C is the quantum yield, $\varepsilon_{\text{abs}}^{\circ}$ is the absorbed light and $k_{\text{C,OH}}$ is the hydroxyl radical rate constant.

Not too many \emptyset_C and $k_{\text{C,OH}}$ values for pesticide degradation are given in literature. An electric energy of 0.5 kWh/m³ is reported for 60 % atrazine photolysis. Under these conditions pesticide degradation varied from 18 % for dicamba to 92 % for mecoprop. (6) Additional research is needed to determine quantum yield and hydroxyl radical rate constants for representative organic micropollutants and to determine the process conditions for UV/H₂O₂ treatment with medium pressure UV lamps.

Disinfection by UV

There is an abundance of literature on the inactivation of fecal coliform bacteria by UV radiation. It has been known for some time that viruses and spore forming bacteria are more resistant to the effect of UV radiation than coliform bacteria. Chang et al (7) showed that viruses, bacterial spores and amoebic cysts required 3 – 4 times, 9 times and 15 times more UV exposure to achieve the same level of inactivation as *Escherichia coli*.

It had been thought that encysted protozoa were insensitive to UV.(8,9) More recent studies have shown that encysted *Cryptosporidium parvum* and *Giardia muris* are relatively sensitive to UV radiation. (10, 11, 12)

Reactivation of pathogenic micro-organisms is a critical parameter with the respect to the treatment of drinking water. It is well known that select pathogenic micro-organisms are capable of reactivating after exposure to UV light. Mechsner et al (13) demonstrated that *E coli* inactivated by low pressure UV repaired its DNA after several days incubation in the dark.

More work is needed to determine the overall reactivation potential of water-borne pathogenic micro-organisms of concern to the water industry.

The ultimate goal for UV disinfection of drinking water is to damage DNA beyond repair.

Additional research is needed to establish dose-response curves for several pathogenic micro-organisms and to establish the UV dosage where DNA is damaged beyond repair.

OBJECTIVES

Disinfection

Three major objectives were pursued in a collaborative study carried out by the University of Alberta and PWN:

- to select representative organisms and characterize UV inactivation by generating UV dose-inactivation curves for MS2 phages, *Bacillus subtilis* endospores, *Giardia muris* cysts and *Cryptosporidium parvum* oocysts using a bench scale collimated beam apparatus;
- to determine the ability of one small medium pressure UV reactor and three larger medium pressure UV reactors to inactivate MS2 phages, *Bacillus subtilis* endospores, *Giardia muris* cysts and *Cryptosporidium parvum* oocysts;
- to examine the reactivation of *Giardia muris* and *Cryptosporidium parvum* ex-vivo and in vivo and to determine more precisely the UV dose required for inactivation of these protozoan parasites in drinking water.

Organic contaminant control

Three additional major objectives were pursued by PWN, partly in collaboration with Trojan Technologies Inc.:

- to select representative organic micropollutants (pesticides) and characterize degradation by UV photolysis and hydroxyl radical reaction for 12 selected pesticides;
- to predict and determine the ability of a medium pressure UV reactor to degrade those 12 priority pollutants;
- to design a full scale UV/H₂O₂ system for both disinfection and organic contaminant control.

Posttreatment

Two additional objectives were pursued by PWN to integrate UV/H₂O₂ treatment in the total treatment scheme:

- the removal of excess H₂O₂ by GAC filtration;
- the removal of AOC by GAC filtration.

INACTIVATION OF MICRO-ORGANISMS

Bench scale experiments

The bacteriophage MS2 has been shown to be relatively resistant to UV inactivation. A reduction of approximately 1 log-unit was achieved when MS2 phages, suspended in PWN water, was exposed to UV doses of 20 – 25 mJ/cm². (Figure 2)

