



Review

A review on photocatalytic ozonation used for the treatment of water and wastewater



Mohammad Mehrjouei*, Siegfried Müller, Detlev Möller

Working Group for Atmospheric Chemistry and Air Quality, Brandenburg Technical University (BTU Cottbus), Volmerstrasse 13, D-12489 Berlin, Germany

HIGHLIGHTS

- Photocatalytic ozonation is a powerful oxidation process for water/wastewater treatment.
- Synergistic effects are observed by combining various photocatalysts with ozone.
- Photocatalytic ozonation is often more cost-effective than ozonation and photocatalysis.
- Photocatalytic ozonation can moderate the poor mass transfer of fixed catalysts.
- Changing the operational conditions can significantly affect the oxidation efficiency.

ARTICLE INFO

Article history:

Received 30 June 2014

Received in revised form 2 October 2014

Accepted 31 October 2014

Available online 14 November 2014

Keywords:

Water and wastewater treatment

Advanced oxidation processes

Photocatalytic ozonation

Photocatalysis

Ozone

ABSTRACT

The present study aims to describe photocatalytic ozonation as a combination of two different techniques for hydroxyl radical generation; photocatalysis and ozonation, and to highlight its advantages for water and wastewater treatment compared to these two technologies. An extensive review on the mechanisms, kinetics and economic aspects of photocatalytic ozonation has been performed to explore the synergistic effects produced by applying this oxidation method to the degradation, mineralisation and detoxification of different organic pollutants in aqueous media. The influence of experimental parameters such as pollutant concentrations, ozone dose, photocatalytic load and properties, solution pH and temperature, irradiation wavelength and intensity and the effect of the presence of some substances on the efficiency of photocatalytic ozonation is discussed. Finally, plasma-induced photocatalytic systems are introduced as a new approach for handling photocatalytic ozonation treatments.

© 2014 Elsevier B.V. All rights reserved.

Contents

1. Introduction	210
2. Mechanisms of photocatalytic ozonation	210
3. Kinetics of photocatalytic ozonation	211
4. Synergy of photocatalytic ozonation	212
5. Economic aspects of photocatalytic ozonation	212
6. Reduction of toxicity by photocatalytic ozonation	213
7. Application of photocatalysts to photocatalytic ozonation reactors	213
8. Plasma-induced photocatalytic ozonation	214
9. Effects of experimental variables	214
9.1. Effect of pollutant concentration in water	214
9.2. Effect of ozone concentration	214
9.3. Effect of photocatalyst loads and properties	214
9.4. pH effect	215
9.5. Effect of irradiation wavelength and intensity	216

* Corresponding author. Tel.: +49 30 6392 5652; fax: +49 30 6392 5654.

E-mail addresses: m.mehrjouei@yahoo.com, meh@btu-lc.fta-berlin.de (M. Mehrjouei).

9.6. Temperature effect	216
9.7. Effect of the presence of other substances	216
10. Conclusions	217
References	217

1. Introduction

Since the beginning of the 1980s, there has been greater interest in water and wastewater treatment, while in the last years, development, extension and advancement of new approaches, ideas or designs which aim to solve new problems or improve existing methods in this field of science have increased. In this way, many studies have focused on enhancing the efficiency of well-known technologies or reducing costs/other disadvantages by merging them with cheaper, sustainable and more environmentally-friendly methods. The application of different technologies with the general title of advanced oxidation processes (AOPs) is one of these developments [1].

Unlike the application of decontamination technologies such as: adsorption, coagulation, flocculation, sedimentation, bio-filtration and gas stripping, which very often shift the pollution issues from water to another medium, the utilisation of AOPs leads to the decomposition and mineralisation of contaminants in water by *in situ* generation of active oxidising reagents such as hydroxyl radical ($\text{OH}\cdot$), superoxide ($\cdot\text{O}_2^-$), ozonide $\cdot\text{O}_3$, photoproducted electron-hole pairs. These oxidative species attack the existing pollutants in water and oxidise them gradually to less harmful substances.

Combinations of ozone, oxygen and, hydrogen peroxide, various homogenous and heterogeneous catalysts, as well as (photo)catalysts in light/dark conditions, have been studied by many groups worldwide. These methodologies are used for the treatment of contaminated water and wastewater to evaluate their capability in the decomposition of pollutants and to assess the treatment efficiencies of these combinations [2,3].

The use of ozone as a powerful oxidising reagent has been applied to the treatment of wastewater samples [4–7]. In addition to its high production cost, ozone has a relatively low solubility and stability in water and selectively reacts with organic compounds at acidic pH. Furthermore, ozone reacts slowly with certain organic substances such as inactivated aromatics or saturated carboxylic acids, and in many cases does not completely mineralise these organic compounds [8,9]. These disadvantages make the application of ozone alone to treat polluted water economically undesirable and is the reason why ozonation processes are sometimes modified by the addition of catalysts and/or irradiation to the oxidation medium to improve oxidation efficiency.

One of these modifications employs photoactivated semiconductors (as photocatalysts) in combination with ozone, resulting in a new advanced oxidation method called photocatalytic ozonation [10,11]. This combination, and the resulting synergistic effects, is thought to be a promising technique for the decomposition of refractory microorganisms and organic compounds in water. For example, Ye et al. [12] showed that among six different advanced oxidation processes, photocatalytic ozonation was the most efficient for complete mineralisation of 4-chloronitrobenzene. Sanchez et al. [13], Li et al. [14], Hsing et al. [15], Yildirim et al. [16], Dominguez et al. [17], Khan et al. [18] and Rajeswari and Kanmani [19] also reported similar results for the mineralisation of aniline, dibutyl phthalate, Acid Orange 6 azo, Reactive Red 194, Acid Red 88 azo, chlortetracycline and carbaryl, respectively, when photocatalytic ozonation was compared with other advanced oxidation techniques. The decomposition effects are primarily attributed to the formation of more reactive but non-selective hydroxyl radicals

in the oxidation medium, which react with almost all organic molecules at a rate of $10^6\text{--}10^9 \text{ M}^{-1} \text{ s}^{-1}$ [20].

Photocatalytic ozonation is still categorised among the more expensive treatment technologies and its use for the removal of biodegradable pollutants from water is not economically justifiable. The particular importance of this oxidation method applies to destroying poorly-biodegradable organic compounds or for improving the biological degradability of wastewater samples containing these compounds [19,21]. In general, particular groups of chemical substances such as pharmaceutical compounds [22,23], surfactants [24,25], detergents [26], colouring matters [15,17], organic herbicides and pesticides [27–29], aromatic and aliphatic organohalogens [30,31], saturated aliphatic carboxylic acids [32,33], nitroaromatics [12,34], are the primary target compounds for photocatalytic ozonation.

In summary, the present review was written to elucidate the benefits of photocatalytic ozonation as an advanced oxidation process for water and wastewater treatment by exploring the most recently published works in this field, the aim of which was to provide new ideas for more effective approaches to water and wastewater treatment. In this review, the reaction mechanisms, kinetics, synergistic effects, economic aspects, reduction of toxicity, application of photocatalysts and the influence of different experimental variables on the decomposition of various contaminants in aqueous media by means of photocatalytic ozonation have been presented and introduction of plasma-induced photocatalytic ozonation has been performed.

2. Mechanisms of photocatalytic ozonation

The presence of photocatalysts (in addition to ozone) in the oxidation medium and the adsorption of ozone and pollutants on its surface can essentially change oxidation mechanisms which indicates photocatalytic ozonation is a different process from ozonation in the absence of a photocatalyst. Principally, photocatalytic reactions commence by photoexciting the surface of photocatalyst with UV-Vis radiation, which can provide the appropriate band gap energy to generate photoactivated electron-hole pairs (R1). In parallel, ozone molecules can adsorb on the surface of the photocatalyst *via* three different interactions: physical adsorption, formation of weak hydrogen bonds with surface hydroxyl groups, and molecular or dissociative adsorption into Lewis acid sites [35], each interaction resulting in the production of active oxygen radicals ($\cdot\text{O}$) (R2). Huang and Li [36] showed these active oxygen radicals react with water molecules to produce hydroxyl radicals (R10) which play a key role in photocatalytic ozonation processes.

