

Prediction of advanced oxidation performance in UV/H₂O₂ reactor systems with LP-UV lamps

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ABSTRACT

Advanced oxidation processes, like UV/H₂O₂ oxidation, are important barriers against organic micro pollutants in drinking water treatment. In order to guarantee safe drinking water, it is important to be able to predict the reactors' performance to adjust the operating conditions to the actual influent water characteristics (like UV transmission) and lamp performance. Therefore, a design tool was developed, which is based on a kinetic model that describes and predicts the direct photolysis and oxidation of organic compounds in pilot experiments, using Low Pressure (LP) UV-lamps. This model has been combined with computational fluid dynamics (CFD), in order to be able to accurately predict the results of pilot and full scale installations, and also to design reactor systems. The model was applied to three model compounds (atrazine, ibuprofen and NDMA) in two different pilot reactors, and it has been shown that reactor performance can be fairly predicted by applying this 'UVPerox' model. The model takes into account the water quality and power of the lamps, and the properties of the compounds involved.

Key words | advanced oxidation processes (AOPs), computational fluid dynamics, kinetic model, pilot reactor, UV/H₂O₂

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INTRODUCTION

(Drinking) water quality may be threatened by the presence of organic contaminants. Advanced oxidation processes (AOPs), like UV/H₂O₂ oxidation, are breaking through as important barriers against organic micro pollutants in full scale water treatment. The performance of UV oxidation is based on photolysis, combined with ·OH radical formation. The advantage of these strong oxidants is their aselective nature. A 'disadvantage' of the UV/H₂O₂ process is the potentially high energy consumption and associated costs. In order to guarantee safe drinking water at acceptable costs, it is important to be able to adjust the process parameters (like UV intensity, H₂O₂ concentration and flow) to the influent water characteristics, without continuously having to carry out pilot trials. Therefore, we developed a design tool: the UVPerox model. At first instance this model was used to compare predicted conversions with

experimental data, but the ultimate goal is to use this model for real-time control of the process.

UV irradiation may induce direct photolysis of micro pollutants and (if H₂O₂ is present) hydroxyl radical formation. These radicals will aselectively oxidize micro pollutants. For most contaminants both direct photolysis and ·OH radical oxidation follow (pseudo) first order kinetics (Crittenden *et al.* 1999). The direct photolysis relates to the UV dose received (in the wavelength range that can be absorbed by the specific compounds). The same holds for the photolysis of H₂O₂ to produce ·OH radicals. These radicals react very fast with various molecules, thus rapidly achieving a steady state equilibrium concentration. Several kinetic models have been proposed (Lay 1989; Yao *et al.* 1992; Glaze *et al.* 1995; Stefan *et al.* 1996), sometimes combined with operation of completely mixed batch reactors

or plug flow reactors. Crittenden *et al.* (1999) developed a kinetic model that incorporates all significant photochemical and chemical reactions. The reactivity of the various contaminants depends on the UV wavelength. The quantum yield of the photolysis process is measured for 254 nm (as emitted by low-pressure lamps), but is not widely measured in the 200–300 nm range (as emitted by medium-pressure lamps). This is also the case for the molar reaction rate constant, both for contaminants and scavengers.

While the kinetic model for photolysis and oxidation has been well developed, so far it has hardly been combined with models that describe the actual flow through a reactor and the related residence time. In most cases, complete mixing is assumed. The flow and residence time distribution can be calculated using Computational Fluid Dynamics (CFD). Alpert *et al.* (2010) and Santoro *et al.* (2010) used CFD modeling for annular reactors.

In this paper a model is proposed describing the kinetics of the UV/oxidation process in combination with CFD calculations to describe real-time flow through reactors equipped with several LP-lamps.

The model was validated for atrazine, ibuprofen and NDMA in pilot reactors at the KWR Watercycle Research Institute and at the drinking water supply company, Dunea.

THEORY

Photolysis

Photolysis starts by absorption of (UV)light, which initiates the degradation process. The theory of photochemical reaction kinetics has been discussed in literature. These kinetics are a function of the quantum yield (a measure of photon efficiency) and the rate of light absorption. The model equations are given by Schwarzenbach *et al.* (1993):

$$\text{Photolysis} \left(\frac{\partial[\text{N}]}{\partial t} \right)_{\lambda} = -E_0(\lambda) \cdot \phi_N(\lambda) \cdot \frac{\varepsilon_N(\lambda) \cdot [\text{N}]}{A_t(\lambda)} \cdot (1 - 10^{-A_t(\lambda)}) \cdot 1000 \quad (1)$$

where E_0 is the photon fluence rate ($\text{J cm}^{-2} \text{s}^{-1}$), t the irradiation time (s), ϕ_N the reaction quantum yield (–), ε_N the molar absorption coefficient ($\text{L cm}^{-1} \text{mol}^{-1}$), $[\text{N}]$ the

concentration of N (mol L^{-1}) and $A_t(\lambda)$ the total absorption of the solution (–). All parameters depend on wavelength λ , and the factor 1,000 is used to convert from (cm^3) to (L).