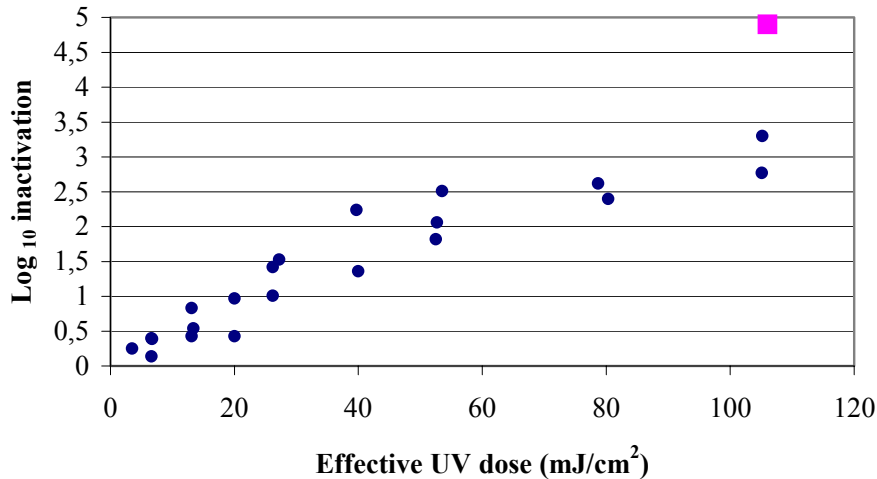


Figure 2 Log Inactivation of MS2 Phages by UV Disinfection

The correlation between log inactivation and effective UV dose demonstrated a near linear relationship, particularly within the UV dose range of up to 50 mJ/cm². This contrasts the UV inactivation curves obtained for *Bacillus subtilis* (Figure 3), *Giardia muris* (Figure 4) and *Cryptosporidium parvum* (Figure 5) where distinct shouldering and tailing effects were observed.

Figure 3 summarizes the results to determine the effect of UV inactivation on *Bacillus subtilis* endospores suspended in PWN water. Similar to data reported by Sommer and Cabaj (14) a distinct shouldering effect was observed when endospores were exposed to UV doses less than 20 mJ/cm².

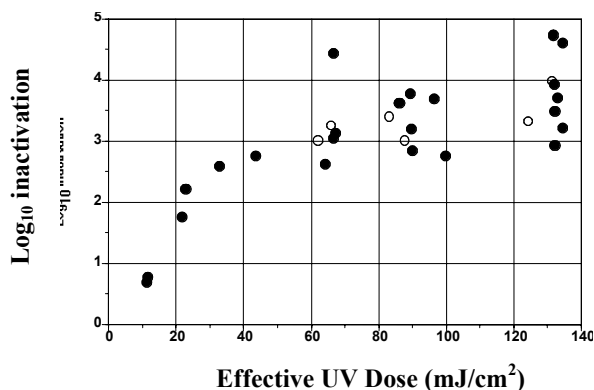


Figure 3 Log Inactivation of *Bacillus Subtilis* Endospores by UV Disinfection

However, unlike the data presented by Sommer and Cabaj a pronounced tailing effect was observed. Sommer and Cabaj reported a log reduction of approximately 4 log units with UV doses of 60 mJ/cm². In this study 3 log and 4 log reduction were achieved at about 60 and 120 mJ/cm² respectively.

Giardia muris cysts suspended in PWN water were shown to be relatively susceptible to UV inactivation. An UV dose of as low as 20 mJ/cm² induced greater than 2 log-unit inactivation of *Giardia muris*. However a pronounced tailing effect in the ability of UV to inactivate the infective potential of *Giardia muris* cysts was observed with UV doses greater than 20 mJ/cm². (Figure 4).