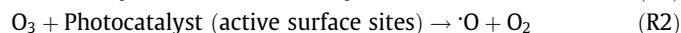
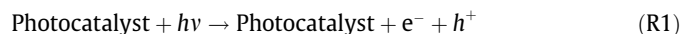
Furthermore, by employing wavelengths shorter than 300 nm, molecules of ozone and hydrogen peroxide would also absorb these wavelengths, producing active oxidising reagents (R3) and (R4) [37]. Hydrogen peroxide molecules are generated as an intermediate in ozone decomposition chain reactions (R14)–(R16). In addition, Beltran [38], Garcia-Araya et al. [39] and Mena et al. [40] described the possibility of hydrogen peroxide formation from the direct reaction of ozone with aromatic compounds, unsaturated carboxylic acids and methanol, respectively.

The photogenerated electrons on the photocatalyst surface (R1) react with adsorbed oxygen and ozone molecules as electron acceptors (R5) and (R6) [41,42], and these reactions are important

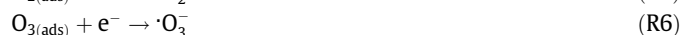
to decreasing the recombination rate of electron–hole pairs. The recombination of electrons and holes negatively affects reduction and oxidation reactions on the photocatalyst surface, quantitatively decreasing the effective interactions and consequently reducing the performance of this technology. The electron affinity of ozone (ca. 2.1 eV) is higher than that of oxygen (ca. 0.44 eV) [43] which can promote photocatalytic reactions in the presence of ozone (photocatalytic ozonation) more positively than in the presence of oxygen (simple photocatalysis). The hydrogen peroxide molecules that are generated can also react with photoexcited electrons on the photocatalyst surface, forming hydroxyl radicals (R7) [40].

The photogenerated holes (R1) are assumed to directly attack the pollutant molecules adsorbed on the photocatalyst surface (R8), or to react with water molecules (acid conditions) or more efficiently with hydroxide anions (alkaline conditions), to produce hydroxyl radicals (R9) which oxidise the pollutant molecules. Other oxidative species such as oxygen atom radicals ($\cdot\text{O}$) and superoxide and ozonide radical anions ($\cdot\text{O}_2^-$ and $\cdot\text{O}_3^-$) are presumed to be generated as reactive intermediates in the photocatalytic ozonation medium, and could potentially oxidise the contaminants directly or reform to produce hydroxyl radicals via different chain reactions (R10)–(R20). Furthermore, water pollutants such as phenols, amines and humic substances are presumed to act as initiators for ozone decomposition to ozonide radical anions ($\cdot\text{O}_3^-$) and then hydroxyl radicals, which consequently accelerate the degradation of these pollutants in water (R21) [9,44]. Hydroxyl radicals produced in the aforementioned processes attack target pollutant molecules and decompose them non-selectively to less harmful substances (R22). Three possible mechanisms are assumed for the decomposition of pollutants by hydroxyl radicals: electron transfer, radical addition and hydrogen abstraction.

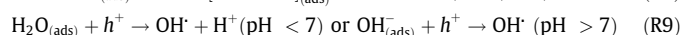
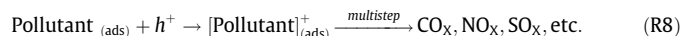
Initial reactions in the presence of photocatalyst, ozone and illumination:



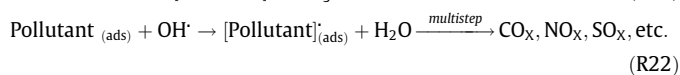
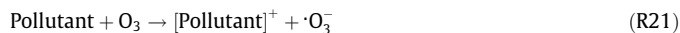
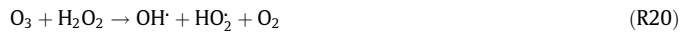
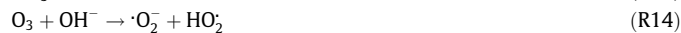
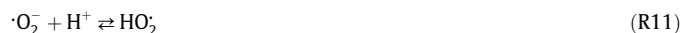
Possible reactions of photogenerated electrons (e^-) on the surface of photocatalyst:



Possible reactions of photogenerated holes (h^+) on the surface of photocatalyst:



Possible further chain reactions in the oxidation medium:



In addition to the aforementioned synergistic effects which occur during photocatalytic ozonation (compared to simple photocatalysis in presence of oxygen), Sanchez et al. [13] and Klare et al. [45] quantitatively showed that one electron must be trapped by ozone to generate a hydroxyl radical (R6), (R12) and (R13), while three electrons were necessary for the generation of one hydroxyl radical when oxygen acts as the electron acceptor (R5), (R11), (R16) and (R17).

3. Kinetics of photocatalytic ozonation

As indicated in the previous section, many partial and parallel events are involved in the photocatalytic ozonation process. First, ozone gas molecules absorb and dissolve in water, and in addition to contaminant molecules in water, they are assumed to diffuse to the surface of photocatalyst via a hypothetical diffusion layer. Ozone, water and pollutant molecules adsorb on the photoactivated surface of the photocatalyst and react with photogenerated hole–electron pairs to generate OH radicals. The OH radicals oxidise the adsorbed pollutants, and the oxidation products leave the surface of the photocatalyst by moving out of the diffusion layer.

These interfacial reactions are well described by the Langmuir–Hinshelwood (L–H) mechanism in many cases, where the oxidation rate ($-\frac{dC_p}{dt}$) of any pollutant which adsorbs on the photocatalyst is determined by its initial concentration (C_p) in water, its adsorption/desorption constant (k_{ads}) on the photocatalyst surface and its oxidation constant (k_{ox}):

$$-\frac{dC_p}{dt} = \frac{k_{\text{ox}}k_{\text{ads}}C_p}{1 + k_{\text{ads}}C_p} \quad (1)$$

However, in addition to this pathway other simultaneous oxidation reactions likely occur, such as the direct attack of ozone on pollutants in the bulk solution, and the oxidation of pollutants by hydroxyl radicals generated from pathways other than photocatalytic surface reactions (R10)–(R20). Therefore, the apparent oxidation rate could be rewritten as:

$$-\frac{dC_p}{dt} = k_{\text{O}_3}C_{\text{O}_3}C_p + k_{\text{OH}}C_{\text{OH}}C_p + \frac{k_{\text{ox}}k_{\text{ads}}C_p}{1 + k_{\text{ads}}C_p} \quad (2)$$

where C_{O_3} and C_{OH} are the ozone and hydroxyl radical concentrations in water respectively and k_{O_3} and k_{OH} are the reaction rate constants of ozone molecules and hydroxyl radicals with the pollutants in water, respectively. It must be noticed that the oxidation effects of other oxidising reagents ($\cdot\text{O}_2^-$, $\cdot\text{O}_3^-$, and H_2O_2) were generalised to the effect of hydroxyl radicals. These simultaneous processes are illustrated in Fig. 1.

Depending on the characteristics of water pollutants and their reaction rates with ozone and hydroxyl radicals or their adsorption properties on the photocatalyst, the overall oxidation rate for photocatalytic ozonation will be the output for the three sections of Eq. (2). For example, Beltran et al. [9] investigated the photocatalytic ozonation of sulfamethoxazole and diclofenac at two concentrations in water where at high concentrations, direct ozonation was the main oxidation approach (first section of Eq. (2)), and at low concentrations, hydroxyl radicals were responsible for the degradation of these pollutants (second section of Eq. (2)), though neither were adsorbed on the photocatalyst during the treatment (third section of Eq. (2)).

