# ADVANCED OXIDATION FOR THE CONTROL OF PESTICIDES AT THE PWN WATER TREATMENT PLANT IN NORTH HOLLAND

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## ABSTRACT

PWN's water treatment plant Andijk was commissioned almost 40 years ago. It services water from the IJssel Lake by conventional surface water treatment. In view of taste and odor problems, the plant was retrofitted with GAC filtration 25 years ago. The finished water quality still complies to all European Commission and Dutch drinking water standards. Nevertheless an upgrade is desired to avoid the use of chlorine and to extend the barriers against pathogenic microorganisms and a broad range of organic micropollutants such as pesticides, rocket fuel by-products (e.g., NDMA), fuel oxygenates (e.g., MTBE), solvents (e.g., 1,4-dioxane), endocrine disruptors, algae toxins, pharmaceuticals, etc. The $UV/H_2O_2$ advanced oxidation treatment process was selected for both primary disinfection and organic contaminant control.

## INTRODUCTION

In 1919, when PWN Water Supply Company North Holland was founded, the demand for drinking water was satisfied by ground water extraction. However, the growing drinking water demand compelled PWN to utilize surface water as an additional water source. Now, at the turn of the 21st century, only 5 % of the drinking water is produced from ground water.

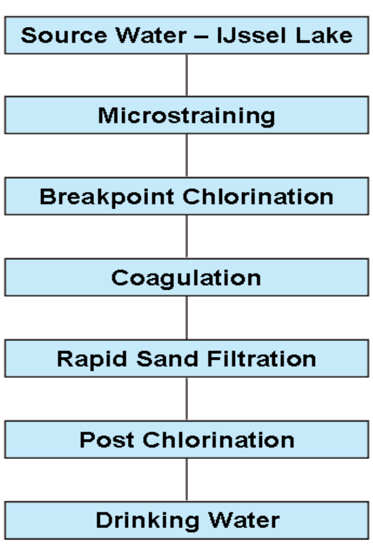


**Figure 1**. Design treatment scheme of the Andijk WTP (1968)

To satisfy the growing surface water demand in the 1960's, the Andijk water treatment plant (WTP) was commissioned for direct drinking water production from IJssel Lake water. The original treatment scheme of the Andijk WTP is presented in Figure 1.

Since 1968 the following modifications in the treatment scheme have been introduced:

- replacement of the post chlorination by a dosage of chlorine dioxide;
- introduction of a pseudo moving bed GAC filtration to remove taste and odor and chlorination by-products (THM's);
- introduction of an additional microstraining following the GAC filtration to remove higher organisms.

From 1978 until 2004 the following treatment was applied (see Figure 2).

After almost 40 years of operation, the water quality of the Andijk WTP still complies with the European Commission (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 by-product (THM) formation;

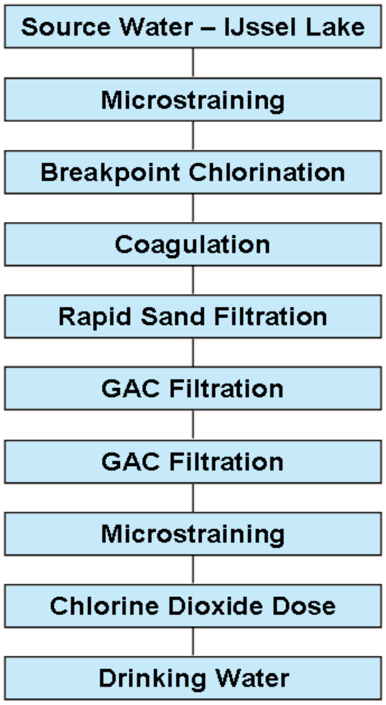


**Figure 2**: Retrofit treatment scheme of the Andijk WTP (1978 – 2004)

- introduction of multiple barriers against pathogenic micro-organisms such as *Giardia* and *Cryptosporidium*;
- introduction of a disinfection credit for treatment steps based on a $10^{-4}$ health risk;
- introduction of a general 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.

Initially, PWN investigated the suitability of the $O_3/H_2O_2$ treatment process for organic contaminant control. Although the results were very promising, the process was not pursued in view of bromate formation (up to 20 $\mu$g/L) in the bromide rich (300 – 500 $\mu$g/L) IJssel Lake water. Subsequently, PWN has pursued the $UV/H_2O_2$ treatment process for both primary disinfection and organic contaminant control.