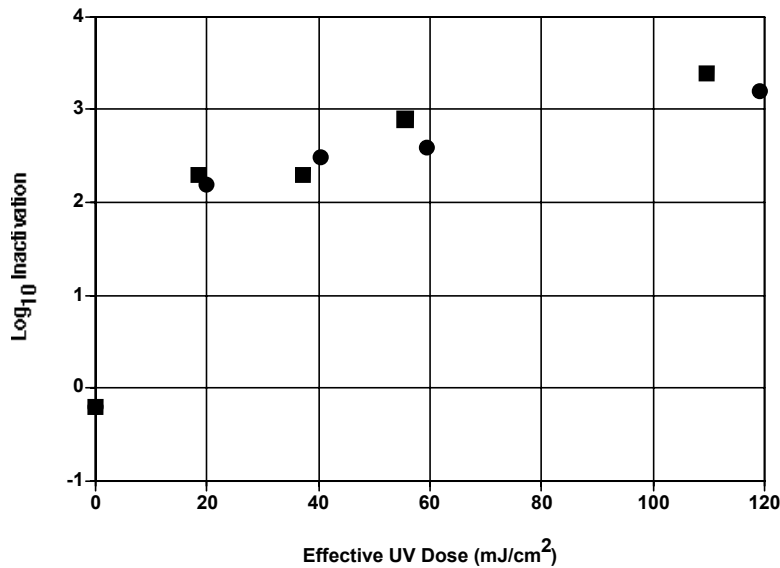


Figure 4 Log Inactivation of *Giardia Muris* Cysts by UV Disinfection

Exposure of *Giardia muris* cysts to UV doses as high as 120 mJ/cm² resulted in only 1 additional log-unit of inactivation compared to UV doses of 20 mJ/cm² only.

Cryptosporidium parvum oocysts suspended in PWN water were extremely susceptible to low doses of UV. Greater than a 3 log-unit reduction in oocyst infectivity was observed in trials where oocysts were exposed to UV doses as low as 20 mJ/cm². For *Cryptosporidium parvum* oocysts the tailing effect of the UV dose-inactivation curve was not as pronounced as that observed for *Giardia muris* cysts (Figure 5). UV doses of approximately 120 mJ/cm² induced greater than 4.5 log-units of inactivation.

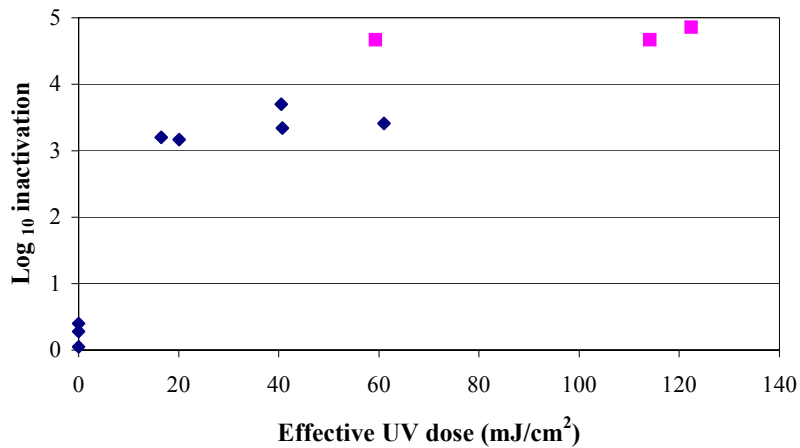


Figure 5 Log Inactivation of Cryptosporidium Parvum Oocysts by UV Disinfection

However, the presence of the tailing suggests that a UV resistant sub-population of oocysts may be present within any given batch of oocysts, which remains to be confirmed using molecular analysis of the resistant sub-population of the (oo)cysts.

Pilot plant experiments

The collimated beam data demonstrate that medium pressure UV radiation effectively inactivated MS2 phages, Bacillus subtilis endospores, Giardia muris cysts and Cryptosporidium parvum oocysts suspended in pretreated IJssel Lake water. The results were confirmed by data obtained with a small scale Berson UV reactor and with three larger scale reactors from Calgon, Berson and Trojan. Of the three larger scale UV reactors the Berson and Trojan reactors showed inactivation levels equivalent to the collimated beam experiments, while the Calgon unit showed a lower inactivation level (Figure 6).

