Impact of Advanced Pretreatment on the Feasibility of UV/H_2O_2 Treatment for Degradation of Organic Micro pollutants

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Abstract

PWN currently researches the feasibility of ion exchange and ultra filtration (IX-UF) to upgrade the existing CSF pretreatment. Advanced oxidation in combination with GAC (UV/ H_2O_2 GAC) as non selective barrier for organic micro pollutants is operational since 2004. Effects of an improved pretreatment on the UV/ H_2O_2 in terms of direct photolysis, OH-radical oxidation and energy consumption are presented. Key water quality parameters are DOC and nitrate for scavenging and competition for UV light. Compared to CSF, the electrical energy per order (EEO) for IX-UF treated water was reduced with about 50%.

Key words: Ultraviolet; Advanced Oxidation; Ion Exchange; Pretreatment

Introduction

PWN Water Supply Company North-Holland started early 20th century with the distribution of dune water. At that time, the focus of the company was on the distribution, because dune water required limited treatment only. Early sixties, PWN had her first experience with direct surface water treatment at wtp Andijk, shifting the focus towards technology. The original treatment of wtp Andijk was conventional treatment consisting of breakpoint chlorination, coagulation-sedimentation-filtration (CSF) and post chlorination. Already after a few years of operation, this treatment was modified, installing post GAC filtration and replacement of the post chlorination by post disinfection with chlorine dioxide. This process was applied until requirements for additional disinfection capacity and a non selective barrier for organic micro pollutants led to the implementation of advanced oxidation process (AOP) UV/H_2O_2 in 2004 (Kruithof et al, 2007).

Two degradation mechanisms play a role in UV/H_2O_2, photolysis and OH-radical oxidation, contributing to the non selectivity of this AOP. Some compounds are only degraded by OH-radical oxidation (1,4 dioxane, pCBA), others mainly by photolysis (NDMA) but the majority of organic micro pollutants is degraded by a combination of photolysis and OH-radical oxidation (atrazine) (figure 1). The efficacy of the UV/H_2O_2 process is impacted by the water matrix. UV-absorbing compounds (nitrate, natural organic matter (NOM)) introduce competition for UV light. Water constituents (DOC, nitrite, carbonate/bi-carbonate), other than the degradation targets, are competing for UV light and OH-radicals (scavenging) as well.

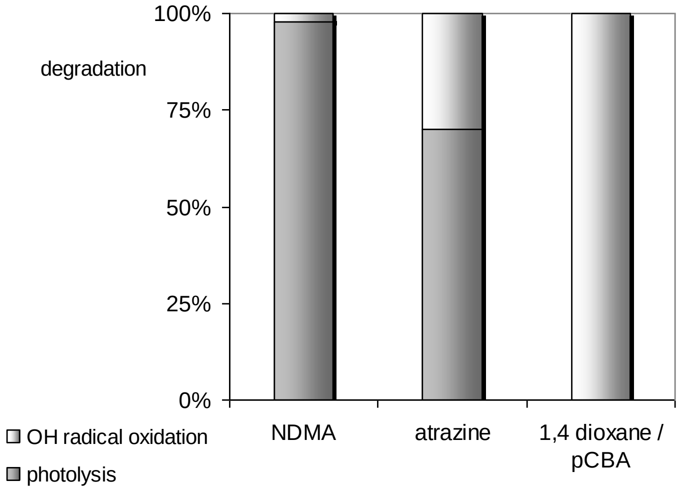

figure 1: degradation mechanisms photolysis and OH-radical oxidation in UV/H_2O_2 treatment

Advanced oxidation with UV/H_2O_2 is increasingly considered as a best available technology (BAT) for organic contaminant control. Already in PWN's collaborative research with UV-supplier Trojan, it was shown that developing an advanced kinetic and CFD model resulted in a reactor design that reduced the power consumption by more than 40% compared to a standard reactor design for conventional disinfection purposes.

Although the required energy consumption by UV/H_2O_2 process in this reactor type is still substantial, the process has proven to be economically feasible for organic contaminant control purposes such as NDMA degradation (Orange County), taste and odor removal (Aurora) and as a non selective barrier against organic micro pollutants (PWN). The economical feasibility would increase significantly with a reduced energy consumption and make this technology even more attractive to solve a wide range of water treatment problems.

Key Water Quality Parameters

A significant reduction of energy consumption of the AOP can be achieved by a strong increase of the UV-transmittance of the water, thereby reducing the competition for UV light and reducing the scavenging by OH-radicals. In a preliminary research effort the composition of the UV absorbing compounds was analyzed. The important water constituents influencing the efficacy of the UV/ H_2O_2 process are natural organic matter (NOM) and nitrate. The NOM (measured as DOC) is regarded as the dominant OH-radical scavenger. Nitrate absorbs UV light at the same wave length as H_2O_2 and has a higher molar absorption, introducing competition for photons (especially when broad spectrum UV light is applied).