## TREATMENT OBJECTIVES

### Disinfection

The disinfection requirements for the Andijk WTP are based on an acceptable infection risk of $10^{-4}$ per person per year. Based on measurements in the IJssel Lake water the required inactivation for six priority microorganisms are calculated. (see Table 1).

The total required inactivation amounted to 4.5 – 5.9 log units, of which 2.0 – 3.0 log units were achieved by the conventional pretreatment steps coagulation and rapid sand filtration. Therefore 1.7 – 3.8 log units had to be achieved by the UV treatment.

PWN considered the perspective of UV treatment for the primary disinfection of surface water very promising. In a collaborative study with the University of Alberta, three major objectives were pursued:

- to establish 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 and *Cryptosporidium parvum* oocysts;

**Table 1**: Concentration of microorganisms, disinfection requirements and required log removals

| Microorganism | Max. content IJssel Lake | Requirement | Log Inactivation | | |
|---|---|---|---|---|---|
| | n/L | n/L | Total Required | In Pre-treatment | Required by UV |
| *EColi* | 6000 | $10^{-2}$ | 5.8 | 2.0 | 3.8 |
| *Faec/Strept.* | 3000 | $10^{-1}$ | 4.5 | 2.5 | 2.0 |
| Spores of SRC | 4500 | $10^{-1}$ | 4.7 | 3.0 | 1.7 |
| Viruses | 0.1 | $1.5 \times 10^{-7}$ | 5.6 | 2.0 | 3.6 |
| *Giardia* | 5.2 | $7.0 \times 10^{-6}$ | 5.9 | 2.5 | 3.4 |
| *Cryptosporidium* | 2.6 | $3.3 \times 10^{-5}$ | 4.9 | 2.0 | 2.9 |

- 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

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, methabenzthiaxuon, dicamba, 2,4-D, TCA and trichlorpyr are found in concentrations up to 1 $\mu$g/L. For these compounds, the standard of the EC and Dutch drinking water act (0.1 mg/L) must be satisfied. In view of the raw water concentrations after storage, the required degradation was set at 80 %.

More recently, monitoring programs have been focussed on the presence of endocrine disruptors and pharmaceuticals. In the raw water sources, up to several hundred ng/L were found for bisphenol A, diethylphtalate, diclofenac, ibuprofen, phenazone, carbamazepine and several antibiotics and X-ray contrast media. For these compounds, no standards have been set at this moment.

UV/$H_2O_2$ treatment, a combination of UV photolysis and hydroxyl radical reactions, was pursued for organic contaminant control. Extensive bench scale and pilot scale testing indicated that 80 % degradation of the organic contaminants could be achieved under realistic conditions.

Again PWN considered the perspective of UV treatment, this time in combination with the addition of $H_2O_2$, for organic contaminant control very promising. Partly in collaboration with Trojan Technologies Inc., three major objectives were pursued:

- to model degradation by UV photolysis and hydroxyl radical reaction for selected priority pollutants (pesticides, endocrine disruptors, pharmaceuticals);
- to predict and determine the ability of a medium pressure UV reactor to degrade those priority pollutants;
- to design a full scale UV/$H_2O_2$ system for both disinfection and organic contaminant control.

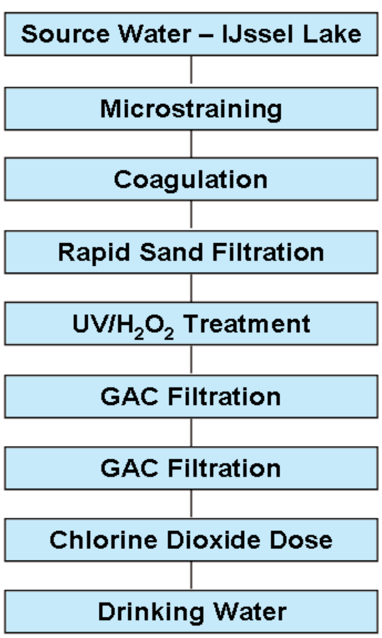


**Figure 3**. Current treatment scheme at the Andijk WTP (2004 - )

## FULL SCALE IMPLIMENTATION OF THE UV/$H_2O_2$ TREATMENT PROCESS

PWN decided to implement UV/$H_2O_2$ treatment process for a full scale treatment plant prior to the two step GAC-filtration already present (see Figure 3). At the same time, the breakpoint chlorination was abandoned.