Absorption is additive, the total absorption being the sum of the absorption of all specific compounds (NOM, organic micropollutants, NO₃, etc.). As the total absorption is low a first-order equation accounts for the attenuation of the light passing through the water (Stefan 2004). The equation becomes:

$$\left(\ln \frac{[\text{N}]_0}{[\text{N}]_t} \right)_{\lambda} = -E_0(\lambda) \cdot \phi_N(\lambda) \cdot \frac{\varepsilon_N(\lambda)}{A_t(\lambda)} \cdot (1 - 10^{-A_t(\lambda)}) \cdot 1000 \cdot t \quad (2)$$

The term $E_0(\lambda) \cdot t$ is a measure for the fluence (J/cm^2) received by the contaminant.

Oxidation

The $\cdot\text{OH}$ radical formation in principle is a photolysis reaction of H₂O₂, which has extensively been described in literature (Bielski *et al.* 1985). According to De Laat *et al.* (1999) the quantum yield for the primary photolysis reaction is 0.5 at 254 nm irradiation. The $\cdot\text{OH}$ radicals react quickly with (organic) contaminants present. Undesired reactions with other compounds in the water matrix (e.g. NOM, carbonate/bicarbonate) will also take place. (Bi)carbonate as well as phosphate acts as an $\cdot\text{OH}$ radical scavenger (Liao *et al.* 2001). Humic substances will both absorb UV light (reducing direct photolysis of micro pollutants) and scavenge $\cdot\text{OH}$ radicals (Hessler *et al.* 1993).

The $\cdot\text{OH}$ radical reduction depends on reaction with contaminants and scavengers. Since $\cdot\text{OH}$ radical formation is the rate determining step, steady state conditions (constant $\cdot\text{OH}$ concentration) can be assumed (Machairas 2004). Then the oxidation rate by $\cdot\text{OH}$ radicals can be described as a pseudo-first order process. The $\cdot\text{OH}$ radical formation rate from H₂O₂ can be described by Equations (3) and (4).

$$\frac{\partial[\cdot\text{OH}]}{\partial t} = -2 \frac{\partial[\text{H}_2\text{O}_2]}{\partial t} \quad (3)$$

$$\frac{\partial[\text{N}]}{\partial t} = -k_{\text{OH},\text{N}} \cdot [\text{N}] \cdot [\cdot\text{OH}] = -k_{\text{OH},\text{N}}' \cdot [\text{N}] \quad (4)$$

Under steady state conditions, $\partial[\text{N}]/\partial t = 0$ (Equation (4)), as the radical formation rate equals the consumption. With both rates in equilibrium, the steady state $[\text{OH}]$ concentration ($[\text{OH}]^{\text{ss}}$) becomes (Yuan *et al.* 2009):

$$[\text{OH}]^{\text{ss}} = 2000 \cdot \phi_{[\text{H}_2\text{O}_2]}(\lambda) \cdot E_0(\lambda) \cdot \varepsilon_{[\text{H}_2\text{O}_2]}(\lambda) \cdot \frac{(1 - 10^{-A_t(\lambda)}) \cdot [\text{H}_2\text{O}_2]}{A_t(\lambda) \cdot (k_{\text{OH,N}} \cdot [\text{N}] + \alpha)} \quad (5)$$

with $\alpha = k_{\text{HCO}_3} \cdot [\text{HCO}_3^-] + k_{\text{CO}_3} \cdot [\text{CO}_3^{2-}] + k_{\text{H}_2\text{O}_2} \cdot [\text{H}_2\text{O}_2] + k_S \cdot [S]$, where S denotes to other components in the water matrix (e.g. humic substances).

The term $k_S \cdot [S]$ describes the influence of the water matrix and is independent of the conversion of N. Therefore it is an important control variable if the model is applied to adjust operating conditions of the reactor.

