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Intensification of the O₃/H₂O₂ advanced oxidation process using a continuous tubular reactor filled with static mixers: proof of concept

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Abstract

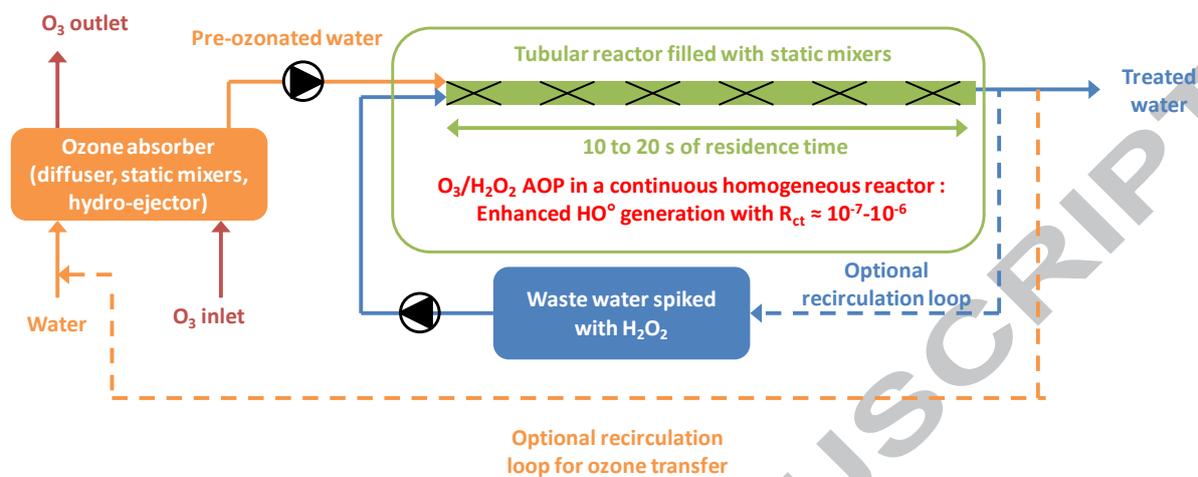
An innovative implementation of the O₃/H₂O₂ advanced oxidation process was proposed to intensify the hydroxyl radical generation. Natural or drinking waters, containing atrazine as a probe compound, were spiked with H₂O₂ and further continuously mixed to a pre-ozonated solution in a homogeneous tubular reactor filled with static mixers. Hydraulic residence times in the range 10 s - 140 s were set at different sampling ports. The experimental results confirmed a very high ozone decomposition rate, concomitant with a high hydroxyl radical exposure (R_{ct} in the range from 10⁻⁷ to 10⁻⁶), especially during the initial ozone decomposition phase (between 10 and 20 s). Equimolar initial concentrations of hydrogen peroxide and ozone were optimal to maximize the hydroxyl radical generation and to minimize their relative consumptions. The influence of the water matrix on the ozone decomposition and the hydroxyl radical generation was limited. This study is a proof of concept that using a homogeneous tubular reactor would be more effective than a gas-liquid reactor to apply the peroxone process.

Keywords

Ozone; hydrogen peroxide; peroxone; advanced oxidation process; tubular reactor; static mixers.

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Graphical abstract



1. Introduction

Several technologies can be applied for emerging contaminants removal such as nanofiltration, adsorption on activated carbon, ozonation and advanced oxidation processes [1]. Through the generation of very reactive hydroxyl radicals HO^\bullet in water, advanced oxidation processes (AOPs) appear particularly appealing [2-5]. They lead to the formation of more biodegradable and often less toxic intermediates and can be advantageously implemented upstream from biological treatments [6-8]. The peroxone AOP ($\text{O}_3/\text{H}_2\text{O}_2$) involves a radical chain mechanism based on the ozone decomposition initiated by the hydroperoxide anion HO_2^- [3, 9-12].

The literature about emerging contaminants removal by the peroxone process is particularly extensive. Except for a few studies implemented in batch homogeneous reactors [13-18], in which a controlled amount of ozone was injected at the initial time in a water spiked with H_2O_2 , these studies were implemented in gas-liquid reactors operated semi-continuously or continuously [8, 19-25]. The use of stirred batch homogeneous reactors, especially by Acero and his coworkers, was motivated by the fact that this configuration allows to control perfectly the initial amount of oxidants and to calculate the hydroxyl radical exposure, often balanced to the corresponding ozone exposure, through the R_{ct} calculation [26]. Thus, using the peroxone process, the total hydroxyl radical exposure is not necessarily higher, with R_{ct} values close to that measured in ozonation, but the hydroxyl radical formation is faster, allowing to design more compact reactors with the peroxone process [14].

Industrial applications of the peroxone process are also implemented in gas-liquid reactors which are often bubble columns. This configuration, which combines the ozone transfer and the chemical reactions in only one equipment, appears natural first since the fast ozone reaction with H_2O_2 might enhance the ozone transfer [12]. Few industrial applications, such as the HiPOx or the PRO₃Mix processes, are based on the use of intensified gas-liquid reactors like static mixers [27, 28]. A major drawback of gas-liquid reactors to apply the peroxone process is the complex control of the oxidants doses since both the ozone mass-transfer rate and the reaction rate are interdependent.

Thus, homogeneous reactors allow potentially to set easily high initial ozone concentrations, contrarily to heterogeneous systems [29]. In 2006, Buffle and his co-workers developed a continuous quench flow system to study the ozonation of natural and waste waters during the initial phase of the ozone decomposition, often called the instantaneous ozone demand (IOD) phase, which last for around 20 s [6, 30, 31]. This outstanding work emphasized that ozone reacts mainly with natural organic moieties during this initial phase, leading to a very high hydroxyl radical production. R_{ct} values (10^{-7} to 10^{-6} orders of magnitude), around two to three orders of magnitude higher than during the second phase (10^{-9} to 10^{-8} orders of magnitude), were measured in both natural and waste waters. Later, Biard and his co-workers measured even high R_{ct} values (10^{-4} order of magnitude) after only 30 ms of reaction time using the peroxone process [32]. Sunder and Hempel used a tubular reactor filled with static mixers to study the perchloroethylene and trichloroethylene oxidations [29]. A pre-ozonated demineralized water (with a flow-rate of 200 L h^{-1}) was continuously mixed to a contaminated water spiked with H_2O_2 (with a flow-rate of 20 L h^{-1}). High conversion rates (close to 100%) were obtained for a reaction time lower than one min but the potential of this configuration was not justified and assessed by comparison to the traditional design of the peroxone process.

Thus, all these observations suggest that this high and fast hydroxyl radical production during the initial phase would be advantageously used to intensify the peroxone process in a homogeneous reactor. Thus, a bench scale process was designed in this study to demonstrate the feasibility of such a process which requires to achieve separately the ozone transfer and the chemical reaction steps. Two different water matrices, a drinking water and a natural water, spiked with H_2O_2 and with atrazine as an efficient hydroxyl radical probe compound [33], were mixed to a pre-ozonated solution in a continuous homogeneous tubular reactor filled with static mixers to improve the micromixing efficiency. Such a tubular reactor was particularly convenient to control the reaction time through the hydraulic residence time in the range 10-140 s, compatible with the duration of the IOD phase. Contrarily to the design of Sunder and Hempel [29], the pre-ozonated solution flow-rate was lower

than the treated water flow-rate. Besides, the pre-ozonated solution was prepared with the same water matrix than the treated water.