Pretreatment impacts the composition of the water matrix. CSF lowers the DOC content, reducing the OH-radical scavenging but does not impact the nitrate concentration. Advanced pretreatment with ion exchange and ultra filtration (IX-UF) removes both nitrate and DOC (Galjaard et al, 2005). It is expected that removal of nitrate benefits the formation of OH-radicals and that the scavenging of OH-radicals is reduced by DOC removal, relative to CSF pretreatment. Additional advantage of IX-UF is that any desired DOC and nitrate reduction can be achieved by setting process conditions. IX-UF pretreatment provides the opportunity to create favorable conditions for the UV/H_2O_2 process, regardless the raw water composition.

Table 1 presents the nitrate concentration in the raw water, after the current CSF pretreatment and after IX-UF pretreatment. Raw water from the Lake IJssel shows seasonal variations in nitrate between 1 and 13 mg/L. The existing CSF treatment does not impact the nitrate concentration substantially. IX-UF lowers the nitrate concentration with 65%, reducing both the fluctuation and the absolute concentration.

table 1: annual min, max and average nitrate concentration in raw water, after CSF treatment and after IX-UF treatment

	min mg NO_3/L	max mg NO_3/L	average mg NO_3/L
raw water	1.2	12.4	6.5
CSF treatment	1.7	9.4	5.8
IX-UF treatment	0.5	4.2	2.3

The DOC content (6.5 mg/L) in raw water is rather stable over the year. DOC, is removed by the existing CSF for approximately 30%. With IX-UF pretreatment, the removal of DOC is increased to 50% on average (table 2).

table 2: annual min, max and average DOC concentration in raw water, after CSF treatment and after IX-UF treatment

	min mg C/L	max mg C/L	average mg C/L
raw water	5.1	7.2	6.0
CSF treatment	2.9	5.1	4.0
IX-UF treatment	2.1	4.4	2.9

The impact of pretreatment on the most relevant water matrix parameters for UV/ H_2O_2, nitrate and DOC, for the PWN situation, are summarized in figure 2.

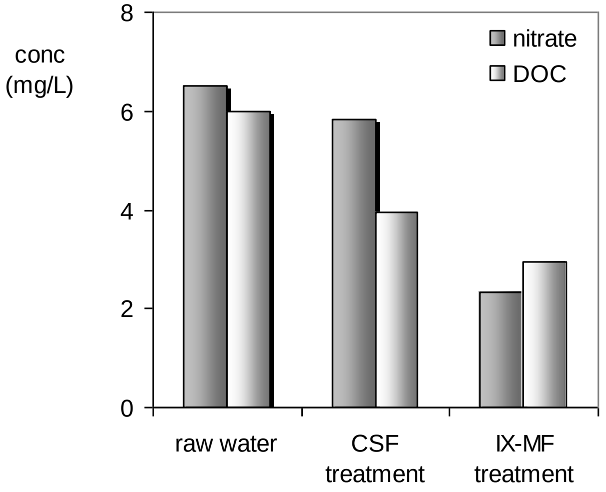

figure 2: annual average nitrate and DOC concentration in raw water, after CSF treatment and in IX-UF treated water

For UV/H_2O_2 purposes both DOC and nitrate content should be lowered by pretreatment as much as possible. In the current situation, CSF lowers the DOC from 6.0 mg/L to 4.0 mg/L. Nitrate removal by CSF is insignificant. Currently, PWN researches the feasibility to replace the existing CSF of her surface wtp Andijk with ion exchange in combination with ultra filtration (IX-UF). For the applied process conditions IX-UF lowers both DOC and nitrate to 2.9mg/L and 2.3 mg/L respectively.

The impact of the improved water quality on the degradation of organic micro pollutants has been studied in collimated beam experiments. Nitrosodimethylamine (NDMA) is selected as a reference compound sensitive for UV photolysis while 1,4-dioxane and pCBA are selected as a reference compound sensitive for OH-radical oxidation only.

The Effect of Pretreatment on Key Water Quality Parameters

The effect of pretreatment on the UV absorption spectrum of the water matrix (panel A, B and C) and the spectrum of H_2O_2 (panel D) are presented in figure 3. DOC and nitrate are measured in all water types. In addition the found contents are spiked in milliQ, simulating the raw water, CSF and IX-UF composition. For raw water (panel A), CSF treated water (panel B) and IX-UF treated water (panel C), a UV-scan (200-300 nm) of natural water is compared to a UV-scan of DOC and nitrate in milliQ.