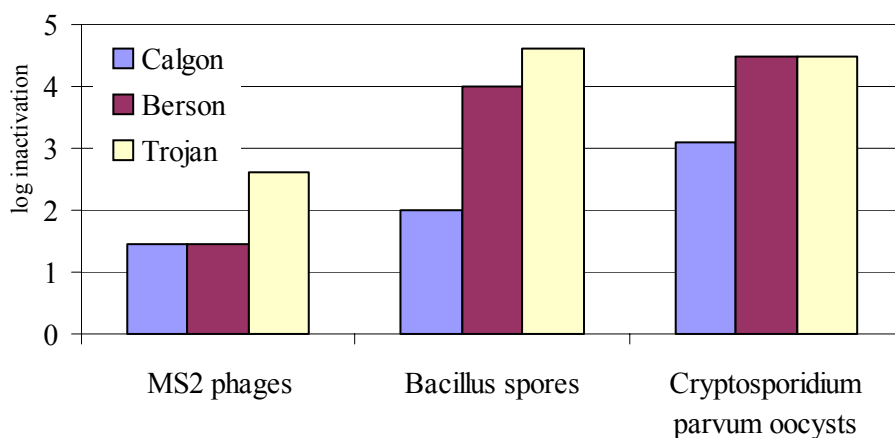


Figure 6 Inactivation of MS2 Phages, Bacillus Subtilis Endospores and Cryptosporidium Parvum Oocysts by UV Disinfection with an UV Dose of 120 mJ/cm²

The findings show that UV disinfection is a very reliable technology for the inactivation of pathogenic micro-organisms in drinking water. A UV dose of 105 mJ/cm² gives a high inactivation of phages and endospores and a complete inactivation of protozoan cysts and oocysts.

REACTIVATION OF MICRO-ORGANISMS

It is important to understand that it is debatable as to whether or not UV-irradiation causes permanent or temporary inactivation of micro-organisms. Relatively little is known about the repair of UV-damaged DNA in encysted water-borne protozoan pathogens. Our data indicated that neither *Giardia muris* cysts nor *Cryptosporidium parvum* oocysts are capable of in vitro reactivation. The results for in vivo reactivation of *Giardia muris* cysts are summarized in table 1.

Table 1 In Vivo Reactivation of *Giardia Muris* Cysts Treated with Medium Pressure UV

Days Post Infection	No. Mice Infected/Total No. Mice			
	< 25 mJ/cm ²		> 60 mJ/cm ²	
5	14/35	0/34	6/20	0/20
10	35/35	1/34	20/20	0/20
15	35/35	1/34	20/20	0/20
20	35/35	5/34	20/20	0/20
25	35/35	6/34	20/20	0/20
30	35/35	7/34	20/20	0/20

From the data it can be concluded that *Giardia muris* cysts are capable of in vivo reactivation after UV treatment when the UV dose applied is as low as 25 mJ/cm². This dose is significantly lower than the UV dose of 105 mJ/cm² needed for a 3.5 log-unit inactivation of MS2 phages.

For *Cryptosporidium parvum* oocysts the in vivo repair could not be tested due to the "end-point" animal model.

DEGRADATION OF ORGANIC MICROPOLLUTANTS

Bench Scale Experiments in Pretreated IJssel Lake Water

Four test runs were carried out with pretreated IJssel Lake water for a first optimization of electric energy input and H₂O₂-dosage. Atrazine degradation is presented in figure 7.

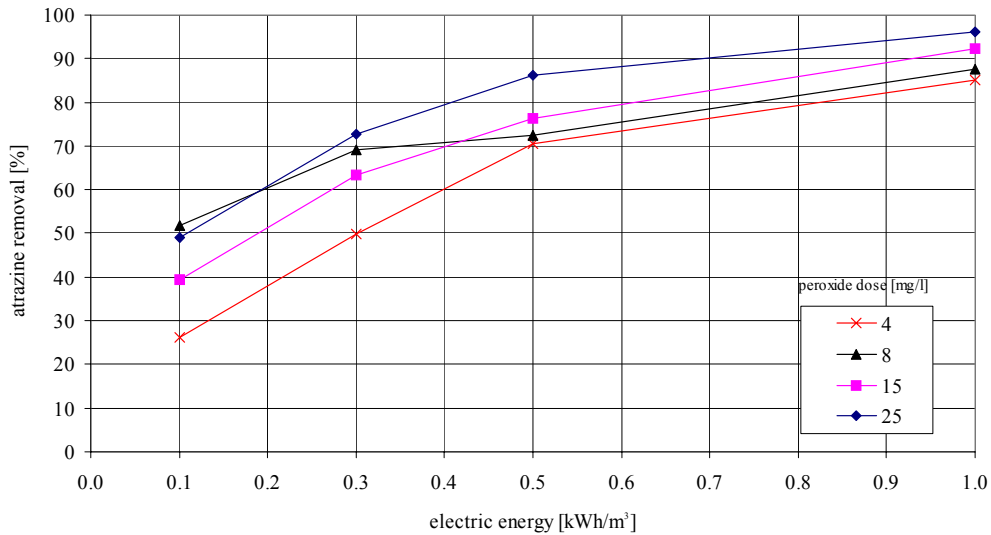


Figure 7: Atrazine Degradation by UV/H₂O₂-Treatment in Bench Scale Experiments in Pretreated IJssel Lake Water

The EE/O was ranging from 0.65 – 1.30 kWh/m³ depending on the H₂O₂-dose (see Table 2).