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2. Material and methods

2.1. Experimental set-up description

The experimental set-up was composed of four main parts (Fig. 1). Pictures of the experimental set-up are available as supplementary material (Figs S1 and S2). The part # 1 was devoted to the ozone generation (at a concentration of nearly 120 g m^{-3} under the normal condition for temperature and pressure) and has been already described in a previous article [34]. The saturated pre-ozonated solution was prepared in the Part # 2 through a continuous bubbling in a temperature controlled gas-liquid reactor (supplied in Pyrex® by Cloup, France) equipped with a glass porous diffuser at the bottom and a mechanically agitated turbine. This reactor was filled with around 2L of the studied water matrix (but free of atrazine and/or H_2O_2) prior to each experiment. The pre-ozonated solution was continuously pumped by a centrifugal pump (Iwaki MD-30FX, Japan) to feed both a dissolved ozone analyzer (ATI Q45H/64 probe supplied by Analytical Instruments) at a flow-rate of 30 L h^{-1} (by-pass line) and the Part #4 of the process. The flow-rate of the by-pass line was measured and controlled by a float-type flow-meter Brooks Sho-Rate R6-15-B (USA).

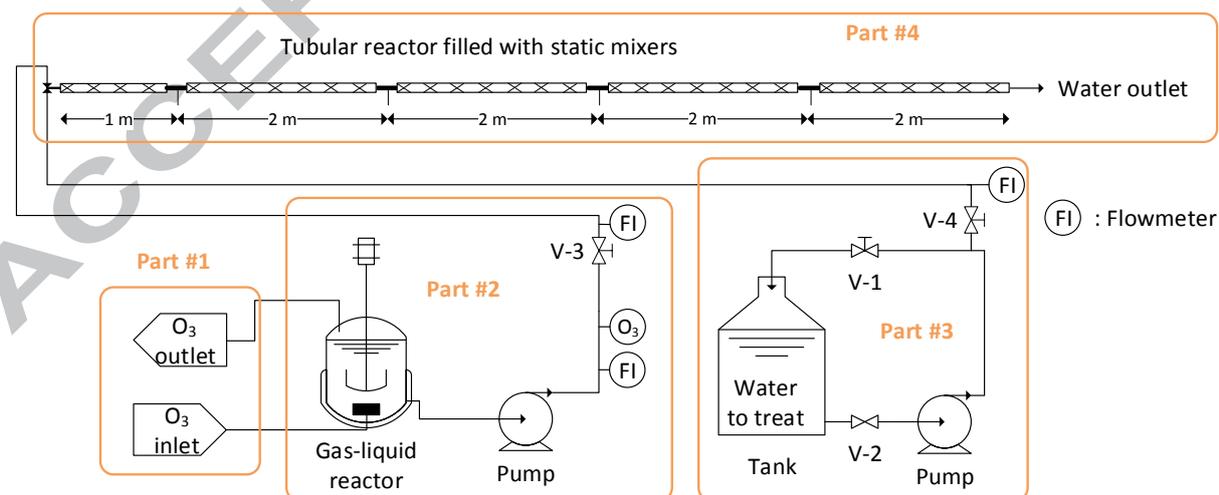


Figure 1: Process flow diagram of the experimental set-up.

The studied water was stored in a 10 L Nalgene tank and spiked with known amounts of H_2O_2 and atrazine (Part #3). H_2O_2 was added at the last time to prevent atrazine oxidation, even if it is unlikely

according to the low reaction rate between H_2O_2 and atrazine [21]. Another centrifugal pump (Iwaki MD-30FX, Japan) was used to feed continuously the Part #4.

Table 1: Summary of the operating conditions.

Variables	Operating conditions range	Regular operating conditions
$C_{HP,0}$ (ppm)	0 – 20	3.5
$C_{Oz,0}$ (ppm)	1.6 – 5	4.5-5
$C_{At,0}$ (ppm)	0 – 4	3.0-3.5
F_1 (L h^{-1})	2 – 8	6
F_2 (L h^{-1})	2 – 8	2
F_T (L h^{-1})	0 – 16	8

The pre-ozonated solution (coming from the Part #2 at a flow-rate F_2) and the solution to treat (coming from the Part #3 at a flow-rate F_1) were continuously mixed (Part #4) in a tubular reactor (6.35 mm of inner diameter) in PTFE®. F_1 and F_2 were measured and controlled by float type flow meters equipped with a valve (Brooks Sho-Rate R6-15-B, USA). The reactor was operated at steady state. The reactive medium was sampled at different hydraulic residence times owing to four sampling ports (made of stainless steel fittings provided by Legris, France) and at the tube outlet. Respectively four and seven helical static mixers of 15 cm length (Koflo, Japan) were regularly inserted in the first section (1 meter length) and in the following sections (2 m length) of the tubular reactor as schematized in Fig. 1. The residence time was deduced from the tube length and diameter, from the total liquid flow-rate ($F_T = F_1 + F_2$) and from the static mixers void fraction ($\varepsilon = 0.709$). Most experiments have been performed with an empty tube superficial velocity of 0.067 m s^{-1} ($F_T = 8 \text{ L h}^{-1}$, Table 1) corresponding to a Reynolds number of 435 (calculating with the empty tube superficial velocity). Such a low Re number is sufficient using helical static mixers to drive to a turbulent regime and a plug flow according to Fang and Lee [35]. In that case, the residence time at the different sampling points was in the range 18 – 137 s. The initial concentrations (Table 1), calculated just after the mixture, at the T-junction, were deduced from F_1 and F_2 and from the concentrations measured at the Parts #2 and #3. Usually, the relative removal efficiency of any species i (η_i) and the relative

consumptions ($\Delta C_{HP}/\Delta C_{Oz}$, $\Delta C_{HP}/\Delta C_{At}$ and $\Delta C_{Oz}/\Delta C_{At}$) were evaluated at different reaction times according to respectively Eqs. 1 and 2:

$$\eta_i = \frac{C_{i,0} - C_i}{C_{i,0}} \quad \text{Eq. 1.}$$

$$\frac{\Delta C_{HP}}{\Delta C_{Oz}} = \frac{C_{HP} - C_{HP,0}}{C_{Oz} - C_{Oz,0}}, \quad \frac{\Delta C_{Oz}}{\Delta C_{At}} = \frac{C_{Oz} - C_{Oz,0}}{C_{At} - C_{At,0}} \quad \text{and} \quad \frac{\Delta C_{HP}}{\Delta C_{At}} = \frac{C_{HP} - C_{HP,0}}{C_{At} - C_{At,0}} \quad \text{Eq. 2.}$$

C_i is the concentration of any species i (expressed in mol L^{-1}). The subscripts HP, Oz and At stand respectively for hydrogen peroxide, ozone and atrazine. The subscript 0 corresponds to the initial time t_0 .