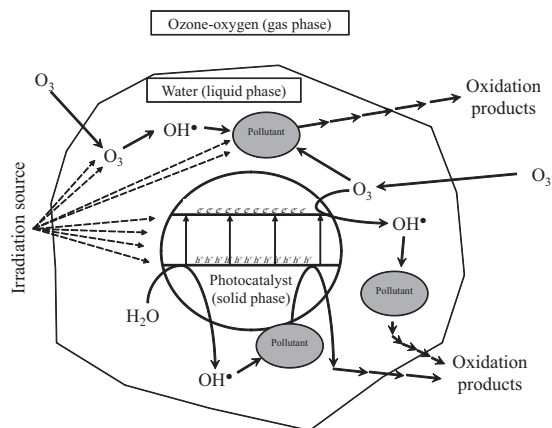


Fig. 1. Schematic diagram of the heterogeneous photocatalytic ozonation.

Most research groups report first order reaction kinetics for the degradation and mineralisation of various water pollutants by photocatalytic ozonation. Beduk et al. [46], Giri et al. [30], Cernigoj et al. [47], Villasenor et al. [48], Balcioglu et al. [49] and Dominguez et al. [17] demonstrated first order kinetics for the oxidation of organophosphorus, chlorinated pesticides, insecticides, phenol, 4-chlorobenzaldehyde and Acid Red 88 azo, respectively, while Ye et al. [12], Beltran et al. [50], Rey et al. [51] and Oyama et al. [52] reported similar kinetics for the mineralisation of 4-chloronitrobenzene, phenol, metoprolol, 2,4-dichlorophenoxyacetic acid, bisphenol-A, and other surfactants. Nevertheless, Li et al. [53] reported pseudo zero-order kinetics for the mineralisation of catechol using photocatalytic ozonation, where variation in the catechol concentration did not influence the mineralisation kinetics. Similarly, Farre et al. [28] reported zero-order kinetics for the photocatalytic ozonation of different pesticides which indicated the rate determining step was the production of OH radicals at the photocatalyst surface. Oddly, Addamo et al. [54] reported a second-order rate constant for the photocatalytic ozonation of oxalate anions at pH 10.

4. Synergy of photocatalytic ozonation

The combination of two oxidation systems, ozonation and photocatalysis, for water treatment under optimum conditions are reported to have increased oxidation efficiencies (synergy) compared to the sum oxidation efficiencies of these two oxidation

systems separately. Many studies have discussed the synergistic effects of photocatalytic ozonation on degradation and removal of different substances from aqueous solutions and the effects are reported in terms of the degradation and/or mineralisation efficiencies or oxidation rate constants of model water pollutants (Table 1).

In addition to the abovementioned synergistic effects, the results obtained by Rajeswari and Kanmani [63] for the degradation of Carbaryl (pesticide) showed the oxidation rate constant using $\text{TiO}_2/\text{UV}/\text{O}_3$ was 2.3 and 4.4 times higher than those of O_3/UV and TiO_2/UV , respectively. Similarly, a synergistic effect between oxidation processes and biological treatment was reported by Li et al. [64] by adding UVC/ TiO_2 to an ozone-BAC (biological activated carbon) oxidation system.

Anandan et al. [65] reported a 4-fold increase in the removal rate of orange II dye from water using photocatalytic ozonation in comparison to simple ozonation and Beltran et al. [8] reported a 10-fold increase in the reactivity of ozone with fluorene by combining it with the TiO_2/UVA system. Likewise, Li et al. [25] indicated that adding ozone to the $\text{In}_2\text{O}_3/\text{UVC}$ system could initiate and accelerate degradation of perfluorooctanoic acid in wastewater. Farre et al. [28] reported that combining photocatalysis with ozone increased the initial degradation rate of pesticides such as Atrazine and Alachlor by two and three times, respectively, in comparison to simple ozonation, while this combination had little effect on the degradation rate of other pesticides such as Chlorfenvinfos and Diuron. Klare et al. [45] reported that photocatalytic ozonation synergy did not occur for the degradation of nitrogen-containing organic compounds, but synergy was observed for the mineralisation of these compounds in both water and real wastewater samples. Müller et al. [66] described photocatalytic ozonation synergy for the mineralisation of 2,4-dichlorophenoxyacetic acid occurred at longer treatment times (after 240 min) when recalcitrant oxidation intermediates accumulated. On the other hand, Melian et al. [67] reported no significant effect from the presence of ozone during photocatalytic degradation of dichlorophenol in a slurry oxidation system.

5. Economic aspects of photocatalytic ozonation

Despite the efficacy of photocatalytic ozonation and its synergistic effects on the decomposition of pollutants in water, economic aspects must also be considered. Comparing photocatalysis in the presence of oxygen (which consumes electricity for UV irradiation sources) to photocatalytic ozonation (which requires additional electrical energy for ozone generation),

Table 1
Synergistic effects of photocatalytic ozonation for the treatment of different pollutants in water and wastewater.

Model pollutant or wastewater	Irradiation source	pH	Oxidation constants/degradation rates/removal or mineralisation efficiencies		
			Photocatalytic ozonation	Sum of photocatalysis and ozonation	Synergy
2-Chlorophenol [52]	Sunlight	6.8	4.7 ppm L/kj	0.71 ppm L/kj	6.6 times
2,4-Dichlorophenoxyacetic acid [30]	UVC	4.3	1.93 h^{-1}	1.28 h^{-1}	1.5 times
4-Chloronitrobenzene [45]	Visible	6.5	0.079 min^{-1}	0.051 min^{-1}	1.5 times
4-Chlorophenol [57]	UVC	Not available	70%	20%	3.5 times
Butyl-naphthalenesulfonate [24]	Sunlight	5.6	100%	29%	3.4 times
Cyanide ion [59]	UVA	11.3	$0.115 \mu\text{M/s m}^2$	$0.084 \mu\text{M/s m}^2$	1.4 times
Formic acid [62]	UVA	3.8	0.209 mg/L min	0.159 mg/L min	1.3 times
Gallic acid [60]	Vis-UVA	3.5	100%	86%	1.2 times
Methanol [40]	UVA	3	$29.1 \mu\text{M/min}$	$18.9 \mu\text{M/min}$	1.5 times
Methylene blue [61]	UVC	Not available	Not available	Not available	2.3 times
Monochloroacetic acid [43]	UVC	3.4	$33 \times 10^{-3} \text{ min}^{-1}$	$4.4 \times 10^{-3} \text{ min}^{-1}$	7.5 times
Oxalic acid [55]	UVA	3	$141 \mu\text{M/min}$	$34 \mu\text{M/min}$	4.1 times
Pharmaceutical wastewater [23]	UVA	4	80%	60%	1.3 times
Phenol [56]	UVC	Not available	52%	25%	2.1 times
p-Nitrophenol [50]	Vis-UVA	4.7	0.0321 min^{-1}	0.0067 min^{-1}	4.8 times
Reused water [58]	UVA	6.7	25.2%	18.3%	1.4 times
Winery wastewater [2]	UVC	3	83%	52%	1.6 times

at first glance, photocatalytic ozonation systems appear to be more expensive than simple photocatalysis and may not be economically justifiable. However, a better cost assessment of these oxidation techniques for water treatment could be determined by evaluating the specific energy consumption for each oxidation system, where the energy consumed during the oxidation process is apportioned to the amount of decomposed materials.