Under no reaction conditions bromate formation was found.

Because the process was considered as cost effective pilot plant research was carried out.

Pilot Plant Experiments Phase 1

Four test runs were carried out with new UV lamps under conditions corresponding with the bench scale experiments.

Atrazine conversion in bench and pilot plant scale testing was in the same order of magnitude.

(see Table 2)

Table 2: EE/O for Atrazine Degradation by UV/H₂O₂-treatment

H ₂ O ₂ g/m ³	EE/O bench scale kWh/m ³	EE/O pilot scale kWh/m ³
4	1.30	1.50
8	1.15	1.30
15	0.90	1.00
25	0.65	0.70

The range of EE/O values for pilot testing was only slightly higher than for bench scale testing: 0.70 – 1.50 kWh/m³ and 0.65 – 1.30 kWh/m³ respectively.

Two conditions being $0.6 \text{ kWh/m}^3 + 15 \text{ g/m}^3 \text{ H}_2\text{O}_2$ and $0.9 \text{ kWh/m}^3 + 4 \text{ g/m}^3 \text{ H}_2\text{O}_2$ were chosen for further research with five selected priority pollutants: atrazine, pyrazone, diuron, bentazone and bromacil. The experiments were carried out with new lamps and after a lamp life of 2000 h.. The results for $0.9 \text{ kWh/m}^3 + 4 \text{ g/m}^3 \text{ H}_2\text{O}_2$ are shown in figure 8.

Degradation (%)

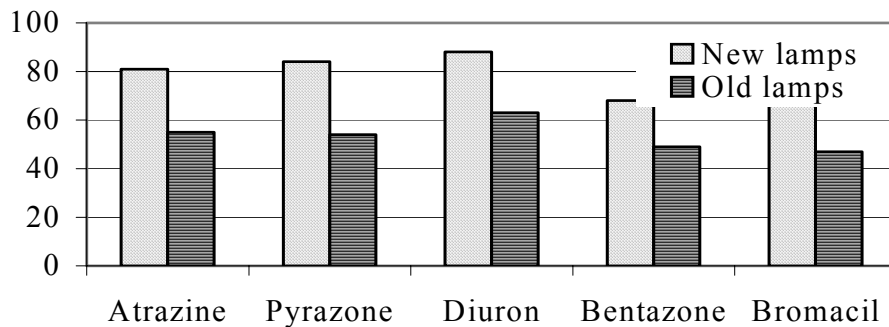


Figure 8: Pesticide Degradation in pretreated IJssel Lake Water as a Function of the Lamp Life

For new lamps pyrazone and diuron were degraded slightly higher than atrazine, while bentazone and bromacil conversion were slightly lower.

After 2000 burning hours pesticide degradation dropped significantly and amounted roughly 50 % of the original degradation. Lamp control showed that the UV-output of the lamps was decreased by 23 – 68 % showing that, in addition to electric energy data, measurement of UV-dose is urgently needed.

Irrespective of reaction conditions no bromate was found.

UV extinction dropped with 20 %, DOC-removal was insignificant.

AOC increased from $10 \mu\text{g/l}$ to $110 - 140 \mu\text{g/l}$. Therefore biological stability after UV/ H_2O_2 -treatment is an important issue.

UV/ H_2O_2 -treatment enables 80 % pesticide degradation without a significant formation of primary pesticide metabolites and bromate. Until now the experiments were focused on the combined effect of UV-photolysis and hydroxyl radical oxidation. In the second phase of the pilot plant research the effect of UV-photolysis only followed by the additional effect of advanced oxidation was studied.