2.2. Analytical methods

Ozone, H_2O_2 and atrazine concentrations were quantified at each sampling point and at the tubular reactor outlet. To avoid the evolution of the solute concentrations between the sampling and the analysis, all the samples were introduced gravitationally quickly in amber glass vials containing adapted amounts of quenching reagents (glycine or sodium thiosulfate as explained later). The time between the sampling and the quenching was estimated to less than 1 s. Thus, the ozone concentration was quantified by the indigo colorimetric method which provides no interaction with H_2O_2 and the atrazine [36]. A Helios UV-Vis spectrophotometer (Shimadzu, Japan) was used for the indigo absorbance measurement, performed a few minutes after the sampling. The H_2O_2 concentration was quantified by the iodometric method in which iodide is catalytically oxidized in iodine at acidic pH. An excess of glycine in powder was previously introduced in the sampling vial to selectively quench O_3 . Indeed, glycine reacts quickly with O_3 ($k = 3.4 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ at $\text{pH} = 8$ according to Pryor et al. [37]) but slowly with H_2O_2 [38], allowing the selective quantification of H_2O_2 . The H_2O_2 concentration was uninfluenced by the glycine addition. The iodine titration by sodium thiosulfate (Titrisol, Merck) was carried out a few minutes after the sampling. An excess of sodium thiosulfate in powder was used to quench the oxidants [5, 39, 40] prior to the atrazine quantification

using an ultra performance liquid chromatograph (UPLC Acquity H-Class) coupled to a tandem mass spectrometer (Quattro Premier triple quadrupole) provided by Waters Corporation (USA). The pH was measured using a pH meter 315i (WTW, Germany) and a pH probe SI Analytics (N1043A, Germany).

2.3. Waters' characteristics

Two water matrices were studied: (i) the drinking water from the city of Rennes in France (pH = 8.05, alkalinity = 1.7 mmol of $\text{HCO}_3^- \text{ L}^{-1}$, total organic carbon (TOC) = 2.39 ppm) and (ii) a raw ground water sampled in a well (pH = 7.13, alkalinity = 0.74 mmol of $\text{HCO}_3^- \text{ L}^{-1}$, total organic carbon (TOC) = 4.06 ppm). This water was filtrated between 17 and 30 μm (Filters 11788722 from Fisher Scientific, USA). These two water matrices were synthetically polluted by known amounts of atrazine, previously dissolved in a stock solution (50 ppm) in an ultrasound bath.

3. Results and discussion

3.1. Atrazine removal by ozonation

Atrazine oxidation by single ozonation (Fig. 2) has been investigated first for two different initial atrazine concentrations (≈ 3 ppm and ≈ 0.3 ppm) targeting ratios $C_{Oz,0}/C_{At,0}$ equal to 7 and 70 ($C_{Oz,0} \approx 10^{-4}$ mol L $^{-1}$). The corresponding concentration time-course plots are available as supplementary material (Fig. S4 and Fig. S6). The atrazine removal efficiency (η_{At}) increased from 17% (10%) to 68% (52%) for reaction times of respectively 18 and 137 s for $C_{At,0} = 3$ ppm (0.3 ppm). In the meantime, the ozone removal efficiency (η_{Oz}) increased from 35% (42%) to 66% (71%) for reaction times of respectively 18 and 137 s for $C_{At,0} = 3$ ppm (0.3 ppm). The better atrazine consumption at 3.0 ppm can be justified by less significant competitive effects.

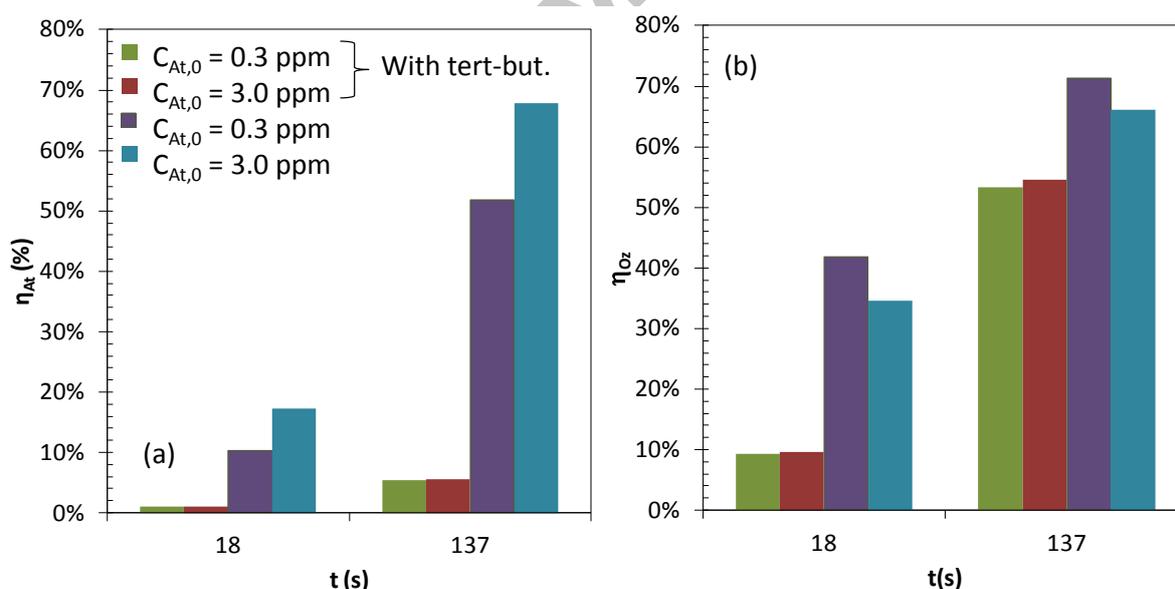


Figure 2: Evolution of η_{At} (a) and η_{Oz} (b) with the reaction time without H_2O_2 for $C_{At,0} = 0.30$ ppm and 3.0 ppm (drinking water, $C_{Oz,0} \approx 10^{-4}$ mol L $^{-1}$, $F_1 = 6$ L h $^{-1}$, $F_2 = 2$ L h $^{-1}$).

To compare the weight of the atrazine oxidation by radicals to the weight of the atrazine oxidation by molecular ozone, the same experiments have been repeated with 0.001 M of tert-butanol at the reactor inlet to quench the radical chain without interaction with molecular ozone [31]. In that case, both the atrazine and the ozone consumptions were slow down (Fig. 2), confirming undoubtedly (i)

the predominance of the atrazine oxidation by radicals and (ii) the influence of the radicals generated on the ozone consumption rate. On the one hand, η_{Oz} with tert-butanol does not depend on $C_{at,0}$ and was not significantly different than the one measured without atrazine and H_2O_2 (section 3.3, Fig. 3 (a)), showing that the ozone decomposition initiation was controlled in that case by reactions with inorganic compounds and with ubiquitous moieties of the natural organic matter, in agreement with the experimental observations of Buffle and Von Gunten (2006) during the instantaneous ozone demand (IOD) phase. It is noteworthy that the reaction of O_3 with the hydroxide anion (at a pH around 8) was too slow to contribute significantly to the ozone decomposition rate [6]. Without tert-butanol, the ozone decomposition was sped up by the reactions with radicals involved in the radical chain. On the other hand, contrarily to the results gathered without radical scavenger (tert-butanol) η_{At} does not depend on $C_{At,0}$ which was characteristics of a pseudo-first order kinetics in excess of ozone, showing that the atrazine consumption in that case was only due to the bimolecular reaction with O_3 .