In our recently published paper on the degradation of oxalic acid and dichloroacetic acid using three different advanced oxidation processes [55], the combination of TiO_2 , UVA, and O_3 showed the highest cost-effectiveness among the oxidation methods assessed with regard to the electrical energy consumed. In the case of oxalic acid decomposition, catalytic ozonation ($\text{TiO}_2/\text{O}_3/\text{dark}$) and photocatalytic oxidation ($\text{TiO}_2/\text{O}_2/\text{UVA}$) were two and nine times more costly than photocatalytic ozonation ($\text{TiO}_2/\text{O}_3/\text{UVA}$), while for the degradation of dichloroacetic acid, catalytic ozonation and photocatalytic oxidation were two and fifteen times more expensive than photocatalytic ozonation with respect to the output. Similarly, Kopf et al. [31] have shown that specific energy consumption for the mineralisation of monochloroacetic acid using photocatalytic ozonation was $\sim 28\%$ and $\sim 5\%$ of that seen for photocatalytic oxidation and ozonation, respectively, and $\sim 9\%$ and $\sim 15\%$ (respectively) for the degradation of pyridine, which demonstrates the cost effectiveness of photocatalytic ozonation. Likewise, in terms of costs per amount of treated pollutant, Mena et al. [40] showed that photocatalytic oxidation and simple ozonation of methanol were 3.3 and 2.8 times more expensive (respectively) than photocatalytic ozonation at pH 3. Beltran et al. [68] reported similar results for a comparison of ozone-based processes in the degradation of sulphamethoxazole, where photocatalytic ozonation was the most efficient process with regards to ozone uptake. After a 60 min reaction, ozone consumption was 78, 20, 25 and 10 mg ozone per mg TOC removed for simple ozonation, ozone photolysis, catalytic ozonation and photocatalytic ozonation, respectively. However, Gilbert [69] compared 4 advanced oxidation technologies for the degradation of 4 different organic pollutants, and found that simple ozonation had the lowest energy consumption per amount of DOC eliminated.

Based upon these studies, it appears that depending on parameters such as pollutant properties, concentration of ozone and pollutant, experimental variables, reactor design, etc., photocatalytic ozonation can be more cost-effective than ozonation and photocatalysis in the oxidation of some pollutants under optimum operational conditions but this conclusion cannot be generalised for all cases.

6. Reduction of toxicity by photocatalytic ozonation

In addition to the degradation and mineralisation of various contaminants in water by photocatalytic ozonation, the process can also reduce contaminant toxicity in water and wastewater. The detoxification and disinfection effects of photocatalytic ozonation have been assessed by several research groups using various standard biotests. Ochiai et al. [70] described that shifting from simple ozonation to photocatalytic ozonation nearly doubled the removal rate constants for waterborne pathogens (evaluated by *Escherichia coli* standard kit). Beltran et al. [68] conducted acute toxicity *Daphnia* tests and reported decreasing the ecotoxicity of sulfamethoxazole solutions from 60% to 10% after a 120 min photocatalytic ozonation treatment. Arana et al. [71] used total coliform determination method and reported complete bacterial disinfection of natural wastewater by combining sunlight, TiO_2 and ozone, while separately, ozonation and irradiated TiO_2 did not prevent the growth of bacteria after treatment. As a measure of detoxification for 2,4-dichlorophenoxyacetic acid solutions, Giri et al. [30] reported a 3-fold greater dechlorination efficiency for

photocatalytic ozonation in comparison to photocatalysis in the presence of oxygen, while the synergistic effect was more clearly observed by applying low ozone concentrations [72]. Similar effects were also reported by other research groups using Daphtox-kit microbio test and Luminescence bacteria test [46], chl-*a* test [73], and *E. coli* standard kit [74].

Nevertheless, Santiago-Morales et al. [3] described that while photocatalytic ozonation of wastewater containing galaxolide and tonalide (as pollutants) presented one of the best oxidation efficiencies among all oxidation systems investigated, the detoxification effects of this oxidation method were minor. In this case, toxicity measurements initially showed a slight decrease (within the first 10 min) which then increased due to the formation and accumulation of toxic transformation products in wastewater.

7. Application of photocatalysts to photocatalytic ozonation reactors

Photocatalysts are used in photocatalytic ozonation processes in two ways. Some researchers mixed photocatalyst particles with polluted water and the suspension was subjected to the photocatalytic process [45,67]. Other research groups used photocatalyst particles immobilised on inert support materials [54,61,75].

It appears that the mass transfer properties of the oxidation system using suspended photocatalyst particles, in comparison with those of immobilised particles, could result in improved degradation efficiency for the suspension. Oyama et al. [52] reported a 50% reduction in mineralisation and dechlorination by photocatalytic ozonation of 2-chlorophenol using immobilised TiO_2 particles compared to suspended TiO_2 particles for the same experimental conditions. Despite efforts to facilitate slurry applications of photocatalysts [51], filtration and recycling of the photocatalyst from treated wastewater in suspension systems is costly, which restricts its application to laboratory experiments only. The immobilisation of photocatalysts on a stable substrate solves this problem, as well as the issue of extinction due to scattering of the UV radiation by the photocatalyst particles.

Diverse designs for immobilised photocatalysts used in photocatalytic ozonation processes have been reported [47,58,61,62,70]. Cernigoj et al. [47] reported the deposition of TiO_2 films on SiO_2 -precoated soda-lime glass slides by sol-gel process and the application of these glass slides fastened radially on a spinning basket which can rotate freely around its axis to improve the mass transfer properties of oxidation system. While Wang et al. [62] reported the utilisation of an annular flow reactor where TiO_2 film was immobilised on the inner surface of a Pyrex glass tube as reactor wall, Zou and Zhu [58] utilised TiO_2 pellets instead of plane thin films of this photocatalyst in a flow reactor to increase its contact surface area with polluted water. For the same aim, Hur et al. [61] immobilised TiO_2 on alumina balls and placed them into 4 reaction tubes inside the batch photoreactor and Ochiai et al. [70] used TiO_2 nanoparticles as modified Ti-mesh sheet for their photocatalytic investigation. But, one of the most effective designs fixed photocatalysts on the surface of plates which were utilised in a multiphase falling film reactor [76,77]. In this design, water or wastewater samples (liquid phase) flow over immobilised TiO_2 particles (solid phase) in proximity to the flow of ozone/oxygen molecules (gaseous phase) under closely-controlled conditions. These conditions provide a high wastewater volume to active photocatalyst surface ratio, which results in improved mass transfer properties of the oxidation system, a major advantage of using falling film reactors. Furthermore, the design of a falling film reactor increases the contact time between ozone molecules and polluted water, in addition to the possible reuse of ozone, which leads to increasing the efficiency of ozone consumption and decreasing ozone production costs.

8. Plasma-induced photocatalytic ozonation

One recently introduced approach to photocatalytic ozonation is the generation of electrical discharge plasma in the presence of a photocatalyst [78–80]. In this technology, the pulsed high voltage discharge is generated in aqueous media to cause various physico-chemical effects which lead finally to the formation of reactive oxidising species there. The most important advantages to the application of plasma to water and wastewater treatment are the simultaneous production of UV/Vis light and reactive reagents such as ozone, hydrogen peroxide and hydroxyl radicals in the oxidation medium in addition to other physical effects such as high electric field, pyrolysis and ultrasonic degradation. Generating plasma close to photocatalyst particles activates the surface and leads to the formation of a photocatalytic ozonation system with synergistic effects for the degradation of pollutants in water. The utilisation of these oxidation systems eliminates the need for external irradiation sources and an ozone generator, though performing electrical discharge in air or a nitrogen atmosphere primarily emits UV light in the UVA band and irradiation intensity lower than UV lamps [81]. Zhang et al. [80] indicated the combination of discharge plasma and TiO₂ favoured the formation of hydrogen peroxide over the formation of ozone, however ozone concentrations of 0.02–0.05 mg/L were produced in the aqueous solution during the plasma-induced oxidation with TiO₂. Even these low concentrations could react with the photoinduced electrons and reduce the recombination rate of the hole–electrons on the TiO₂ surface and improve oxidation efficiency.

As an example of the synergy produced by this combination, the results of Hao et al. [79] on the degradation of 4-chlorophenol in water showed that the oxidation rate constant of this contaminant during pulsed-discharge plasma and energy consumption efficiency of the oxidation system in the presence of TiO₂ were 1.8- and 2.3-fold higher than in the absence of TiO₂ particles, respectively. Similar effects were observed by Lukes et al. [78] on the degradation of phenol by a plasma-induced oxidation system combined with TiO₂, where results were attributed to the prohibitive effects of plasma-generated active species on the recombination of photogenerated electron–hole pairs.