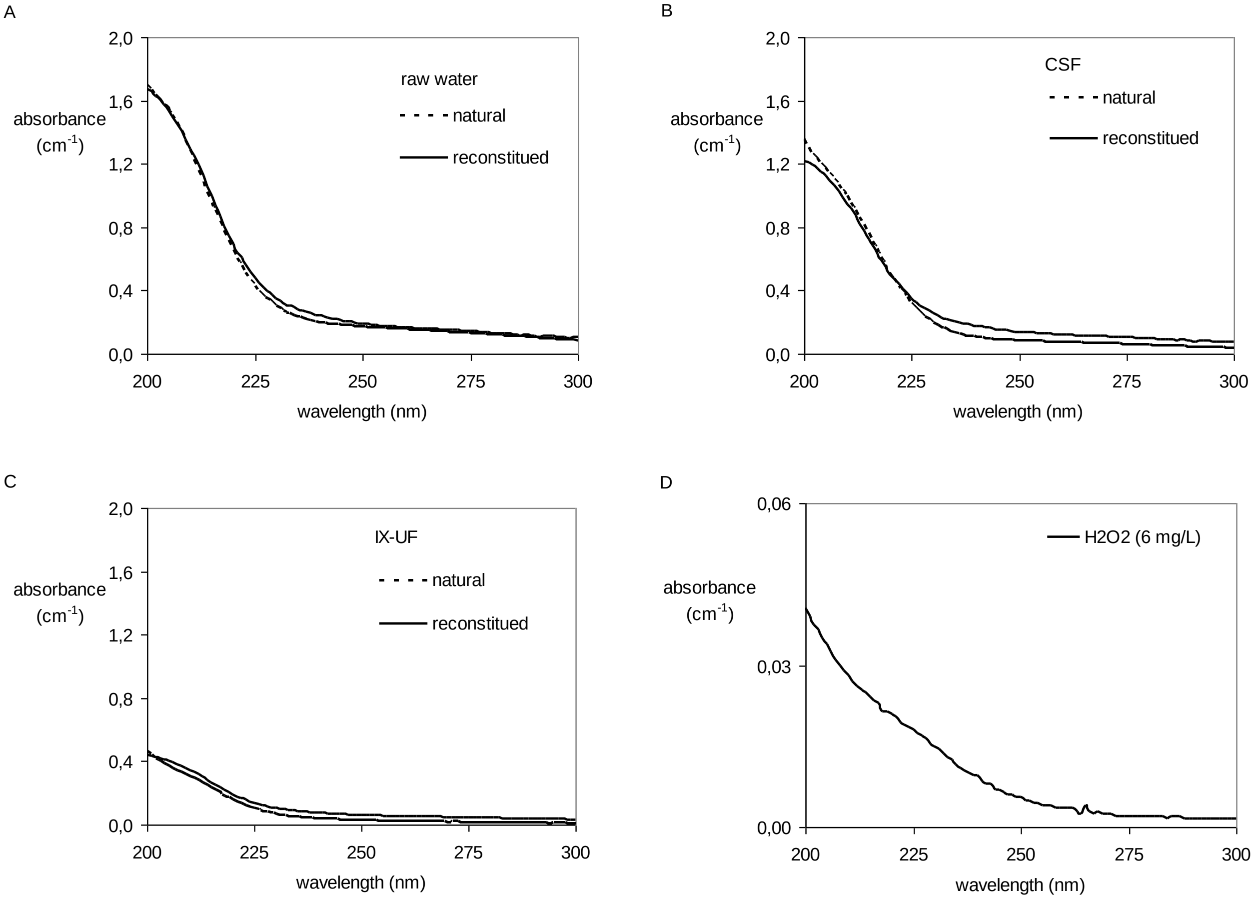

figure 3: absorbance of raw water and reconstituted water (panel a), CSF treated water and reconstituted water (panel b), after IX-UF treatment and reconstituted water (panel c) for the average water quality and the absorbance of 6 mg/L H_2O_2 solution (panel d)

The absorption spectra confirm that DOC and nitrate are the major UV absorbing constituents. Please note that H_2O_2 absorbs in the same wavelength range but with much lower absorption values.

The available fraction of UV-radiation for the formation of OH-radicals by photolysis of H_2O_2 is determined for two wavelengths, 240 nm and 254 nm, in raw water, CSF treated water and in IX-UF treated water (table 3). All three water types show a higher UV absorbance by H_2O_2 at lower wavelength. This indicates that OH-radical formation at 254 nm (LP UV) is less efficient than at lower wavelengths, for instance 240 nm (MP UV) (table 3). The effect of pretreatment on the UV-absorption is illustrated as well by the results from table 3. An increase of approximately 2-2.5 times in available UV between CSF pretreatment and IX-UF pretreatment is observed.

table 3: absorption of H_2O_2 (6 mg/L) in raw water, CSF treated water and after IX-UF treatment for two wave lengths (240 nm and 254 nm)

	240 nm	254 nm
raw water	4.5%	2.6%
CSF treated water	8.2%	5.3%
IX-UF treatment	19.4%	14.7%

Based upon the emission spectrum of MP UV, relative to the total photon flow, the absorbed photon flow for the water matrix, the H_2O_2 dosage and the indicator compounds (NDMA for photolysis and 1,4 dioxane for OH-radical oxidation) are calculated (table 4) (Bolton, 2001). Due to experimental constraints, a high NDMA concentration was applied, resulting in a comparable absorbed photon flow for NDMA and H_2O_2.

table 4: absorbed photon flow by the water matrix, H_2O_2 (6 mg/L), NDMA (500 ug/L) and 1,4 dioxane (200 ug/L) in raw water, CSF treated water and after IX-UF treatment. Collimated beam data, normalized to 100% absorption to represent full scale reactor conditions

	raw	CSF treated water	IX-UF treatment
% photon flow absorbed by matrix	89%	85%	72%
% photon flow absorbed by H_2O_2	4%	6%	11%
% photon flow absorbed by NDMA	7%	9%	17%
% photon flow absorbed by 1,4 dioxane	0%	0%	0%

Compared to the results of table 3 where only the absorption spectrum of the water matrix and H_2O_2 were taken into account, the effect of the pretreatment is less pronounced, but still substantial.