To quantify the radical production, the ratio of the hydroxyl radical exposure to the ozone exposure (R_{ct}) was calculated according to Eq. 3 [33]:

$$R_{ct} = \frac{1}{k_{HO^\circ}} \left[\frac{\ln \left(\frac{C_{At}}{C_{At,0}} \right)}{\int_0^t C_{Oz} dt} - k_{O_3} \right] \quad \text{Eq. 3.}$$

With k_{HO° , the second-order reaction constant between HO° and atrazine ($3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [41]) and k_{O_3} , the second-order reaction constant between O_3 and atrazine ($6.3 \text{ L mol}^{-1} \text{ s}^{-1}$ at neutral and basic pH, [42]). The R_{ct} values were around 10^{-12} using tert-butanol and confirmed an efficient radical scavenging. Without tert-butanol, an average R_{ct} value at 137 s, equal to 5.5×10^{-8} (4.0×10^{-8}) for 3 ppm (0.3 ppm) of atrazine, consistent with the order of magnitude found in the literature [43, 44], have been measured. The R_{ct} calculated after only 18 s of reaction time had the same orders of magnitude.

Regarding the quick ozone consumption after 18 s, it stressed a fast radical generation, taking into account advantageously the first second of the IOD phase [6, 30, 31].

3.2. Ozone decomposition and H₂O₂ consumption without atrazine

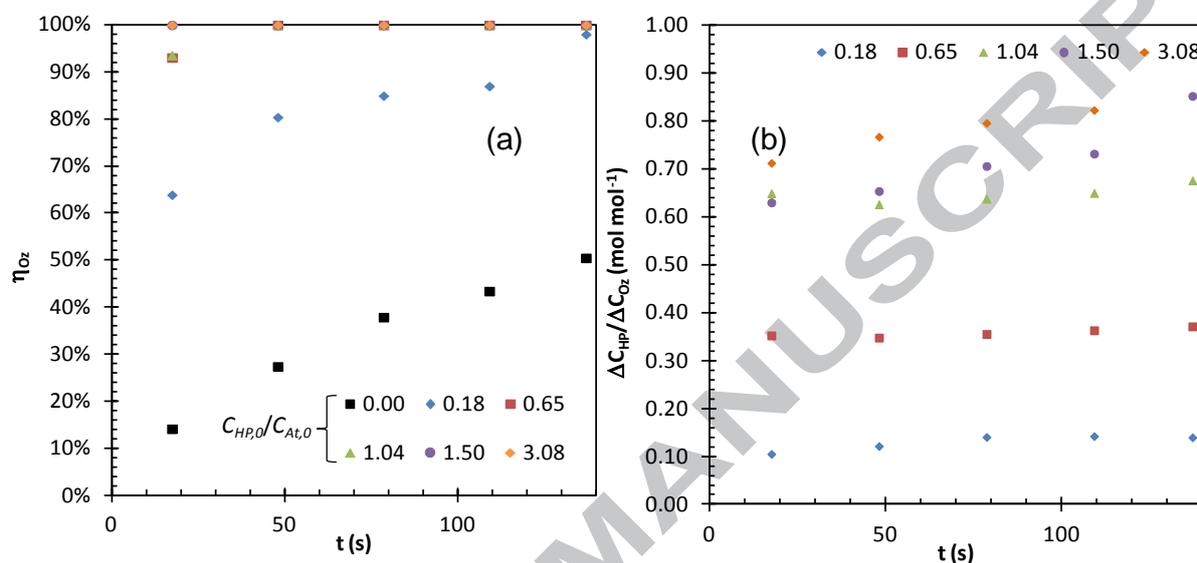


Figure 3 : Evolution of η_{O_3} (a) and of $\Delta C_{HP}/\Delta C_{O_3}$ (b) with the reaction time without atrazine for different ratios $C_{HP,0}/C_{O_3,0}$ in the range 0-3.08 (drinking water, $C_{O_3,0} \approx 10^{-4}$ mol L⁻¹, $F_1 = 6$ L h⁻¹, $F_2 = 2$ L h⁻¹).

Different initial H₂O₂ concentrations (in the range 0-9.50 ppm/0-2.79 10⁻⁴ mol L⁻¹) were applied to assess the influence of the ratio $C_{HP,0}/C_{O_3,0}$ (in the range 0-3.08 mol mol⁻¹) on the O₃ and H₂O₂ removal efficiencies without atrazine (with $C_{O_3,0} \approx 10^{-4}$ mol L⁻¹). The corresponding concentration time-course plots are presented as supplementary material (Fig. S3).

For $C_{HP,0} \leq C_{O_3,0}$, η_{O_3} increased with the reaction time and was complete after 137 s in presence of H₂O₂. For $C_{HP,0} > C_{O_3,0}$, the ozone concentration cannot be quantified even at the first sampling points (reaction time of 18 s) owing to a fast ozone decomposition rate (Fig. 3 (a)). This large ozone consumption rate cannot be attributed solely to the initiation reaction with the hydroperoxide anion and involves significant parallel reactions with radicals formed after the mixing of the two solutions, with inorganic compounds and with ubiquitous moieties of the natural organic matter [30]. The lower ozone decomposition rates involved in the study of Sunder and Hempel [29] were probably

related to a lower ozone demand induced by the higher proportion of pre-ozonated water (90% compared to 25% in this study).

Without H_2O_2 , η_{Oz} without atrazine was lower at any time than the ones measured with atrazine (whatever the atrazine concentration) according to Fig. 2 (b) and Fig. 3(a). It indicates that atrazine should play the role of a promoter of the ozone decomposition since it poorly affects the R_{ct} but enhance the ozone decomposition [43]. Nonetheless, the choice of an initial atrazine concentration of 3.0 ppm in addition of experiments at 0.3 ppm was necessary since at 0.3 ppm, atrazine could not be quantified while $C_{\text{HP},0} \geq C_{\text{Oz},0}$ (part 3.3).