9. Effects of experimental variables

9.1. Effect of pollutant concentration in water

The pollutant concentration in water is an important factor for determining the oxidation efficiency and the synergistic effects of photocatalytic ozonation processes. Rey et al. [51] indicated the synergistic effects of photocatalytic ozonation on the mineralisation of metoprolol were greater at a higher initial concentration of this pollutant (compared with low concentrations). The variations in the synergy parameter can also change the oxidation mechanisms in the photocatalytic ozonation medium [9]. In most reported cases, increasing the initial concentration of pollutant(s) in water led to an increased oxidation rate by photocatalytic ozonation, which was due to increased availability of pollutants for oxidative reactions with active oxidising species, either adsorbed on the photocatalyst or in the bulk solution. For example, the degradation of fuel oxygenation additives in water by photocatalytic ozonation showed that a 10-fold increase in the initial concentration of methyl *t*-butyl ether (MTBE), ethyl *t*-butyl ether (ETBE) and *t*-amyl ethyl ether (TAEE) in aqueous solution increased their degradation rate by 14, 7.5 and 6.5 times, respectively. These differing increases in initial oxidation rates were attributed to the different adsorption levels and reaction rates of these fuel additives with ozone and hydroxyl radicals [82]. Similar results were reported by Beltran

et al. [83] for the photocatalytic ozonation of sulfamethoxazole. However, Yildirim et al. [16] described an inverse effect, where a decrease in the decolourisation rate constant and an increase in the half-life of Reactive Red 194 were observed by increasing the initial concentration of this pollutant in a photocatalytic ozonation system, which was due to the enhanced scattering effect caused by the coloured molecules of Reactive Red 194 on the light absorption of TiO₂ particles.

9.2. Effect of ozone concentration

For the effective degradation of pollutant molecules using photocatalytic ozonation, ozone molecules should dissolve in the aqueous solution, diffuse and adsorb onto the surface of the photocatalyst to continue the oxidation process. Therefore, variations in ozone concentration of the oxidation medium can significantly influence many aspects of photocatalytic ozonation. For example, the results for photocatalytic ozonation of oxalate anions in alkaline solutions showed the adsorption constant value for oxalate anions increased when the ozone concentration in the liquid phase was increased [54]. This was attributed to the stabilisation of the photogenerated positive holes on the photocatalyst surface as a result of the reaction between photogenerated electrons and adsorbed ozone molecules, which led to increased adsorption of oxalate anions on the positively-charged photocatalyst surface. Likewise, Jing et al. [84] showed that for the mineralisation of dimethyl phthalate by photocatalytic ozonation, the effect of increasing ozone concentration was greater than simple ozonation or photo-ozonation, indicating a positive role for ozone adsorption and decomposition processes on the photocatalyst surface.

Other interesting results were reported by Rodriguez et al. [23] and Beltran et al. [83] indicating the photocatalytic ozonation of different pharmaceuticals (atenolol, hydrochlorothiazide, ofloxacin, trimethoprim and sulfamethoxazole) at low ozone concentrations (<10 mg/L) was primarily by hydroxyl radicals, and by increasing ozone up to a critical concentration (in this case ≈20 mg/L), the contribution of direct ozonation was more important. Li et al. [5], Cernigoj et al. [47], and Giri et al. [72] in dealing with photocatalytic ozonation systems, indicated an optimal ozone concentration must be applied to reach an optimal specific ozone consumption and for synergy between photocatalysis and ozonation to occur. The critical/optimal ozone concentration, being defined by various parameters such as chemical structure of pollutant, reactor design, pH, light specifications, must be determined for each individual photocatalytic ozonation system.

The literature reported an increase in the oxidation and/or mineralisation rates of different water pollutants by photocatalytic ozonation when the concentration of ozone in water was increased [13,26,40,53,58,73,85]. However, some research groups reported a maximum effective ozone concentration for their photocatalytic ozonation setups, where higher ozone concentrations did not increase the oxidation or mineralisation rates and efficiencies considerably [12,83], as the concentration value depended on the characteristics of pollutants and their oxidation by-products in the oxidation matrix.

9.3. Effect of photocatalyst loads and properties

Due to its chemical stability, high photocatalytic activity and low toxicity, TiO₂ is the most reported photocatalyst used for photocatalytic ozonation processes. This photocatalyst is relatively inexpensive and commercially available as Degussa P-25, BDH, PSB-P200, TP-2, Sachtleben Hombikat UV100 and Millennium TiONA PC50 [72,86,87]. Some research groups reported preparation of TiO₂ [51,62,64] and also the modification of TiO₂ particles by doping or mixing with activated carbon [5,71], metal oxides

[3,34,48,88] and noble metals [73,89] in order to improve photocatalytic properties. However, photocatalysts other than TiO_2 are also used for photocatalytic ozonation treatments [65,90].

Good adsorption and interaction between the pollutant molecule, ozone molecules and photocatalyst surface groups are required for photocatalytic ozonation. Therefore, the structure and properties of the photocatalyst play a significant role. Photocatalyst morphology and crystallinity, ratio between crystal lattice oxygen to surface oxygen atoms, presence of active surface group(s), porosity (BET surface area), are some important characteristics which can indicate the lifetime of photogenerated electron–hole pairs, light absorption properties and the adsorption capacity. Hernandez-Alonso et al. [86] compared the photoactivity of two different types of TiO_2 , Degussa P25 (80% anatase, 20% rutile) and BDH (100% anatase). Despite the lower BET surface area of BDH ($10 \text{ m}^2/\text{g}$) in relation to P25 ($50 \text{ m}^2/\text{g}$), higher oxidation and adsorption constants were reported when BDH was used as the photocatalyst for photocatalytic ozonation of cyanide ions. The higher photoactivity of BDH was attributed to the higher content and lower band gap energy of anatase, the most photoactive crystalline form of TiO_2 . Evaluating the adsorption of two different catalysts showed the amount of cyanide adsorbed increased with decreasing surface area and increasing crystal size [59]. The results of Cernigoj et al. [27] on the degradation of thiacloprid using different photocatalysts with various surface areas and photocatalytic activities showed the higher surface area of a photocatalyst increased the degree of synergy between ozonation and photocatalysis regardless of the photocatalytic activity. This was due to increased amounts of adsorbed ozone molecules on the surface and their further reactions with photogenerated electrons.

In addition to the properties of the photocatalyst, photocatalyst content in the reaction medium has also been found to be important in photocatalytic ozonation treatments. Unlike the efficiency of immobilised photocatalyst applications, that of suspended systems has been reported as being dependent on the photocatalyst load [13,16,29,83] and increasing the content of photocatalyst in the suspension up to a critical level would increase the oxidation and mineralisation rates/efficiencies. This ideal level of photocatalyst, which usually varies from 1 g/L to 2 g/L, corresponds to the optimal light absorption condition of the photocatalyst particles [2,12,45,46,52], while higher photocatalyst content reduced oxidation efficiency.

When modifying the photocatalytic activity of TiO_2 , Li et al. [14] and Arana et al. [71] reported that doping carbon black into TiO_2 enhanced steric hindrance for grain growth and made the crystallite smaller while increasing surface area and porosity of the photocatalyst, leading to increased photoactivity. Similarly, Villasenor et al. [48] reported a 3-fold increase in the BET surface area of TiO_2 by co-gelling with 10 wt.% MnO_2 . This enhancement was accompanied by increasing the anatase extent of the photocatalyst and increased surface acidity, which indicated creation of additional interfacial acidic sites. Nevertheless, this modification led to an increase in the degradation efficiency of phenol by catalytic ozonation (in the dark) but did not improve photocatalytic ozonation considerably. These results were explained by the insertion of manganese ions in the TiO_2 lattice shifting the ability of TiO_2 to produce less hole and electron pairs and consequently, hydroxyl radicals. Likewise, Tomova et al. [34] showed that doping TiO_2 with WO_3 and Au slightly decreased the BET surface area but increased the degradation rate of 2,4,6-trinitrotoluene by photocatalytic ozonation. These results were explained by the increased Bronsted and Lewis types of surface acidity for the composite and an increased degree of charge separation of electron–holes in the photoexcited composite, which increase both the adsorption capacity of photocatalyst and the life time of photogenerated electron–hole pairs. Similarly, increased Pb (II) removal efficiency was

reported by Murrini et al. [89] when Pt– TiO_2 (instead of pure TiO_2) was used as the photocatalyst for photocatalytic ozonation. However, in this case the photocatalytic removal was inhibited at the final stages due to the formation of oxidised Pt products on the surface of the photocatalyst.