Effect of Pretreatment on Photolysis

NDMA has a high absorption within the UV-C spectral range 200-260nm and a relatively high quantum yield. The compound was chosen because degradation is almost entirely due to photolysis showing little degradation by OH-radical oxidation (Stefan et al, 2002).

In MP UV collimated beam experiments, the degradation of NDMA was studied in milliQ water, CSF treated water and IX-UF treated water for several H_2O_2 dosages. The irradiance time was calculated according to Bolton (Bolton et al, 2002).

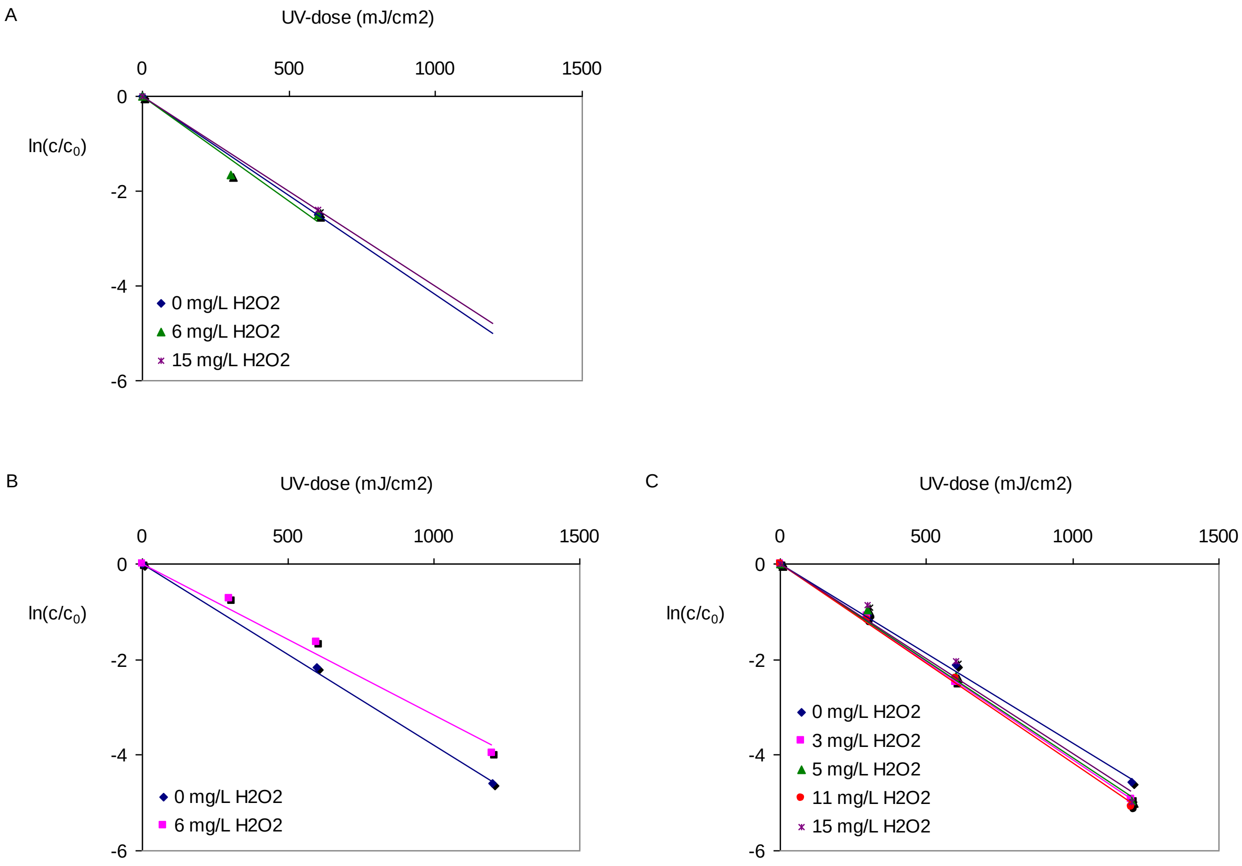

figure 4: NDMA degradation (MP UV collimated beam experiments) in milliQ (panel a), in CSF treated water (panel b) and after IX-UF treatment (panel c) for a range of H_2O_2 concentrations

The quantum yield was determined based upon the experimental results (figure 4). Literature values (Stefan et al, 2002) where consistently lower (approximately 15%) than quantum yields determined in this study (table 5) due to a lower molar absorption coefficient.

table 5: experimentally obtained quantum yield for NDMA

	milliQ	CSF treatment	IX-UF treatment
□	0.431	0.394	0.392

The results from the collimated beam experiments confirm that the predominant nature of the degradation mechanism of NDMA is photolysis and that matrix effects (competition for UV-light) are taken into account by setting the correct irradiation time.

For MP UV pilot experiments, at a range of H_2O_2 dosages, the EEO required for NDMA degradation in IX-UF treated water was calculated. For a single H_2O_2 dosage, the EEO for NDMA degradation in CSF treated water was calculated as well (figure 5).