In the meantime, in agreement with a corresponding fast ozone consumption, η_{HP} increased sharply before the first sampling point and was in the range 23%-60% after 18 s of reaction time (Fig. S5). Then, η_{HP} increasing was narrower after the first sampling point and the almost complete ozone disappearance. This slight increasing might be due to reactions with both residual radicals or with by-products. The literature usually supports a consumption of one mol of H_2O_2 for two mol of O_3 using the peroxone process ($\Delta C_{\text{HP}}/\Delta C_{\text{Oz}} = 0.5$) whereas the initiation reaction involved the consumption of one mol of HO_2^- for one mol of O_3 [11, 17, 45, 46]. Thus, $\Delta C_{\text{HP}}/\Delta C_{\text{Oz}}$ was most of time in the range 0.5-1 (Fig 3.b) when H_2O_2 was introduced in excess ($C_{\text{HP},0}/C_{\text{Oz},0} \geq 1$). However, for $C_{\text{HP},0}/C_{\text{Oz},0} < 1$, $\Delta C_{\text{HP}}/\Delta C_{\text{Oz}}$ was lower than 0.5. Thus, low inputs of H_2O_2 are beneficial to enhance the ozone decomposition but with a limited H_2O_2 consumption. Addition of atrazine in the part 3.3 will allow to confirm if this enhanced ozone decomposition is concomitant with an intensified radical generation.

3.3. Atrazine removal using the peroxone process

The corresponding concentration time-course plots are presented as supplementary material (Figs S4-S6). Both the ozone and H_2O_2 concentration time-courses were poorly affected by the atrazine addition compared to the reference experiments without atrazine (section 3.3) achieved with the same oxidants concentrations. However, the combination of O_3 and H_2O_2 enhanced the atrazine

oxidation with a major extent, even at low H_2O_2 inputs (Fig. 4). Indeed, the atrazine removal efficiency was in the range 80-90% (60-100%) after only 18 s at $C_{At,0} = 3.0$ ppm ($C_{At,0} = 0.3$ ppm). Except for ratios $C_{HP,0}/C_{Oz,0}$ lower than 1, the atrazine concentration did not vary significantly after the first sampling point (18 s), in agreement with a complete ozone decomposition (section 3.2), emphasizing that the tubular reactor is more beneficial during the first seconds of reaction time corresponding to the IOD phase. Besides, the H_2O_2 addition leads to R_{ct} values (10^{-7} order of magnitude), calculated between 0 and 18 s, around one order of magnitude higher than without H_2O_2 (10^{-8}) with the same operating conditions (Table 3). They were also around one or two orders of magnitude higher than in traditional ozone-based advanced oxidation processes with different water qualities such as the catalytic ozonation or the peroxone process applied in homogeneous stirred batch reactors, in which the R_{ct} was not significantly different than with the ozonation process but with a fastest ozone decomposition [14, 16, 17, 26, 33, 44, 47]. Using a homogeneous tubular reactor filled with static mixers to improve the micromixing efficiency, both the amount of HO° radicals produced and their generation rates were higher, *i.e.* more radicals were formed within a shorter time at identical initial oxidants inputs. It is noteworthy that such high R_{ct} values imply that atrazine reacted only with HO° radicals and not directly with molecular ozone [26].

On the one hand, both the R_{ct} and the ozone consumption, quantified through the ratio $\Delta C_{Oz}/\Delta C_{At}$, were poorly influenced by the initial hydrogen peroxide concentration when $C_{HP,0}/C_{Oz,0}$ was roughly higher than 1 (Table 3) for which both the atrazine and ozone consumptions were almost total. On the other hand, the hydrogen peroxide consumption, quantified through the ratio $\Delta C_{HP}/\Delta C_{At}$, tends to increase with $C_{HP,0}/C_{Oz,0}$, excepted for a local minimum obtained for a molar ratio $C_{HP,0}/C_{Oz,0}$ around 1. Therefore, to maximize the radical production and to limit the hydrogen peroxide consumption, a molar ratio $C_{HP,0}/C_{Oz}$ roughly equal to one was optimal.

The R_{ct} values obtained for a low initial atrazine concentration of 0.3 ppm (Table 3) were close to those obtained using 3.0 ppm for $C_{Oz,0}/C_{At,0}$ lower or equal to 0.67. For higher $C_{Oz,0}/C_{At,0}$ ratios,

atrazine was not detected at the sampling point and the R_{ct} was not quantified justifying the selection of both a low and a high atrazine concentrations for the assessment of the proposed process. Indeed, even if a high atrazine concentration can slightly affect the R_{ct} determination and the ozone chemistry, R_{ct} order of magnitude should be close to the one obtained at lower and more realistic atrazine concentrations. Since the ozone and hydrogen peroxide consumptions are mainly related to their self-reaction and to the radical chain, $\Delta C_{HP}/\Delta C_{At}$ and $\Delta C_{Oz}/\Delta C_{At}$ values were very high for $C_{At,0} = 0.3$ ppm.

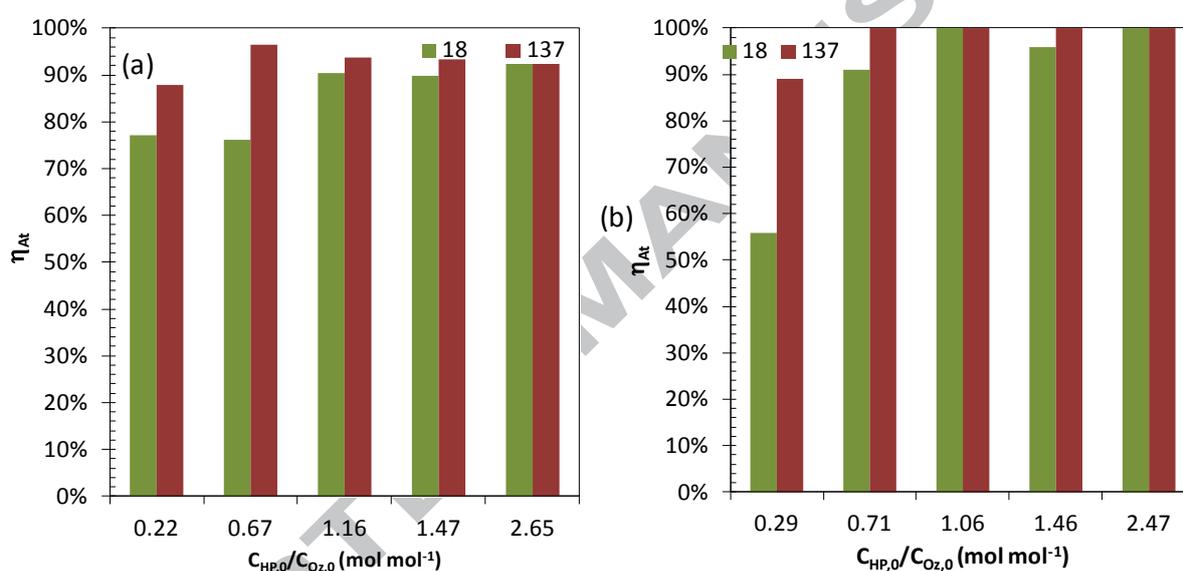


Figure 4: Evolution of η_{At} with the reaction time for various ratio $C_{HP,0}/C_{Oz,0}$ for $C_{At,0} = 3.0$ ppm (a) and 0.30 ppm (b) (drinking water, $C_{Oz,0} \approx 10^{-4}$ mol L⁻¹, $F_1 = 6$ L h⁻¹, $F_2 = 2$ L h⁻¹).

