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Intensification of the O_3/H_2O_2 advanced oxidation process using a continuous tubular reactor filled with static mixers: Proof of concept

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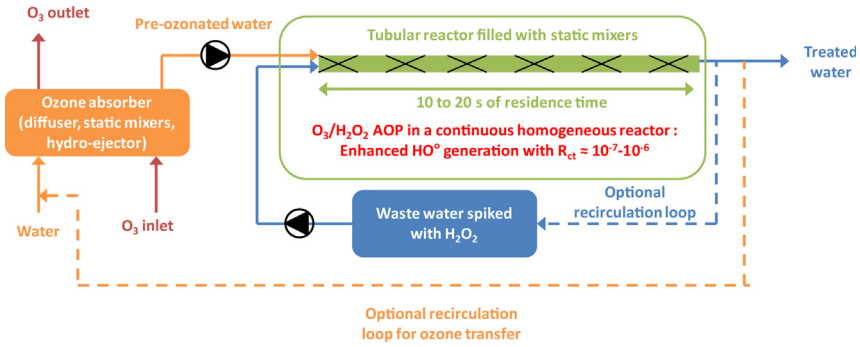
HIGHLIGHTS

- A homogeneous tubular reactor was used to apply the O_3/H_2O_2 process.
- Static mixers allowed to improve the micromixing efficiency within the reactor.
- Outstanding R_{ct} ranging 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.

GRAPHICAL ABSTRACT



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ABSTRACT

An innovative implementation of the O_3/H_2O_2 advanced oxidation process was proposed to intensify the hydroxyl radical generation. Natural or drinking waters, containing atrazine as a probe compound, were spiked with H_2O_2 and further continuously mixed to a pre-ozonated solution in a homogeneous tubular reactor filled with static mixers. Hydraulic residence times ranging from 10 to 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.

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° 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 (O_3/H_2O_2) involves a radical chain mechanism based on the ozone decomposition initiated by the hydroperoxide anion HO_2^- [3,9–12].

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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)

The literature about emerging contaminants removal by the peroxone process is particularly intensive. 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 those 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 PRO_3Mix 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 mainly reacts 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 higher 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 in comparison with 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 ranging from 10 to 140 s, compatible with the duration of the IOD phase. Contrarily to

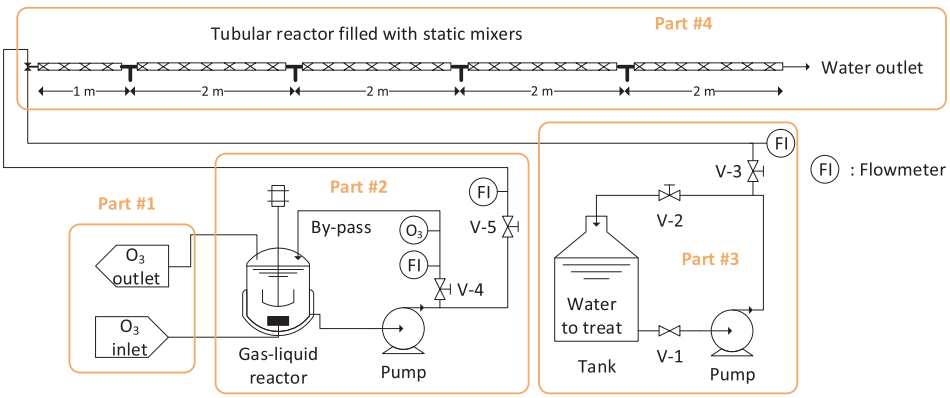

Fig. 1. Process flow diagram of the experimental set-up.