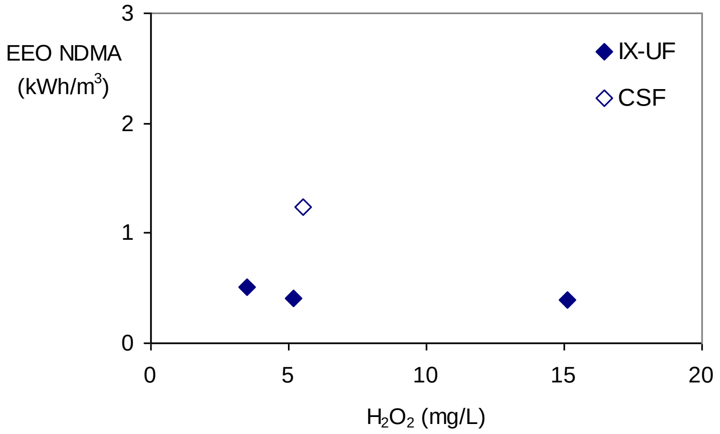

figure 5: electrical energy per order for NDMA as function of H_2O_2 concentration for CSF treated water and after IX-UF treatment (pilot experiments)

Independent of the H_2O_2 dosages, the same EEO for NDMA degradation in IX-UF treated water was calculated, confirming the photolytic character of NDMA degradation. The higher EEO for NDMA in CSF treated water is due to the water matrix, creating more competition for UV light. The EEO for NDMA in IX-UF treated water (0.41 kWh/m^3), compared to the EEO for NDMA in CSF treated water (1.24 kWh/m^3) exceeds the estimate based upon the photon flow. Reason for this may be the increasing efficacy of the UV-reactor with higher UV-transmittance.

Effect of Pretreatment on OH-radical Oxidation

1,4-dioxane was chosen for this study because its degradation is entirely due to hydroxyl radical oxidation. The degree to which 1,4-dioxane degradation occurs is an indicator of the influence of the water matrix on OH-radical production and radical scavenging.

The degradation of 1,4 dioxane was studied in MP UV collimated beam experiments in milliQ, CSF treated water and IX-UF treated water. The irradiance time was calculated according to Bolton (Bolton et al, 2002).

In milliQ water, in the absence of H_2O_2, no degradation of 1,4 dioxane is observed (figure 6, panel A). The minor 1,4 dioxane degradation in CSF treated water and in IX-UF treated water without H_2O_2 dosage is due to photo induced OH-radical formation (figure 5, panel B, C).