The overall kinetics can be described by the total of contaminant conversion due to photolysis and oxidation:

$$\left(\frac{\partial[\text{N}]}{\partial t}\right)_\lambda = -E_0(\lambda) \cdot \varphi_N(\lambda) \cdot \frac{\varepsilon_N(\lambda) \cdot [\text{N}]}{A_t(\lambda)} \cdot (1 - 10^{-A_t(\lambda)}) \cdot 1000 - k_{\text{OH,N}}' [\text{N}] \quad (6)$$

This is a first order reaction equation that was applied to experiments carried out in a collimated beam set-up. The reaction constants used in the calculations are shown in Table 1.

This kinetic model predicts the conversion of a compound as a function of the UV dose applied. However, in a reactor there will always be a 'UV dose distribution', due to the flow through the reactor. This can be modeled by

means of CFD (Lyn & Blatchely 2005). A detailed description of the procedure followed here is given by Wols *et al.* (2011). By combining the UV dose distribution with the kinetic model, the reduction of contaminant concentration is calculated for each individual trajectory while passing through the UV system. Based on these data the reduction of a specific contaminant can be calculated.

MATERIALS AND METHODS

Reagents

Lab grade reagents (J. T. Baker) were used: H₂O₂ (30%, CAS No. 7722-84-1) and Na₂SO₃ (CAS No. 7757-83-7). Atrazine (dr. Ehrenstorfer, GmbH, CAS No. 1912-24-9), ibuprofen (Sigma Aldrich Chemie BV, CAS No. 15687-27-1) and NDMA (Supelco, CAS No. 62-75-9).

Test water

Collimated Beam tests were conducted in Milli Q (Deionized water) Millipore Academic A10, and surface water from the river Meuse, pretreated by means of coagulation, sedimentation, microsieves and sand filtration at Dunea. The water quality of the Dunea water used during the different tests is shown in Table 2.

Analyses

The UV scan was performed with a Thermo Spectronic Unicam UV500 spectrophotometer at a wavelength of 254 nm at a path length of 1 cm.

Table 1 | Reaction constants used for the UVPerox model calculations

Compound	Molar mass (g/mol)	Quantum yield (mol/Einstein) ϕ	Molar abs. coeff. (mol ⁻¹ cm ⁻¹) ε_N	Reaction constant (L/mol/s) k_N	Lit. ref.
H ₂ O ₂	34	0.5	18.6	2.7×10^7	De Laat <i>et al.</i> (1999)
Atrazine	215.72	0.045	3.86×10^5	2.7×10^9	Nick <i>et al.</i> (1992)
NDMA	74.08	0.30	1.974×10^5	3.3×10^8	Sharpless & Linden (2003)
Ibuprofen	206.3	0.1923	256	6.77×10^9	Yuan <i>et al.</i> (2009)

Table 2 | Water quality of the Dunea water used during the various tests

Experiment	pH	HCO ₃ ⁻ (mg/L)	NPOC ^a (mg C/L)	UV-T (254 nm) (%)
Collimated beam	7.9	140	3.4	82
KWR reactor	8.0	190	3.9	78
Dunea reactor	8.0	150	4.0	75
	7.9	135	3.3	82

^aNon Purgable Organic Carbon.

Analysis of the model compounds was performed by 'The Water Laboratory' in Haarlem, The Netherlands using an Ultra Performance Liquid Chromatograph (UPLC, Waters Acquity) equipped with a quaternary pump, combined with a Quattro Xevo triple quadrupole Mass Selective Detector (Waters Micromass) (UPLC BEH C18 column; 0.1% formic acid in water and methanol). Standard deviation for ibuprofen analysis was 0.6 µg/L, and for atrazin 0.003 µg/L.

Collimated beam experiments

The UV/H₂O₂ oxidation experiments were made with a collimated beam unit (CB unit) available at KWR. In this way, a value for the term $k_S \cdot [S]$ (describing the influence of the water matrix) was obtained. The set-up of the collimated

beam unit was described by Ijpelaar *et al.* (2006). Experiments were conducted with a low pressure lamp, whose intensity was determined using an IL 1,700 Research Radiometer and an SED sensor. The water was spiked with a mixture of atrazine (2 µg/L), ibuprofen (20 µg/L) and NDMA (2 µg/L). The H₂O₂ was added just before the start of the irradiation of a sample. The reaction was not quenched after irradiation. Samples were checked to see if the presence, over several weeks, of H₂O₂ in visible light affected the concentrations of the model compounds.