Nishimoto et al. [90] compared TOC removal of phenol solutions by photocatalytic ozonation using two different photocatalysts, WO_3 and N-doped TiO_2 . Despite the fact that N- TiO_2 had a considerably higher BET surface area ($97.4 \text{ m}^2/\text{g}$) compared to WO_3 ($3.6 \text{ m}^2/\text{g}$), TOC removal was improved slightly by utilising WO_3 . Similarly, Li et al. [25] reported 8.4 times higher photocatalytic activity for In_2O_3 (compared to TiO_2) in the degradation of perfluorooctanoic acid which was attributed to better coordination of this pollutant on the surface of In_2O_3 and its reaction with photogenerated holes (compound is reported as being inert to hydroxyl radicals). Anandan et al. [65] described an increase in the degradation rate of orange II dye using a $\text{Bi}_2\text{O}_3/\text{O}_3$ /visible light system by doping Bi_2O_3 with Au, which was explained by the increased photocatalyst crystallinity, enhanced adsorption capacity of photocatalyst and decreased electron–hole recombination.

9.4. pH effect

Solution pH is another key experimental variable which can influence the performance of photocatalytic ozonation processes in three ways. (1) Increasing the pH will shift the oxidation surface reactions to an alkaline media where higher levels of hydroxide anions (OH^-) react more efficiently with photoexcited holes on the photocatalyst surface, accelerating the generation of hydroxyl radicals (R9) [91]. (2) pH variations may change the electrostatic attractive effects between the charged surface of photocatalyst and pollutant molecules. The latter can influence both the adsorption level of contaminants on the photocatalyst surface and the interfacial electron transfer. For a better characterisation, the pH of the isoelectric point (pH_{iep}) or point of zero charge (pzc) are defined for any photocatalyst as the pH level at which the surface of the photocatalyst carries neither a negative nor a positive charge. It is evident that, according to the pzc, the surface of the photocatalyst is negatively- or positively-charged under different pH conditions. As a result, the adsorption of cationic pollutants is accelerated when the surface is negatively-charged and a positively-charged photocatalyst surface has a greater tendency to attract anionic compounds. (3) The pH of aqueous solutions determines the stability of dissolved ozone molecules in water and also indicates the manner in which the ozonation process occurs. A critical pH value is defined for each chemical in the liquid phase which is expected to vary for different solutions. Below the critical pH, oxidation reactions develop via molecular ozone, while above this critical pH level, hydroxide anions (OH^-) react as initiators to accelerate ozone decomposition, yielding hydroxyl radicals (OH^\cdot) more rapidly (R14) and (R18) [92].

Garcia-Araya et al. [39] and Beltran et al. [68] indicated that performing photocatalytic ozonation at pH 7 using buffered solutions led to a decrease in the mineralisation efficiency compared to unbuffered acidic solutions. This was explained by the formation of bicarbonate ions (as oxidation by-products) which can accumulate in water at pH 7 and scavenge the hydroxyl radicals produced, reducing oxidation efficiency. At acidic conditions, mineralisation of organic pollutants results in the formation of carbon dioxide gas which escapes the solution. However, it must be mentioned that utilising photocatalytic ozonation in the treatment of unbuffered solutions frequently leads to a gradual decrease in pH due to the generation of organic and inorganic acids during oxidation.

Published studies indicated acidic pH being preferred for photocatalytic ozonation treatments due to higher oxidation and mineralisation efficiencies [2,8,13,16]. Similarly, Rajeswari and Kanmani

[19] and Cernigoi et al. [47] reported the synergistic effect of photocatalytic ozonation in the degradation of pesticides and insecticides was seen at acidic and neutral pH, but not at basic pH, due to faster ozone decomposition under alkaline conditions. Furthermore, Rodriguez et al. [23] described that while pH variations did not have significant effects on the removal rate of model pharmaceuticals from water, the greatest ozone consumption efficiency for mineralisation was observed at pH 4, suggesting the photocatalytic ozonation of these pollutants in acidic solutions would be more economically favourable.

Other research groups reported photocatalytic ozonation treatments at neutral pH values resulted in better oxidation and/or mineralisation efficiencies [12,40,66,93]. Khan et al. [18] described the degradation of chlortetracycline at pH 7 was more efficient than at pH 2 because of the higher ozone decay to $\cdot\text{OH}$ and better attraction between ionised chlortetracycline and TiO_2 particles at pH 7. While only one study [94] reported alkaline pH was optimal for photocatalytic ozonation of carbendazim, the oddest results were reported by Piera et al. [29] where TOC removal efficiency of 2,4-dichlorophenoxyacetic acid using photocatalytic ozonation was nearly independent of solution pH (pH 2–10).

To summarise, depending on the different parameters present in photocatalytic ozonation systems (chemical structure of contaminants, characteristics of utilised photocatalysts, applied ozone concentration, wastewater content and, temperature), the effect of pH on the efficiency of oxidation systems would be an output of three aforementioned aspects.

9.5. Effect of irradiation wavelength and intensity

A wide range of light wavelengths have been applied to activate the surface of photocatalysts during photocatalytic ozonation; UVC [46,86], UVB [22,68], UVA [16,40] and visible light [3,65]. Since the utilisation of light sources with wavelengths shorter than 300 nm facilitates the generation of more reactive oxidising radicals by direct irradiative decay of ozone and hydrogen peroxide (R3) and (R4) in addition to surface reactions with photoinduced electron–hole pairs, it is reasonable to conclude that moving towards shorter wavelengths should lead to an increased efficiency of the oxidation system. However, Zou and Zhu [58] reported the use of UVC irradiation instead of a UVA under the same experimental conditions did not considerably improve the decolourisation efficiency (84.3% vs. 87.2%) and TOC removal (34.3% vs. 37.3%) of a real wastewater sample. Unfortunately, this effect was not investigated for photocatalytic ozonation of other pollutants.

In terms of light intensity, results from the degradation of oxalic acid and dichloroacetic acid showed that increasing the light intensity of the irradiation source led to increased oxidation rates [55]. Similar results were reported by Wu et al. [73] for the remediation of ballast water. Zou and Zhu [58] found no significant differences in colour removal from wastewater using three different UVA light intensities (11.1, 21.1 and 32.3 W/m^2), while Rivas et al. [95] reported a higher quantum yield of photocatalytic ozonation for *n*-alkanoic acids at lower light intensities. Piera et al. [29] reported a half-order dependence between TOC removal of 2,4-dichlorophenoxyacetic acid and light intensity in a $\text{TiO}_2/\text{UVA}/\text{O}_3$ system which indicated a significant electron–hole recombination and photon energy loss in the range of light intensities investigated.

9.6. Temperature effect

Water/wastewater temperature can influence photocatalytic ozonation by promoting or hindering oxidation, where the influence of temperature on degradation efficiency for each oxidation

setup is a consequence of many co-current and/or counter-current functions. For instance, increasing temperature should lead to higher rates for chemical reactions involved in heterogeneous oxidations and moreover, should decrease the thickness of the diffusion layer around the photocatalyst providing better mass transfer conditions. On the other hand, increased temperature reduces the half-life and solubility of ozone in an aqueous solution and any shortage in the concentration of ozone will negatively affect the output of photocatalytic ozonation. Furthermore, according to the Langmuir adsorption isotherm, as the temperature increases at a constant pressure (or concentration), the adsorption rate of pollutants on the photocatalyst surface is reduced and the quantity adsorbed increases more slowly, leading to a decrease in the degradation of adsorbed contaminants.