Pilot Plant Experiments Phase 2

Degradation of 10 pesticides atrazine, pyrazon, diuron, bentazone, bromacil, methabenzthiaxon, dicamba, 2,4-D, TCA, trichlorpyr and the atrazine metabolite desethyldeisopropylatrazine by UV-photolysis was studied. The electric energy was ranging from $0.25 - 2.0 \text{ kWh/m}^3$ (see Figure 9).

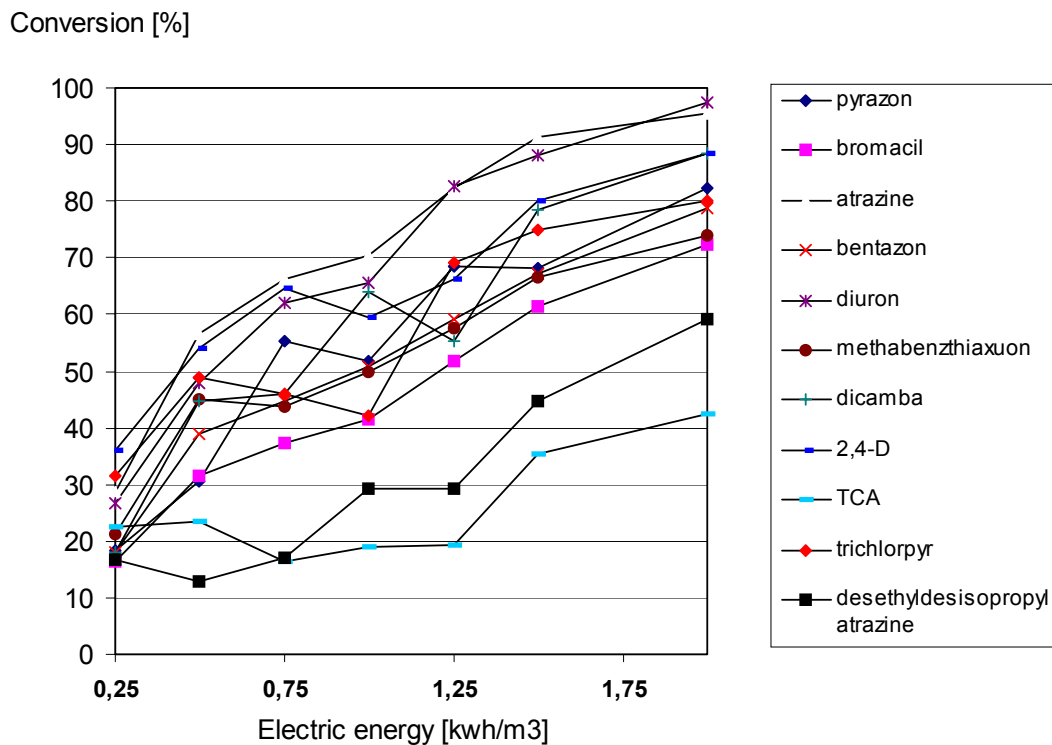


Figure 9: Pesticide Degradation by UV-Photolysis as a Function of the UV-Dose

All priority pollutants showed a significant degradation by UV-photolysis. The conversion for an electric energy of 1 kWh/m³ is summarized in table 3.

Table 3: Pesticide Degradation by UV-Photolysis with 1 kWh/m³

Pesticide	Degradation (%)	Pesticide	Degradation (%)
Atrazine	70	Dicamba	63
Pyrazon	52	2,4-D	58
Diuron	65	TCA	18
Bentazone	50	Trichlorpyr	52
Bromacil	42	Desethyldeisopropyl-atrazine	30
Methabenzthiaxon	50		

By UV-photolysis with 1 kWh/m³ degradation ranged from 18 % for trichloroacetic acid (TCA) to 70 % for atrazine. The criterion of 80 % conversion had to be achieved by an additional H₂O₂-dosage to initiate a supplementary hydroxyl radical reaction. Examples for a compound with a low and a high UV-photolysis conversion are shown in figure 10 and 11.