Flow through experiments

KWR reactor

The stainless steel pilot UV unit (1–5 m³/h) was equipped with four quartz sleeves perpendicular to the flow direction. The reactor was equipped with LP lamps supplied by Philips Lighting BV (Roosendaal, the Netherlands). Lamp output and water flow were monitored frequently. The lamp intensity was measured with a calibrated sensor (MUV2.4WR UV-referenzradiometer with 'SUV20.2A2Y1R/150/UVD6 (RO001)' sensor, IL Metronic Sensortechnik GmbH) placed at the reactor wall (Figure 1).

The H₂O₂ dose during all tests was 0, 5, or 10 mg/L. After sampling, reactions were quenched with 1 g/L sodium sulfite, to neutralize the residual H₂O₂.

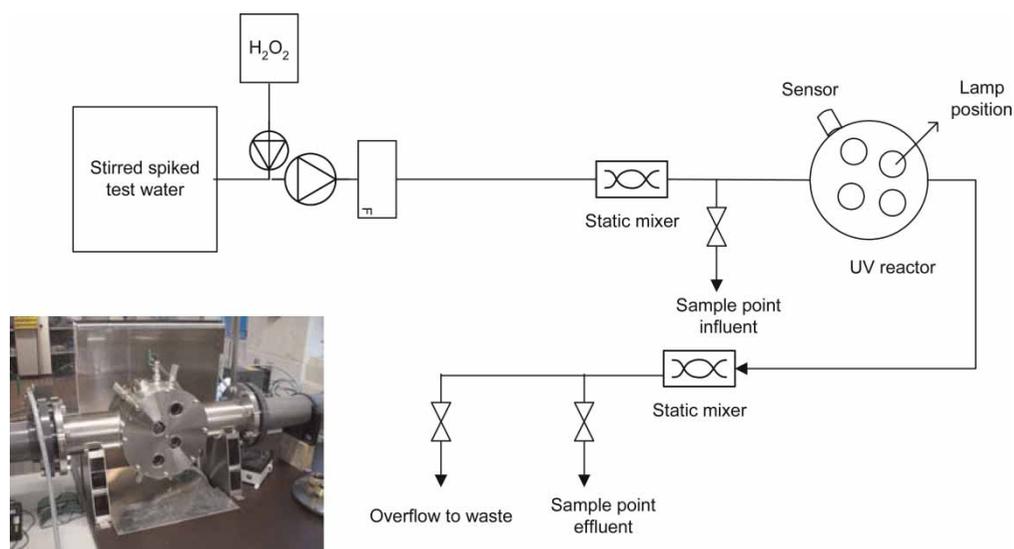


Figure 1 | Schematic depiction of the pilot reactor at KWR.