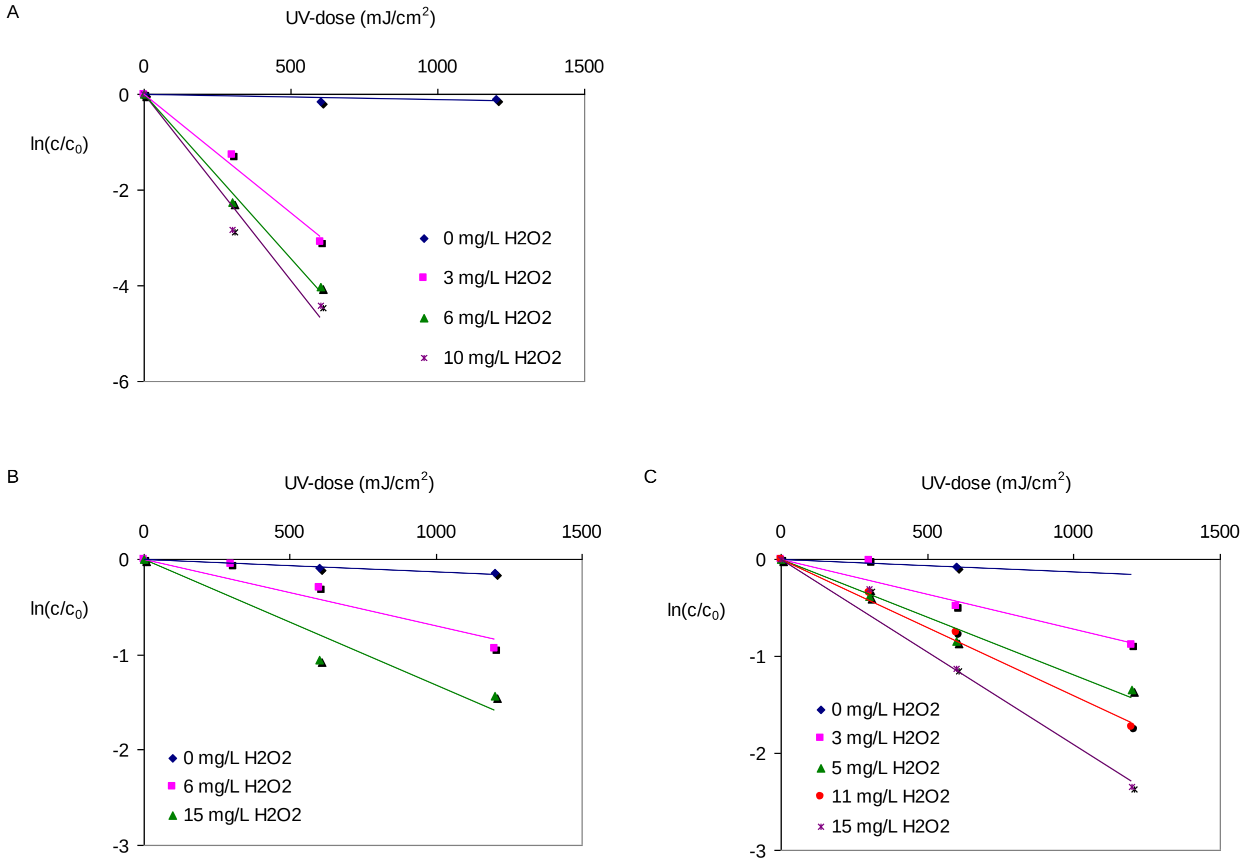

figure 6: 1,4 dioxane degradation (MP UV collimated beam experiments) in milliQ (panel a), in CSF treated water (panel b) and after IX-UF treatment (panel c) for a range of H_2O_2 concentrations

The primary reason for the observed increased 1,4 dioxane degradation in IX-UF treated water is the restricted OH-radical scavenging (figure 6, panel B and C).

In MP UV pilot experiments, for a range of H_2O_2 dosages, the required EEO of 1,4 dioxane degradation in IX-UF treated water was determined. For a single H_2O_2 dosage, the EEO needed for the degradation of 1,4 dioxane in CSF treated water was calculated as well (figure 7).

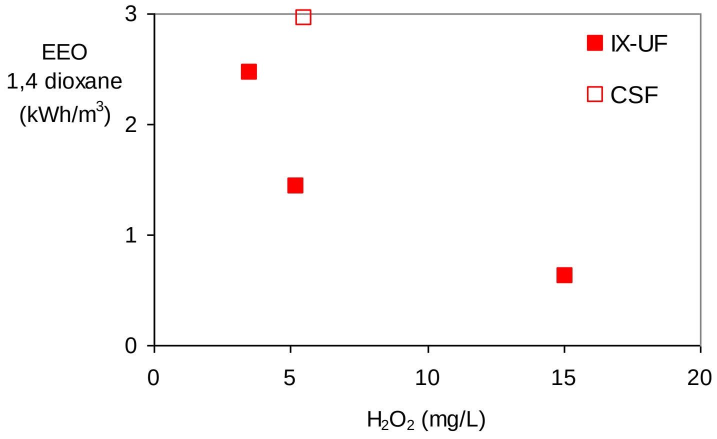

figure 7: electrical energy per order for 1,4 dioxane as function of H_2O_2 concentration for CSF treated water and after IX-UF treatment (pilot experiments)

Contrary to the NDMA data, in IX-UF pretreated water the H_2O_2 dosage shows a substantial impact on the EEO for 1,4 dioxane, ranging from 2.5 kWh/m^3 at 3.5 mg H_2O_2/L to 0.6 kWh/m^3 at 15 mg H_2O_2/L (figure 7). For one H_2O_2 dosage (5 mg/L), the EEO of 1,4 dioxane in CSF treated water was determined as well. Comparing this EEO (3.0 kWh/m^3) to the EEO in IX-UF treated water (1.4 kWh/m^3), shows a reduction with a factor of 2.1. This improvement by pretreatment is due to both reduced OH-radical scavenging and less competition for UV light for OH-radical formation.

$R_{OH,\ UV}$ Modeling for Effect of Pretreatment

For both 1,4 dioxane and pCBA, the $R_{OH,UV}$ concept, developed by Rosenfeldt (Rosenfeldt et al, 2007) was applied. The $R_{OH,UV}$ concept is defined as the experimentally determined OH• radical exposure per UV fluence. $R_{OH,\ UV}$ was determined by examining the degradation of both 1,4 dioxane and para-chlorobenzoic acid (pCBA) as probe compound. The following equation for $R_{OH,\ UV}$ was developed by Rosenfeldt:

$$R_{OH,UV} = \frac{\int_0^t [\bullet OH]dt}{H} = \frac{k_T^{'D} - k_d^{'D}}{k_{OH,probe}}$$

Where:

$k_d^{'D}$ is the fluence based rate constant of the probe destruction by direct UV photolysis in the water matrix;

$k_T^{'D}$ is the fluence based rate constant of the probe destruction by both OH-radical oxidation and direct photolysis in the water matrix;

$k_{OH,probe}$ is the rate constant for the probe destruction by OH-radical oxidation;

$k_{OH,pCBA}$ is 5,0*10^9 M^{-1} s^{-1} (Rosenfeldt et al, 2007)

$k_{OH,1,4-dioxane}$ is 2,8*10^9 M^{-1} s^{-1} (Stefan et al, 1998)

Figure 8 shows the $R_{OH,\ UV}$ in milliQ as function of the H_2O_2 concentration, using both 1,4 dioxane (figure 5) and pCBA as probe (MP UV collimated beam experiments). In our experiments, the probe selection does not influence the $R_{OH,UV}$ significantly. Also plotted in figure 8 are the results for $R_{OH,\ UV}$ in milliQ from Rosenfeldt, using pCBA as a probe (MP UV collimated beam experiments).