In this respect, results from the degradation of oxalic acid by photocatalytic ozonation showed that increasing temperature from 10 °C to 55 °C increased the removal rate of oxalic acid from water, while higher temperatures up to 70 °C had a negative effect and reduced the degradation rate compared to that observed at 55 °C [33]. A similar effect was observed by Giri et al. [72] where the degradation rate constants for solutions of 2,4-dichlorophenoxyacetic acid at 10, 20 and 30 °C were 2.65, 3.35 and 2.25 h^{-1} , respectively. Decomposition of dichloroacetic acid increased from 0.294 mM/h to 0.633 mM/h as the solution temperature was increased from 10 °C to 70 °C [11].

9.7. Effect of the presence of other substances

In addition to the aforementioned experimental parameters, the presence of certain chemical substances in the oxidation medium of photocatalytic ozonation systems can either promote or inhibit the oxidation process and increase or decrease the oxidation efficiency. Beltran et al. [68] and Garcia-Araya et al. [39] described that the inhibitory influence of phosphate ions on photocatalytic ozonation of sulfamethoxazole and diclofenac in water was due to their reactions with hydroxyl radicals (as a scavenger) as well as their role in the deactivation of the photocatalyst surface. Likewise, Santiago-Morales et al. [3] reported a lower efficiency of hydroxyl radical formation during photocatalytic ozonation of wastewater (compared to that of pure water), due to the presence of bicarbonates and other radical scavengers such as phosphate and, chloride in the wastewater. However, Tong et al. [88], Oppenländer [96], and Zhang and Jian [97] indicated the high reaction rate constant of pollutant molecules with hydroxyl radicals or other oxidative radicals ($>10^9$ L/mol s) could minimise the effect of radical scavengers such as phosphate, bicarbonate or carbonate ions which usually reacted with these radicals at reaction rate constants of 10^6 – 10^7 L/mol s. Unexpectedly, Arana et al. [71] reported the presence of phosphate ions in aqueous solution stimulated photocatalytic ozonation of *p*-nitrophenol.

t-Butanol is another well-known radical scavenger and its presence in water or wastewater can negatively influence photocatalytic ozonation [83]. However, Beltran et al. [9] reported an increase in the photocatalytic ozonation rate of sulfamethoxazole and diclofenac by the addition of *t*-butanol to the oxidation medium. These effects were attributed to *t*-butanol reducing the surface tension and viscosity of the aqueous solution, increasing the ozone concentration in the film layer closest to the gas–water interface which increased the efficiency of the oxidation process. These results, and similar results reported by Villasenor et al. [48] on the degradation of phenol, indicated the oxidation of these pollutants occurred by direct ozonation rather than by interaction with free radicals. However, Villasenor et al. [48] also reported the presence of *t*-butanol increased the concentration of degrada-

tion intermediates, which demonstrated the role of radicals in the degradation of oxidation intermediates. Another inhibiting effect was reported by Beltran et al. [83] for iodide ions, due to their scavenging reactions with photogenerated holes.

In terms of stimulatory substances, Rodriguez et al. [93] reported higher mineralisation efficiencies and reaction rates for the degradation of a pharmaceuticals mixture after the addition of Fe^{3+} to $\text{TiO}_2/\text{UVA}/\text{O}_3$. These results were explained by the initiation of a photo Fenton process and its synergy with existing oxidation processes in the oxidation medium. Similar effects for Fe^{2+} on the degradation of *t*-butanol as a model water pollutant were recently reported [85].

10. Conclusions

- As far as the oxidation and mineralisation of recalcitrant organic contaminants in water and wastewater are concerned, the combination of ozone, appropriate photocatalyst(s), optimum design and optimised conditions will lead to higher degradation, removal rates and efficiencies compared to using ozonation and photocatalysis separately. The synergistic effects of this combination have been observed in many cases and are primarily attributed to the intensive generation of highly oxidative and non-selective reagents (such as hydroxyl radicals) in the oxidation medium of photocatalytic ozonation.
- The high mineralisation rates of nearly all model pollutants in water by photocatalytic ozonation, and the simplicity of this process, make it an excellent alternative to other oxidation treatment methods.
- In addition to choosing a suitable photocatalyst, a proper irradiation source and an optimum ozone concentration for photocatalytic ozonation treatments, developing new operative designs for oxidation reactors, where these factors are combined and utilised together, is important. An effective reactor design could considerably stimulate the synergistic effects and benefits of photocatalytic ozonation systems.
- Much like other successful technologies, in order to move this treatment method from the lab to commercial utilisation, more attention should be focused on the immobilisation of photocatalyst particles onto inert substrates, as slurry applications of photocatalytic ozonation are not economically justifiable, due to the additional high costs of photocatalyst filtration after treatment. Fortunately, photocatalytic ozonation can moderate the relatively poor mass transfer properties of immobilised photocatalysts in photocatalytic treatments.
- In most reported cases, increasing the concentration of pollutant(s) and ozone led to an increased oxidation rate by photocatalytic ozonation. However, an optimal ozone concentration must be applied to reach an optimal specific ozone consumption and for synergy between photocatalysis and ozonation to occur.
- The structure, properties and concentration of applied photocatalyst play a significant role in the oxidation efficiency of photocatalytic ozonation. Using shorter wavelengths and increasing the light intensity of the irradiation source usually led to increased oxidation rates. However, employing photocatalysts able to absorb natural sunlight and moving towards visible wavelengths can significantly reduce cost.
- Most published studies indicated acidic pH being preferred for photocatalytic ozonation treatments due to higher oxidation and mineralisation efficiencies.
- The presence of chemical substances in the oxidation medium of photocatalytic ozonation systems can either promote or inhibit the oxidation process.