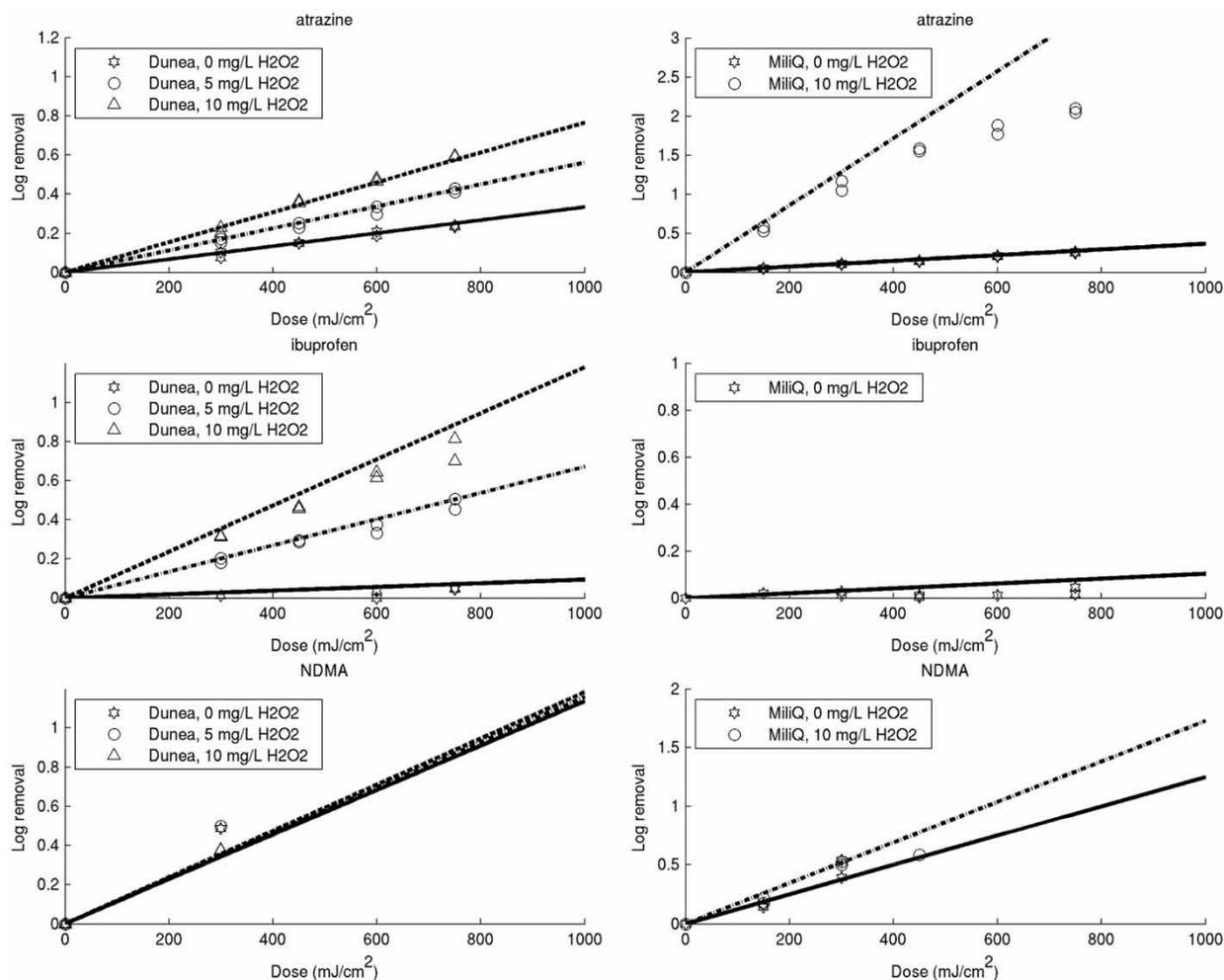


Figure 2 | Predicted (line) and actual (dots) conversion of atrazine, ibuprofen and NDMA with a LP-lamp in the CB set-up.

Dunea reactor

For pilot trials at Dunea, a commercial reactor (ITT Wedeco), including an immersed pre-calibrated UV monitor, were installed: a U-shaped reactor with four LP lamps parallel to the flow direction.

CFD modeling

The reactor geometry including inlet and outlet connections was meshed and solved for the appropriate flow. Flow trajectories were obtained (5,000 for the KWR reactor and 1,000 for the Dunea reactor) identifying both time and position inside the UV system. The Dunea LP reactor had 674,858 elements, 1,000 particles, all zero initial conditions,

boundary condition inlet velocity of 0.0786 m/s (corresponding to a flow rate of 5 m³/h) and zero pressure at the outlet.

The KWR reactor had 74,354 elements, 5,000 particles, all zero initial conditions, boundary condition inlet velocities of 0.190 m/s (corresponding to a flow rate of 2.1 m³/h) and 0.272 m/s (3 m³/h) and zero pressure at the outlet.

RESULTS AND DISCUSSION

The kinetic model describing the reduction of contaminants was evaluated in the CB set-up (equipped with an LP-lamp) for a mixture of atrazine, ibuprofen and NDMA in milli-Q water and Dunea water.