Table 3: Values of $\Delta C_{Oz}/\Delta C_{At}$, $\Delta C_{HP}/\Delta C_{At}$, $\Delta C_{HP}/\Delta C_{Oz}$ and of the R_{ct} for a reaction time of 18 s (drinking water, $C_{Oz,0} \approx 10^{-4}$ mol L⁻¹, $F_1 = 6$ L h⁻¹, $F_2 = 2$ L h⁻¹)

$C_{HP,0}/C_{Oz,0}$ (mol mol ⁻¹)	$\Delta C_{Oz}/\Delta C_{At}$ (mol mol ⁻¹)		$\Delta C_{HP}/\Delta C_{At}$ (mol mol ⁻¹)		$\Delta C_{HP}/\Delta C_{Oz}$ (mol mol ⁻¹)		$10^7 \times R_{ct}$	
$C_{At,0}$ (ppm)	3.0	0.30	3.0	0.30	3.0	0.30	3.0	0.30
0	14.0	278	-	-	-	-	0.42	0.25
0.22	4.54	90	0.93	24	0.21	0.29	2.12	2.51
0.67	6.38	62	3.69	28	0.58	0.45	7.23	8.14
1.16	7.02	68	2.37	38	0.34	0.56	9.63	UD ^a
1.47	6.85	74	6.16	50	0.90	0.67	8.74	UD
2.65	6.82	80	8.92	48	1.31	0.60	9.32	UD

^a: UD = undetermined

3.4. Influence of the initial oxidants concentration on the atrazine removal

The influence of the oxidants concentration with an optimal ratio $C_{HP,0}/C_{Oz,0}$ ratio of nearly 1 and at a constant atrazine initial concentration ($C_{At,0} = 3.0$ ppm) was assessed targeting a ratio $C_{Oz,0}/C_{At,0}$ in the range 2.25-6.79. Only the results at 18 s of reaction time are presented but the corresponding concentration time-course plots are presented as supplementary material (Fig. S7 and Fig. S8). The R_{ct} increased slightly with the ratio $C_{Oz,0}/C_{At,0}$ (Table 4), proving that atrazine does not inhibit the radical chain [43]. The R_{ct} increasing with the ratio $C_{Oz,0}/C_{At,0}$ might be justified by a lower competition between O_3 (which is a promoter) and atrazine regarding hydroxyl radicals. Thus, high initial oxidants concentrations respecting a ratio $C_{HP,0}/C_{Oz,0}$ close to one would be effective to enhance the radical production.

The atrazine degradation by HO^\bullet radicals leads to the formation of many by-products which does not allow to predict the overall reaction stoichiometry [19, 41]. However, the order of magnitude of $\Delta C_{Oz}/\Delta C_{At}$ is reasonable. For example, Acero et al. measured $\Delta C_{Oz}/\Delta C_{At}$ in the range from 8.5 (for an atrazine yield of 29%) to 25 (for a total atrazine consumption) using the peroxone process in a batch homogeneous reactor and initial concentrations close to those used in this study [41].

Table 4: Values of η_{Av} , η_{Oz} , η_{HP} , $\Delta C_{Oz}/\Delta C_{Av}$, $\Delta C_{HP}/\Delta C_{At}$ and of the R_{ct} for a reaction time of 18 s and for $C_{At,0} \approx 3.0$ ppm (drinking water, $C_{Oz,0}/C_{HP,0} \approx 1.1$, $F_1 = 6$ L h^{-1} , $F_2 = 2$ L h^{-1}).

$C_{Oz,0}/C_{At,0}$ (mol mol ⁻¹)	η_{At} (%)	η_{Oz} (%)	η_{HP} (%)	$\Delta C_{Oz}/\Delta C_{At}$ (mol mol ⁻¹)	$\Delta C_{HP}/\Delta C_{At}$ (mol mol ⁻¹)	$10^7 \times R_{ct}$
2.25	45.1	84.1	39.5	4.20	2.15	5.87
2.94	61.4	90.9	29.3	4.35	1.62	7.73
3.68	64.7	94.7	28.7	5.38	1.78	6.94
4.89	79.5	95.6	16.4	5.88	1.11	8.58
6.08	88.2	96.8	29.9	6.67	2.34	9.14
6.79	90.4	93.5	27.1	7.02	2.37	9.63

3.5. Influence of the reaction time on the atrazine oxidation

The sections 3.2 and 3.3 clearly highlighted that the process is more beneficial before the first sampling point, *i.e.* for a reaction time lower than roughly 10 to 20 seconds, corresponding to the IOD phase. To assess the influence of the reaction time at this first sampling point, the flow-rates F_1 and F_2 were adjusted to target reaction times in the range 9-35 s (F_T was in the range 4-16 L h⁻¹).

Table 5: Values of η_{At} , η_{Oz} , η_{HP} and of the R_{ct} for a reaction time of 18 s and for $C_{At,0} = 2.0$ ppm (drinking water, $F_1 = F_2$, $C_{Oz,0} \approx 6.55 \times 10^{-5}$ mol L⁻¹, $C_{HP,0} = 8.08 \times 10^{-5}$ mol L⁻¹, $C_{At,0} = 9.08 \times 10^{-6}$ mol L⁻¹).

t (s)	$F_1 = F_2$ (L h ⁻¹)	η_{At} (%)	η_{Oz} (%)	η_{HP} (%)	$10^7 \times R_{ct}$
35.2	2	82.2	99.6	38.1	4.96
23.4	3	83.3	99.5	36.6	7.69
14.1	5	83.9	94.5	41.2	12.5
11.7	6	83.5	92.4	41.2	14.5
10.0	7	83.1	89.3	42.8	16.3
8.8	8	82.8	83.8	44.3	17.5

On the one hand, η_{At} (around 83%) is not significantly affected by the reaction time whereas η_{Oz} increased with the reaction time (from 84 to more than 99%) according to the Table 5. On the other hand, η_{HP} decreased surprisingly with the reaction time (*i.e.* increased with the liquid superficial velocity and flow-rate) although the initial oxidants and atrazine concentrations were unmodified. This H₂O₂ consumption increasing with the liquid superficial velocity suggests that the micromixing efficiency might limit the overall kinetics. Indeed, even if helical static mixers are recognized for their high mixing efficiency, the micromixing time would be in the range 1-50 ms [35]. However, with comparable reaction time orders of magnitude, Biard et al. (2011), Buffle and von Gunten (2006) and Buffle et al. (2006a,b) observed significant amounts of ozone and parachlorobenzoic acid consumed, with and without hydrogen peroxide in natural, waste and drinking waters. Nonetheless, the quite low Reynolds numbers (calculated considering an empty tube), in the range 218-871, were sufficient using helical static mixers to induce a turbulent flow [35]. Thus, the almost constant atrazine yield

might be justified by the fact that the lower reaction times were counterbalanced by a more efficient radical production. Indeed, the R_{ct} increased when the reaction time decreased, in agreement with the experimental observations of Buffle et al. [31]. Using static mixers, this phenomenon might be reinforced by the micromixing efficiency improvement at higher liquid flow-rate. Thus, outstanding R_{ct} values higher than 10^{-6} were obtained.