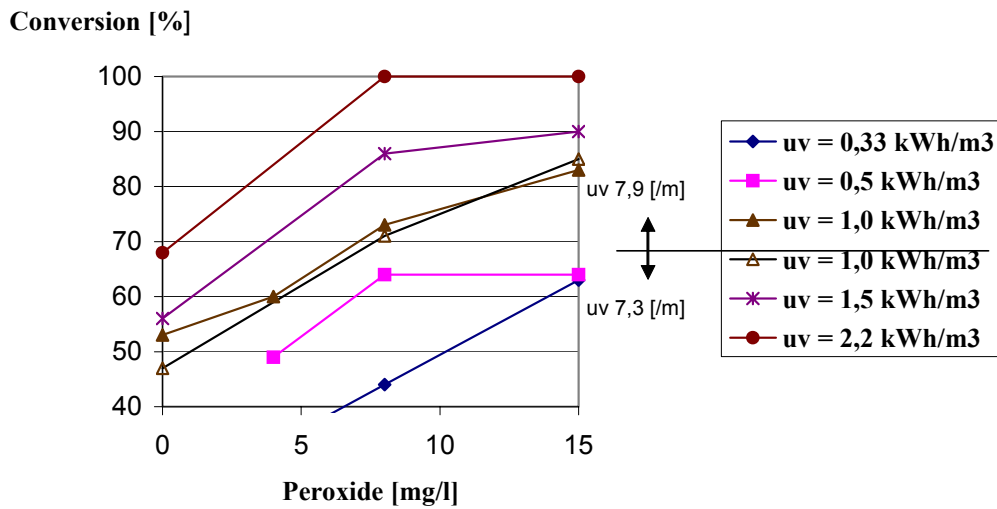


Figure 10: Bromacil Degradation by Combined UV-Photolysis and Hydroxyl Radical Oxidation for UV/H₂O₂-treatment

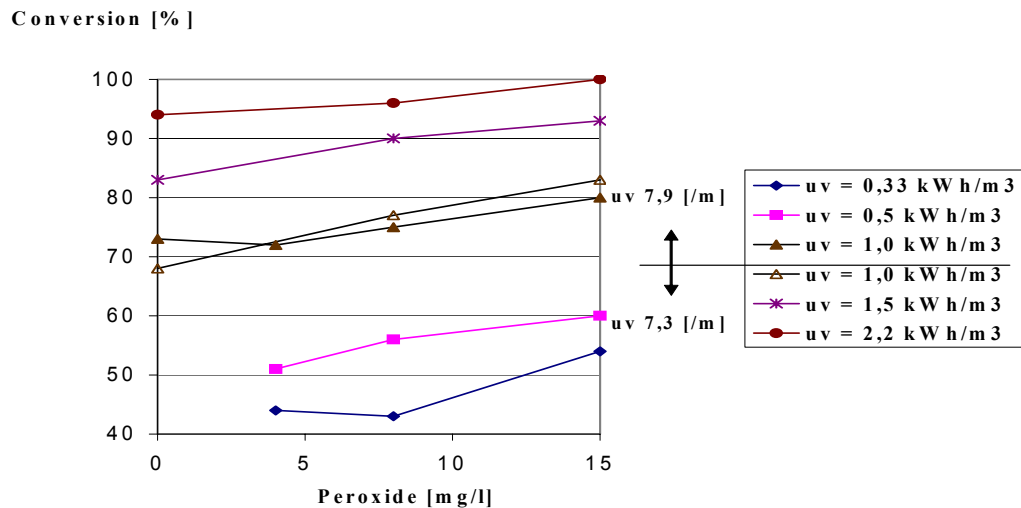


Figure 11: Atrazine Degradation by Combined UV-Photolysis and Hydroxyl Radical Oxidation for UV-H₂O₂-treatment

Degradation of atrazine by an electric energy of 1 kWh/m³ amounted 70 %. This degradation was increased to the desired 80 % by adding 13 g/m³ H₂O₂. Atrazine degradation was caused primarily by photolysis with a polishing effect of hydroxyl radical oxidation.

Degradation of bromacil by an electric energy of 1 kWh/m³ amounted 42 %. This degradation was increased to the desired 80 % by adding 15 g/m³ H₂O₂. For bromacil degradation hydroxyl radical oxidation played a much more important part.

For most priority pollutants a degradation of 80 % can be achieved. Depending on UV-absorbance and quantum yield on the one side and chemical structure (double bonds, H-atoms) on the other side

photolysis or hydroxyl radical reactions will play a predominant part. Only for TCA and desethyldeisopropylatrazine 80 % degradation may not be achieved.