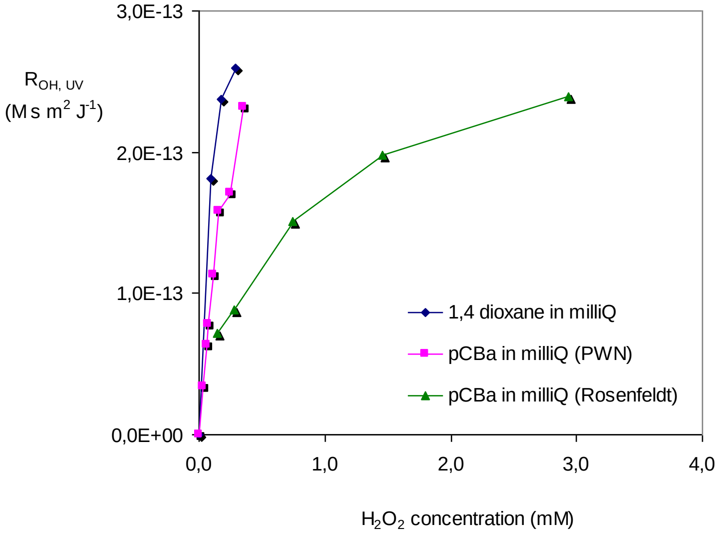

figure 8: $R_{OH,\ UV}$ determined in milliQ for 1,4 dioxane and pCBA, compared to pCBA literature values (Rosenfeldt et al, 2007)

Our $R_{OH,\ UV}$ data for 1,4 dioxane and pCBA relate very well. The results from Rosenfeldt (Rosenfeldt et al, 2007) are in the same order of magnitude although his $R_{OH,\ UV}$ values are significantly lower. This may be caused by a lower quality of milliQ water.

The $R_{OH,\ UV}$ for milliQ, CSF treated water and IX-UF treated water for a range of H_2O_2 concentrations (up to 0,5 mM H_2O_2) (MP UV) is presented (figure 9). The fluence based rate constants k'^{D}_{T} and k'^{D}_{d} (table 6) are derived from collimated beam experiments (figure 6).

table 6: pseudo first order rate constants by direct photolysis and direct and indirect photolysis for 1,4 dioxane and pCBA in milliQ (6 ppm H_2O_2), CSF treated water (6 ppm H_2O_2) and IX-UF treated water (5 ppm H_2O_2)

	k'^{D}_{d} (m^2 J^{-1}) 1,4 dioxane	k'^{D}_{d} (m^2 J^{-1}) pCBA	k'^{D}_{T} (m^2 J^{-1}) 1,4 dioxane	k'^{D}_{T} (m^2 J^{-1}) pCBA
milliQ	$7.94*10^{-6}$	$3.21*10^{-5}$	$6.73*10^{-4}$	$8.22*10^{-4}$
IX-UF	$1.23*10^{-5}$	n.a.	$1.12*10^{-4}$	n.a.
CSF	$1.22*10^{-5}$	n.a.	$8.16*10^{-5}$	n.a.

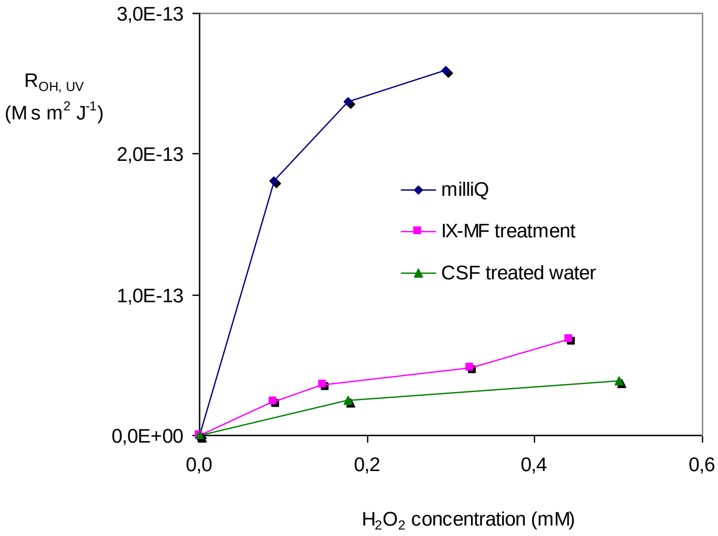

figure 9: $R_{OH, UV}$ for milliQ, CSF treated water and after IX-UF treatment as function of H_2O_2 concentration

Relative to the $R_{OH, UV}$ in milliQ, $R_{OH, UV}$ values for CSF treated water and IX-UF treated water illustrate the very substantial impact the water matrix is having. Comparing the $R_{OH, UV}$ at a H_2O_2 concentration of 0.15 mM (5 mg/L) for CSF treated water and IX-UF treated water to the EEO results from the pilot experiments (figure 7), indicate similar behavior.