This set of experiments confirmed the benefits of a low reaction time, using a high superficial velocity, to improve the mixing efficiency and the radical production and to limit the ozone consumption. For the development of an industrial process based on this concept, a shorter tubular reactor length and a higher superficial velocity, combined with a recirculation loop would be a feasible option to achieve a very high degradation rate in a compact process and with a limited oxidants consumption.

3.6. Influence of the water matrix

The optimal conditions of the section 3.3 ($C_{Oz,0}/C_{HP,0}$ around 1 with $C_{Oz,0} \approx 10^{-4} \text{ mol}^{-1}$, $F_1 = 6 \text{ L h}^{-1}$, $F_2 = 2 \text{ L h}^{-1}$) determined using drinking water were applied to a ground water (well water) with an initial atrazine concentration of 3.0 ppm and without atrazine. The corresponding concentration time-course plots are presented as supplementary material (Fig. S9 and Fig. S10).

Without atrazine, both the hydrogen peroxide and ozone consumptions were slowed down in the ground water compared to the drinking water (Table 6). On the one hand, the alkalinity of the ground water is nearly 2.5 times lower. Hydrogenocarbonate and carbonate anions are considered as the main radical scavengers in natural water but they also play the role of promoters in the peroxone process [48]. On the other hand, the ground water has a pH one unity lower than the drinking water. Thus, an initiation rate significantly lower is expected since the H_2O_2 conjugated base (HO_2^-) is involved as the main initiator of the ozone decomposition. Consequently, the lower O_3 and H_2O_2 consumptions for the ground water might be mainly attributed to its lower pH.

R_{ct} and η_{At} after 18 s of reaction time were respectively around two times and 16% lower using well water compared to the drinking water (Table 7). Nonetheless, even using a raw water, which has never been previously ozonated (a high ozone demand should be expected) and with a high organic content, the radical generation potential remained important. The ozone consumption was even lower. Thus, this set of experiments shows that the influence of the water matrix on the HO° generation remains limited. The pH seems to be the most influential parameter through its influence on the H_2O_2/HO_2^- balance but it should be confirmed with other water matrices, especially waste waters.

Table 6: Comparison in drinking and ground waters of the values of η_{Oz} , η_{HP} and $\Delta C_{HP}/\Delta C_{Oz}$ for reaction times of 18 s and for 137 s without atrazine ($C_{Oz,0} \approx 10^{-4} \text{ mol L}^{-1}$, $C_{Oz,0}/C_{HP,0} \approx 1.16$, $F_1 = 6 \text{ L h}^{-1}$, $F_2 = 2 \text{ L h}^{-1}$).

t (s)	Drinking water			Ground water		
	$\Delta C_{HP}/\Delta C_{Oz}$ (mol mol ⁻¹)	η_{HP} (%)	η_{Oz} (%)	$\Delta C_{HP}/\Delta C_{Oz}$ (mol mol ⁻¹)	η_{HP} (%)	η_{Oz} (%)
18	0.65	58.3	93.6	0.32	25.50	80.3
137	0.68	64.3	> 99	0.49	49.21	> 99

Table 7: Comparison in drinking and ground waters of the values of η_{At} , η_{Oz} , η_{HP} , $\Delta C_{Oz}/\Delta C_{At}$, $\Delta C_{HP}/\Delta C_{At}$ and of the R_{ct} for a reaction time of 18 s ($C_{At,0} \approx 3.0 \text{ ppm}$, $C_{Oz,0} \approx 10^{-4} \text{ mol L}^{-1}$, $C_{Oz,0}/C_{HP,0} \approx 1.16$, $F_1 = 6 \text{ L h}^{-1}$, $F_2 = 2 \text{ L h}^{-1}$).

Water nature	$\Delta C_{HP}/\Delta C_{At}$ (mol mol ⁻¹)	$\Delta C_{Oz}/\Delta C_{At}$	η_{HP} (%)	η_{Oz} (%)	η_{At} (%)	$10^7 \times R_{ct}$
Drinking water	2.37	7.02	27.13	93.52	90.38	9.02
Ground water	2.05	5.79	22.85	65.77	76.48	4.17

3.7. Discussion – comparison with a traditional gas-liquid reactor

Using a traditional semi-batch gas-liquid reactor, with a high initial hydrogen peroxide concentration of 0.025 mol L^{-1} (around $10^{-4} \text{ mol L}^{-1}$ in this study) and an atrazine concentration of $6.95 \cdot 10^{-5} \text{ mol L}^{-1}$ (corresponding to a concentration of round 15 ppm) in a synthetic water matrix, Prado et al. (1999) determined an atrazine half-life of nearly 10 min at pH 7 [21]. In this study, using a ground water with a similar pH, the atrazine half-life was lower than 10 s. Since the experimental conditions of Prado et

al. (1999) were not necessarily optimized, with a very high initial H_2O_2 concentration, the gas-liquid reactor implemented for the ozone transfer (Part #2) was used to undertake two semi-batch reference experiments with the drinking water matrix with an initial atrazine concentration of around 4 ppm. The ozone gas concentration was set at 20 g Nm^{-3} to target a dissolved ozone concentration at the equilibrium of nearly $10^{-4} \text{ mol L}^{-1}$ (such as in the part 3.3) with a flow-rate of 80 NL h^{-1} . With a low H_2O_2 initial concentration of 4 ppm corresponding to nearly $10^{-4} \text{ mol L}^{-1}$, the time necessary to obtain an atrazine removal efficiency of 90% was around 130 s and H_2O_2 was completely consumed after 140 s.

These results confirm the higher potential of a homogenous tubular reactor compared to a traditional gas-liquid reactor. Using a gas-liquid reactor, the dissolved ozone concentration was negligible as long as H_2O_2 was present in solution. It shows that the initiation reaction between O_3 and HO_2^- was fast in the liquid film surrounding the gas-liquid interface with a Hatta number higher than 5 [12]. Thus, hydroxyl radicals would be generated in the liquid film. Since, these radicals are very reactive and do not diffuse in solution, most of them should react in the liquid film to the detriment of the liquid bulk in which the pollutants concentrations is maximal. Thus, the pollutants oxidation by hydroxyl radicals might be limited by their transport from the liquid bulk to the interface. The use of a homogeneous reactor enables the generation of the radical species directly in the liquid bulk with no mass-transfer and transport limitations. Besides, the process operation would be simplified compared to a traditional gas-liquid reactor due to the fact that both the hydrogen peroxide and ozone concentrations can be controlled independently whereas the dissolved ozone and H_2O_2 concentrations in a gas-liquid contactor are interdependent.