PERSPECTIVE

At water treatment plant Andijk UV/H₂O₂-treatment will be implemented. For primary disinfection the breakpoint chlorination will be replaced by UV-disinfection. A dose of 105 mJ/cm² gives a high inactivation of phages (viruses) and spores and an complete inactivation of Giardia muris and Cryptosporidium oocysts. Although some reactivation of Giardia muris cysts is observed, this will not take place at UV-doses as high as 105 mJ/cm².

UV/H₂O₂-treatment will be implemented for organic contaminant control prior to the two step GAC-filtration already present.

A pesticide degradation of 80 % can be achieved for a broad range of process conditions (i.e. from 0.4 kWh/m³ and 15 g/m³ H₂O₂ to 0.9 kWh/m³ and 4 g/m³ H₂O₂). This UV dose is much higher than needed for disinfection. Under these conditions bromate formation is completely absent, while primary metabolite formation is insignificant.

PWN decided to pursue UV/H₂O₂-treatment for full scale application. Important issues were removal of residual H₂O₂ and biological stability. Removal of H₂O₂ by GAC-filtration is presented in Figure 12.

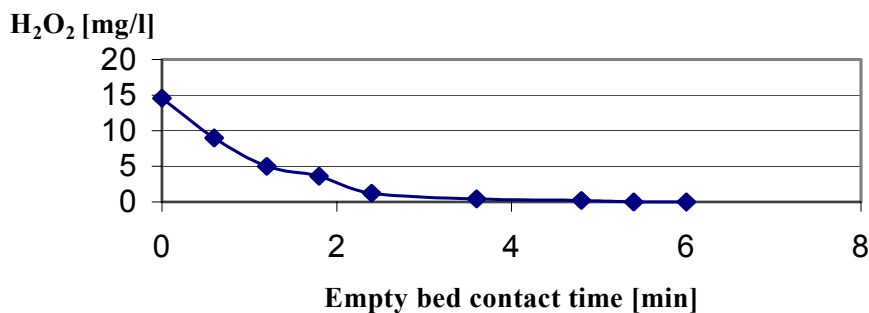


Figure 12: H₂O₂-removal by GAC-filtration as a Function of the Empty Bed Contact Time

Removal of 15 g/m³ proved to be complete within 5 minutes. After GAC-filtration with an empty bed contact time of 40 minutes the biofilm formation rate remained very low (~ 2 pg/cm².d) during the total filter run, although AOC increased from 10 to 40 µg Ac C eq/l.

Based on these results PWN will upgrade water treatment plant Andijk to the following configuration (Figure 13).

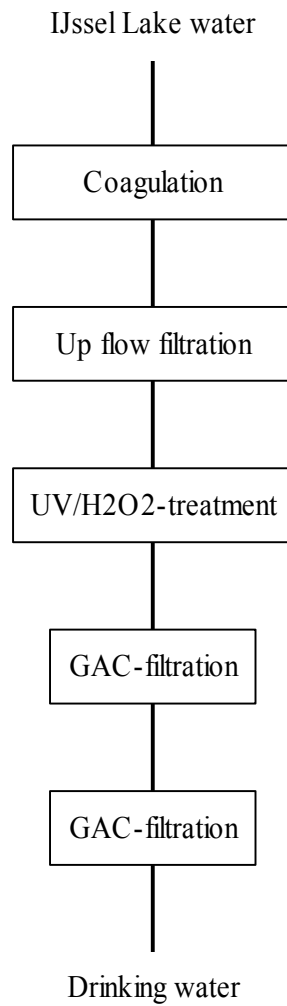


Figure 13: Projected Water Treatment Plant Andijk

The combination UV/H₂O₂-treatment / GAC-filtration provides a very reliable and flexible process for:

- removal / inactivation of micro-organisms;
- organic contaminant control.

ACKNOWLEDGEMENT

The authors thank P. Hoogzaad, R. Kooijman (PWN), D.W. Smith, N.F. Neumann, S. Craik (University of Alberta), M.I. Stefan (Trojan Technologies Inc.) and J.R. Bolton (Bolton Enterprises) for their stimulating discussions and their assisting in realizing this study.

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