The impact of the dominant water matrix constituents, DOC and nitrate, on the $R_{OH, UV}$ has been studied in MP UV collimated beam experiments, using pCBA as probe. MilliQ was spiked with a range of DOC concentrations and a range of nitrate concentrations at comparable H_2O_2 concentrations. The $R_{OH, UV}$ of the given H_2O_2 concentration was used as reference (figure 9).

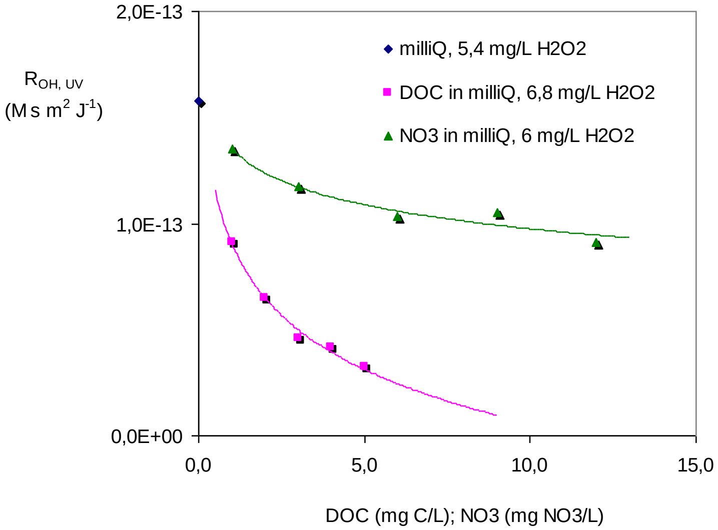

figure 10: $R_{OH, UV}$ for 6 mg/L H_2O_2 as a function of the DOC concentration and NO_3 concentration in milliQ; pCBA was used as probe, results from MP UV collimated beam experiments

The impact of DOC over the observed annual range in CSF treated water (3-5 mg C/L) and IX-UF treated water (2-4 mg C/L) is predominantly determining the capacity of the OH-radical oxidation. The impact of nitrate on the $R_{OH, UV}$ is less pronounced. From this perspective a further decrease of DOC by the IX-UF process should be pursued (i.e. by selection of process conditions for IX-UF).

Conclusions

In view of the foreseen new pretreatment for PWN's surface wtp Andijk, the effect of this pretreatment on the in 2004 installed UV/ H_2O_2 process was studied. The existing pretreatment is based on CSF; the foreseen new pretreatment is IX-UF.

Compared to CSF, IX-UF improves the water quality in terms of UV transmittance, extended DOC removal (to 1.0 mg/L) and significant nitrate removal (to 0.2 – 4.0 mg nitrate/L). This improves the conditions for post UV/H_2O_2 treatment. The scavenging of OH-radicals is reduced and, since PWN applies medium pressure UV-lamps, the generation of OH-radicals by photolysis of H_2O_2 becomes more favorable.

NOM (DOC) and nitrate are the predominant water parameters, influencing the UV/ H_2O_2 process. CSF pretreatment removes 30% DOC and does not affect the nitrate concentration. For the tested IX-UF process settings, DOC is removed for 50% and nitrate for 70%.

Based on UV absorbance (200-300 nm) of the water matrix and H_2O_2, treatment with IX-UF resulted in an increase of the available UV light for H_2O_2 by a factor 2, relative to CSF pretreatment (table 3). This behavior was confirmed in a more detailed study, calculating the absorbed photon flow taking the MP UV lamp emission spectrum into account (table 4).

The absorbance of UV by H_2O_2 at a wave length of 240 nm is higher than at 254 nm. This is shown for both CSF pretreated water (UVT_{254} ~80%) and IX-UF treated water (UVT_{254} ~90%).

For the MP UV collimated beam experiments and pilot experiments, NDMA was used as compound to monitor photolytic processes and 1,4 dioxane and pCBA were used to monitor the OH-radical oxidation. Based on pilot work, the electrical energy per order (EEO) is calculated.

The quantum yield for NDMA was determined in MP UV collimated beam experiments and compared to literature values. It is observed that the experimental values are off by 25%, mainly due to a difference in the molar absorption. In the pilot, the expected degradation by photolysis of NDMA was confirmed. IX-UF pretreatment compared to CSF pretreatment reduced the EEO to a third.

Rosenfeldt's $R_{OH, UV}$ concept was used to compare the OH-radical oxidation in the water matrices. Results from MP collimated beam experiments were used as input. The OH-radical oxidation, measured by the increase of $R_{OH, UV}$, improved with 40%, applying IX-UF instead of CSF. In pilot plant experiments, a reduction of the EEO by a factor 2 was observed when CSF was replaced by IX-UF.

Additional MP UV collimated beam results, using pCBA as probe, on DOC and nitrate spiked milliQ, have been used to determine the dominant water matrix constituent for the OH-radical oxidation. The $R_{OH, UV}$ concept was applied, showing that DOC has the major impact on the efficacy of the OH-radical oxidation. In view of the potentially very high removal of DOC by IX-UF, this treatment looks very promising as pretreatment for UV/H_2O_2.

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