Based on bench and pilot scale experiments, it was decided to use a dose of 6 mg/L $H_2O_2$. However, the $H_2O_2$ concentration (post UV) was >5 mg/L. Fortunately, the GAC filtration steps very effectively remove (to less than 0.1 mg/L) the residual $H_2O_2$.

The AOC in the source water varied between 5 - 33 $\mu$g Ac C eq/L; however, after the UV/$H_2O_2$ treatment the AOC increased to 45 - 142 Ac C eq/L. Nevertheless, the GAC filtration lowered the AOC back down to 3 - 31 Ac C eq/L. These values are higher than the recommendation for biological stability of 10 Ac C eq/L. However, the biofilm formation rate after GAC filtration remained lower than the recommended value for biological stability (< 5 pg/cm$^2$.d) for more than one year.

PWN has now installed a Trojan Technologies Inc. UV/$H_2O_2$ system at the Andijk WTP consisting of 12 SWIFT 16L30 reactors (see Fig. 4), arranged in three lines with four reactors each. The total UV power is 2.4 MW, making this installation currently the largest UV system for water treatment in the world. The system is intended to provide primary disinfection and destruction of a wide range of pesticides, endocrine disrupting compounds, algae toxins, pharmaceuticals, etc. The system was designed to provide 80% destruction of atrazine at a flow rate of 4,000 m$^3$/h at a UV transmittance of 80% at 254 nm (1 cm path length). The actual destruction under these conditions proved to be 77 ± 9%, easily within the designed range.

The UV-dose of 560 mJ/cm$^2$ is needed to degrade organic micro-pollutants with the UV/$H_2O_2$ treatment process. However, the UV dose needed for disinfection only amounts to a fifth of that. Consequently, the UV dose applied for the degradation of organic micro-pollutants determines the design of the reactor. At the same time, the disinfection criteria are fully satisfied as well.

## DISCUSSION AND CONCLUSIONS

The Andijk WTP not only degrades pesticides but also inactivates microorganisms. Also, the removal of health-threatening substances, such as pharmaceuticals and endocrine disruptors and the carcinogenic NDMA is safeguarded for the future. The UV-hydrogen peroxide treatment therefore promises to be an international success-story. Anywhere where drinking water is extracted from surface water, this process can provide answers on the subject of organic contaminant control.

The great thing about the UV/$H_2O_2$ process is that the technology is 'future proof'. Substances that don't exceed present standards, may do so in the future. The first pesticides measured in surface water could still be adsorbed onto activated carbon. Now there is a tendency toward application of more environmentally friendly pesticides. Unfortunately, 'more environmentally friendly' means: more soluble in water. That in turn means, that activated carbon is less suitable in removing these substances from water. For example, the modern pesticide Glyfosate is not economically removable by carbon. But the UV/$H_2O_2$ process does it easily. The installation at Andijk is scaled to the contaminants that can be reasonably expected.

In North America, N-nitrosodimethylamine (NDMA), a substance that originates as a waste product of rocket fuel production, is known to be present in some drinking water sources. It is not only highly carcinogenic, but also difficult to remove. Air stripping and activated carbon filtration do not suffice. The substance even slips through the membrane filtration process of reverse osmosis. With 1,4-dioxane, it is the same story. However, the hydroxyl radicals in the UV/$H_2O_2$ process react with almost all organic contaminants degrading all these substances.

A technology may look attractive, but if too expensive, it will not catch on. Here is where the advantage of a combined step is apparent. The trajectory of the research and development was complex, but the definitive process is actually very simple. Moreover, the technology can be fit into already existing treatment systems. Not much more is needed than the fitting in of flanges and reactors in an existing pipe.

A lot of hard work has gone into reducing the high energy consumption. By application of a new type of UV reactor, the energy-efficiency is now twice as high. The energy consumption dropped from 1.0 to 0.55 kWh per $m^3$. Then operating costs are moderate. Absolutely reliable drinking water from Andijk costs only 0.01 cent per liter more than it did before. How does that compare to the costs of one bottle of water from the store?

In conclusion, the UV/$H_2O_2$ system at the Andijk WTP is extremely innovative and provides a viable option to other WTPs with similar micro-contaminant problems.


**Figure 4**: UV reactors in the full scale UV/$H_2O_2$ system at the Andijk WTP.