Furthermore, a continuous tubular reactor appears more beneficial than stirred homogenous reactors used in other studies focused on the peroxone process [14-17, 49], with R_{ct} values around 1 or 2 orders of magnitude higher. Two reasons can be proposed. Firstly, a low hydraulic residence time, corresponding to the initial ozone decomposition phase in which the radical generation is

enhanced, can be set with a tubular reactor. To achieve a desired oxidation level, a recirculation loop would be advantageously implemented between the tubular reactor outlet and the treated water feed. Secondly, the use of on-line mixers with a high micromixing efficiency allows to reduce the mixing time to an order of magnitude comparable to those corresponding to the initiation reaction (section 3.5).

3.8. Prototype proposal based on this proof of concept

This process might be applied both batch wise and continuously to industrial and urban wastewater (Fig. 5). In this study, the ozone transfer, performed in a gas-liquid agitated vessel, was not optimized yet. An intensified gas-liquid contactor such as a hydro-ejector or static mixers, in which a high ozone partial pressure can be applied to reach a high dissolved ozone concentration, should be used. Furthermore, the low hydraulic residence time in this kind of contactor would allow to limit the ozone consumption during the transfer step. The make-up water used to prepare the pre-ozonated solution could be derived from the water to treat if its ozone demand is not too high, or a fraction of the wastewater plant outlet can be recirculated. To maximize the ozone transfer efficiency, a recirculation loop on the ozone flux would be beneficial. Thus, the wastewater to treat would be continuously spiked with a desired amount of H_2O_2 pumped with a metering pump from a commercial solution to respect an optimal ratio $C_{HP,0}/C_{O_2,0}$ around one. Control loops based on the ozone and H_2O_2 dissolved concentrations measurement must be implemented. Then, both the pre-ozonated solution and the treated water would be pumped in a short tubular reactor to achieve a reaction time of a few seconds. A recirculation loop would allow to control the pollution level at the process exit. The next step of the process development will be to implement a lab-scale prototype based on these observations, trying to optimize the ozone transfer, the H_2O_2 injection, the control of initial H_2O_2 and O_3 concentrations and the reaction step.

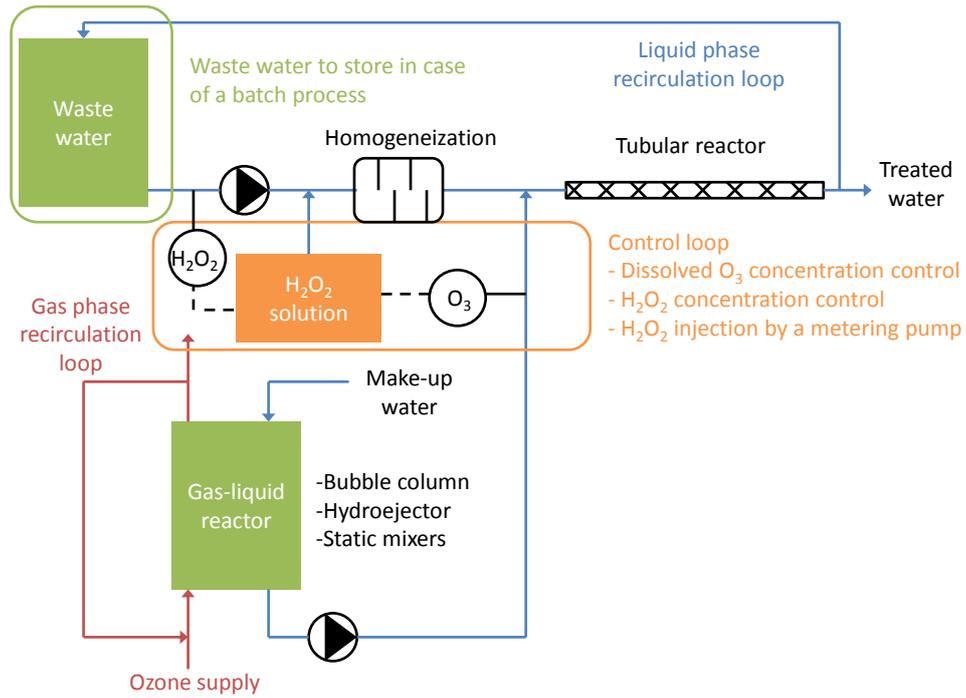


Figure 5: Industrial process proposal

5. Conclusions

The feasibility of using a homogeneous tubular reactor filled with static mixers to intensify the radical generation using the O_3/H_2O_2 advanced oxidation process was evaluated. A pre-ozonated solution was continuously mixed to the polluted water spiked with hydrogen peroxide and atrazine. The results emphasized a very high radical generation, with R_{ct} values with orders of magnitude in the range from 10^{-7} to 10^{-6} , particularly during the first tens of seconds of reaction time, concomitant with a high ozone decomposition rate corresponding to the IOD phase. An optimal ratio of the initial oxidants concentration $C_{HP,0}/C_{Oz,0}$ around one, which correspond to the stoichiometry of the initiation reaction between O_3 and HO_2^- , was optimal to enhance the radical generation and to limit the hydrogen peroxide consumption, whereas the ozone consumption was almost complete.

In addition of an intensified hydroxyl radical generation, this configuration allowed advantageously to carefully control the initial O_3 and H_2O_2 concentrations and the reaction time through the hydraulic residence time. An increasing of the liquid superficial velocity within the static mixers to increase the turbulences was beneficial to improve the micromixing efficiency, the ozone decomposition rate and the R_{ct} value. Both a drinking and a ground waters were studied. The influence of the water matrix on the ozone consumption and on the radical generation was limited but this should be confirmed with other water matrices, especially waste waters with a high ozone demand. A lab scale prototype including a recirculation loop to obtain a desired level of mineralization was proposed and will be tested in the future.

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Glossary

AOP: advanced oxidation process

C_i : concentration of any species i (in mol L⁻¹ or ppm depending on the situation)

F_1 : flow-rate of the waste water at the tubular reactor inlet (L h⁻¹)

F_2 : flow-rate of the pre-ozonated solution at the tubular reactor inlet (L h⁻¹)

F_T : total liquid flow-rate in the tubular reactor (L h⁻¹)

IOD: instantaneous ozone demand

k_i : reaction rate constant between the atrazine and a species i (L mol⁻¹ s⁻¹)

R_{ct} : ratio of the hydroxyl radical exposure to the ozone exposure

Re : Reynolds number

t : reaction time (s)

Greek letters:

η_i : removal efficiency of any species i

$\Delta C_i / \Delta C_i'$: ratio of the amount of the species i consumed over the amount of the species i' consumed at a reaction time t

Subscripts:

At: atrazine

HP: hydrogen peroxide

Oz: ozone

0: at the initial time (corresponding to the tubular reactor inlet)

ACCEPTED MANUSCRIPT

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Highlights

- A homogeneous tubular reactor was used to apply the O₃/H₂O₂ process
- Static mixers allowed to improve the micromixing efficiency within the reactor
- Outstanding R_{ct} in the range from 10⁻⁷ to 10⁻⁶ were measured
- The first seconds of the ozone decomposition phase were the most beneficial
- Equimolar initial hydrogen peroxide and ozone concentrations were optimal