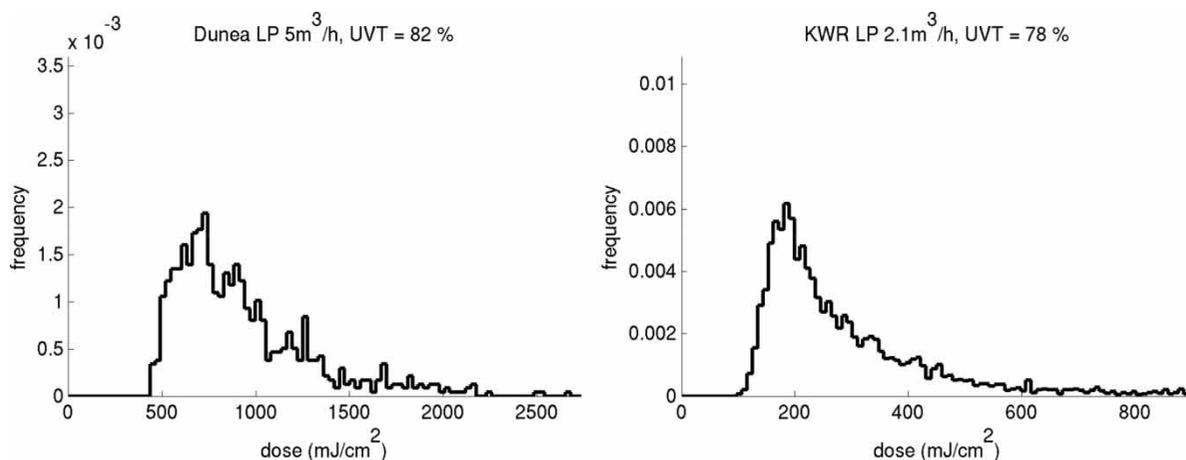


Figure 3 | LP dose distribution in the KWR pilot reactor at a flow of 2.1 m³/h, and in the Dunea reactor at a flow of 5 m³/h.

CB results obtained in milli-Q water showed that experimental data fit well with the model using the constants shown in Table 1. By means of CB measurements in Dunea water, the term k_S [S] for this water matrix was determined for atrazine. This k_S [S] should only depend on the matrix, which was confirmed by good predictions obtained with ibuprofen and NDMA in Dunea water, as is shown in Figure 2.

For ibuprofen, in milli-Q water with 10 mg H₂O₂/L the concentration quickly decreased until below the detection limit, explaining why there are no more data in this graph.

For NDMA we were only able to measure a few points, due to rapid conversion of the NDMA below the detection point. However, these measurements also show a reasonable accordance between theory and practice.

CFD calculations for the KWR pilot reactor and the Dunea pilot reactor were made. UV dose distributions were calculated. The results are shown in Figure 3.

The UV dose in the KWR reactor was varied by adjusting the flow through the reactor. At a flow of 2.1 m³/h a mean calculated dose of 306 mJ/cm² was achieved, and at 3.0 m³/h the mean dose applied was 212 mJ/cm². Experiments were carried out using Dunea water. A similar procedure was applied to the Dunea pilot reactor. The flow through this reactor was 5 m³/h, and the UV-C output was 150 W per lamp (so 600 W in total).

The dose of each trajectory was plugged into the kinetic equations, after which the average degradation of the compound was calculated (Table 3).

From these results it can be concluded that for atrazine the difference between the predicted and the measured

Table 3 | Conversion of atrazine, ibuprofen and NDMA, according to the UVPerox model and experimentally determined

Reactor	Mean dose mJ/cm ²	H ₂ O ₂ (mg/L)	Atrazine		Ibuprofen		NDMA	
			Exp. (%)	UVPerox (%)	Exp. (%)	UVPerox (%)	Exp. (%)	UVPerox (%)
KWR $T = 78\%$	306	0	21	22	0	6.2	–	–
	306	10	43	39	66	51	–	–
	212	0	14	16	0	4	–	–
	212	10	29	29	58	40	–	–
Dunea $T = 75\%$	741	0	35	44	11	14	88	80
	741	5	52	58	32	63	100	81
	741	10	64	70	54	81	84	82
Dunea $T = 82\%$	927	0	43	53	10	18	91	88
	927	5	61	69	63	73	92	88
	927	10	73	73	69	89	89	89

conversion in the KWR pilot reactor is within the experimental uncertainty. For the Dunea pilot reactor the predicted values are a little higher than the actually measured values (in contrast with the results obtained by Alpert *et al.* (2010), whose model rather underpredicted the conversion). This may be due to uncertainties in the lamp output.

The resemblance between model and actual data in general is good, not only for photolysis (0 mg H₂O₂/l) but also for the combined system of photolysis and oxidation by [•]OH radicals.

For ibuprofen in the KWR reactor the model predicts lower values than actually measured, whereas for the Dunea reactor the model predicts considerably higher values than measured. These differences can probably be attributed to uncertainties in the determination of the ibuprofen concentration.

The conversion of NDMA in the KWR reactor appeared to be quick, as a result of which the concentration immediately dropped below the lower detection limit. In the Dunea reactor we could carry out some measurements, but here too the resulting NDMA concentration quickly became very low.

CONCLUSIONS

The UVPerox model showed a rather good resemblance between predicted and experimental data for the compounds tested. It can be applied to describe and predict the performance of different pilot reactors, equipped with more than one LP lamp. Best results will be obtained when the reactor geometry and lamp characteristics are well known. Thus, this performance can be calculated as a function of the water matrix characteristics and reactor geometry. The main disadvantage for the UVPerox model is that accurate kinetic constants (reaction rate constant with hydroxyl radicals, quantum yield) are required for all compounds. These are not yet always available.

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