References

- [1] W. Glaze, J.W. Kang, D.H. Chapin, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, *Ozone Sci. Eng.* 9 (1987) 335–352.
- [2] O. Gimeno, F.J. Rivas, F.J. Beltran, M. Carbajo, Photocatalytic ozonation of winery wastewaters, *J. Agric. Food Chem.* 55 (2007) 9944–9950.
- [3] J. Santiago-Morales, M.J. Gomez, S. Herrera, A.R. Fernandez-Alba, E. Garcia-Calvo, R. Rosal, Oxidative and photochemical processes for the removal of galaxolide and tonalide from wastewater, *Water Res.* 46 (2012) 4435–4447.
- [4] M. Mehrjouei, S. Müller, K. Sekiguchi, D. Möller, Decolorization of wastewater produced in a pyrolysis process by ozone: enhancing the performance of ozonation, *Ozone Sci. Eng.* 32 (2010) 349–354.
- [5] L. Li, P. Zhang, W. Zhu, W. Han, Z. Zhang, Comparison of O_3 -BAC, UV/O_3 -BAC and $\text{TiO}_2/\text{UV}/\text{O}_3$ -BAC processes for removing organic pollutants in secondary effluents, *J. Photochem. Photobiol. A* 171 (2005) 145–151.
- [6] S. Preis, S. Kamenev, J. Kallas, R. Munter, Advanced oxidation processes against phenolic compounds in wastewater treatment, *Ozone Sci. Eng.* 17 (1995) 399–418.
- [7] D. Wu, Z. Yang, W. Wang, G. Tian, S. Xu, A. Sims, Ozonation as an advanced oxidant in treatment of bamboo industry wastewater, *Chemosphere* 88 (2012) 1108–1113.
- [8] F.J. Beltran, F.J. Rivas, O. Gimeno, M. Carbajo, Photocatalytic enhanced oxidation of fluorene in water with ozone: comparison with other chemical oxidation methods, *Ind. Eng. Chem. Res.* 44 (2005) 3419–3425.
- [9] F.J. Beltran, A. Aguinaco, A. Rey, J.F. Garcia-Araya, Kinetic studies on black light photocatalytic ozonation of diclofenac and sulfamethoxazole in water, *Ind. Eng. Chem. Res.* 51 (2012) 4533–4544.
- [10] T.E. Agustina, H.M. Ang, V.K. Vareek, A review of synergistic effect of photocatalysis and ozonation on wastewater treatment, *J. Photochem. Photobiol. C* 6 (2005) 264–273.
- [11] M. Mehrjouei, S. Müller, D. Möller, Synergistic effect of the combination of immobilized TiO_2 , UVA and ozone on the decomposition of dichloroacetic acid, *J. Environ. Sci. Health A* 47 (2012) 1073–1081.
- [12] M. Ye, Z. Chen, X. Liu, Y. Ben, J. Shen, Ozone enhanced activity of aqueous titanium dioxide suspensions for photodegradation of 4-chloronitrobenzene, *J. Hazard. Mater.* 167 (2009) 1021–1027.
- [13] L. Sanchez, J. Peral, X. Domenech, Aniline degradation by combined photocatalysis and ozonation, *Appl. Catal. B* 19 (1998) 59–65.
- [14] L. Li, W. Zhu, L. Chen, P. Zhang, Z. Chen, Photocatalytic ozonation of dibutyl phthalate over TiO_2 film, *J. Photochem. Photobiol. A* 175 (2005) 172–177.
- [15] H.J. Hsing, P.C. Chiang, E.E. Chang, M.Y. Chen, The decolorization and mineralization of Acid Orange 6 azo dye in aqueous solution by advanced oxidation processes: a comparative study, *J. Hazard. Mater.* 141 (2007) 8–16.
- [16] A.Ö. Yildirim, S. Gül, O. Eren, E. Kusvuran, A comparative study of ozonation, homogenous catalytic ozonation and photocatalytic ozonation for C.I. Reactive Red 194 azo dye degradation, *Clean: Soil, Air, Water* 39 (2011) 795–805.
- [17] J.R. Dominguez, J. Beltran, O. Rodriguez, Vis and UV photocatalytic detoxification methods (using TiO_2 , $\text{TiO}_2/\text{H}_2\text{O}_2$, TiO_2/O_3 , $\text{TiO}_2/\text{S}_2\text{O}_8^{2-}$, O_3 , H_2O_2 , $\text{S}_2\text{O}_8^{2-}$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{C}_2\text{O}_4^{2-}$) for dyes treatment, *Catal. Today* 101 (2005) 389–395.
- [18] M.H. Khan, H.S. Jung, W. Lee, J.Y. Yung, Chlortetracycline degradation by photocatalytic ozonation in the aqueous phase: mineralization and the effects on biodegradability, *Environ. Technol.* 34 (2012) 495–502.
- [19] R. Rajeswari, S. Kanmani, A study on synergistic effect of photocatalytic ozonation for carbaryl degradation, *Desalination* 242 (2009) 277–285.
- [20] R. Andreozzi, V. Caprio, A. Insola, R. Marrota, Advanced oxidation processes (AOP) for water purification and recovery, *Catal. Today* 53 (1999) 51–59.
- [21] E.A. Emam, Effect of ozonation combined with heterogeneous catalysts and ultraviolet radiation on recycling of gas-station wastewater, *Egypt. J. Petrol.* 21 (2012) 55–60.
- [22] F.J. Rivas, F.J. Beltran, A. Encinas, Removal of emergent contaminants: integration of ozone and photocatalysis, *J. Environ. Manage.* 100 (2012) 10–15.
- [23] E.M. Rodriguez, G. Marquez, E.A. Leon, P.M. Alvarez, A.M. Amat, F.J. Beltran, Mechanism considerations for photocatalytic oxidation, ozonation and photocatalytic ozonation of some pharmaceutical compounds in water, *J. Environ. Manage.* 127 (2013) 114–124.
- [24] T. Oyama, T. Otsu, Y. Hindano, T. Koike, N. Serpone, H. Hidaka, Remediation of simulated aquatic sites contaminated with recalcitrant substrates by TiO_2 /ozonation under natural sunlight, *Appl. Catal. B* 91 (2009) 242–246.
- [25] X. Li, P. Zhang, L. Jin, T. Shao, Z. Li, J. Cao, Efficient photocatalytic decomposition of perfluorooctanoic acid by indium oxide and its mechanism, *Environ. Sci. Technol.* 46 (2012) 5528–5534.
- [26] K. Krapfenbauer, N. Getoff, Comparative studies of photo- and radiation-induced degradation of aqueous EDTA. Synergistic effects of oxygen, ozone and TiO_2 (acronym: CoPhoRaDe/EDTA), *Radiat. Phys. Chem.* 55 (1999) 385–393.
- [27] U. Cernigoi, U.L. Stangar, J. Jirkovskv, Effect of dissolved ozone or ferric ions on photodegradation of thiacloprid in presence of different TiO_2 catalysts, *J. Hazard. Mater.* 177 (2010) 399–406.
- [28] M.J. Farre, M.I. Franch, S. Malato, J.A. Ayllon, J. Peral, X. Domenech, Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation, *Chemosphere* 58 (2005) 1127–1133.

- [29] E. Piera, J.C. Caple, E. Brillas, X. Domenech, J. Peral, 2,4-Dichlorophenoxyacetic acid degradation by catalyzed ozonation: $\text{TiO}_2/\text{UVA}/\text{O}_3$ and $\text{Fe(II)}/\text{UVA}/\text{O}_3$ systems, *Appl. Catal. B* 27 (2000) 169–177.
- [30] R.R. Giri, H. Ozaki, R. Takanami, S. Taniguchi, Heterogeneous photocatalytic ozonation of 2,4-D in dilute aqueous solution with TiO_2 fiber, *Water Sci. Technol.* 58 (2008) 207–216.
- [31] P. Kopf, E. Gilbert, S.H. Eberle, TiO_2 photocatalytic oxidation of monochloroacetic acid and pyridine: influence of ozone, *J. Photochem. Photobiol. A* 136 (2000) 163–168.
- [32] I. Ilisz, A. Bokros, A. Dombi, TiO_2 -based heterogeneous photocatalytic water treatment combined with ozonation, *Ozone Sci. Eng.* 26 (2004) 585–594.
- [33] M. Mehrjouei, S. Müller, D. Möller, Degradation of oxalic acid in a photocatalytic ozonation system by means of Pilkington Active™ glass, *J. Photochem. Photobiol. A* 217 (2011) 417–424.
- [34] D. Tomova, V. Iliev, S. Rakovsky, M. Anachkov, A. Eliyas, G. Li Puma, Photocatalytic oxidation of 2,4,6-trinitrotoluene in the presence of ozone under irradiation with UV and visible light, *J. Photochem. Photobiol. A* 231 (2012) 1–8.
- [35] K.M. Bulanin, J.C. Lavalley, A.A. Tsyganenko, IR spectra of adsorbed ozone, *Colloids Surf. A* 101 (1995) 153–158.
- [36] H. Huang, W. Li, Destruction of toluene by ozone-enhanced photocatalysis: performance and mechanism, *Appl. Catal. B* 102 (2001) 449–453.
- [37] M.D. Gurol, A. Akata, Kinetics of ozone photolysis in aqueous solution, *AIChE J.* 42 (1996) 3283–3292.
- [38] F.J. Beltran, *Ozone Reaction Kinetics for Water and Wastewater Systems*, Lewis Publishers, Boca Raton, Florida, 2004.
- [39] J.F. Garcia-Araya, F.J. Beltran, A. Aguinaco, Diclofenac removal from water by ozone and photolytic TiO_2 catalyzed processes, *J. Chem. Technol. Biotechnol.* 85 (2010) 798–804.
- [40] E. Mena, A. Rey, B. Acedo, F.J. Beltran, S. Malato, On ozone-photocatalysis synergism in black-light induced reactions: oxidizing species production in photocatalytic ozonation versus heterogeneous photocatalysis, *Chem. Eng. J.* 204–206 (2012) 131–140.
- [41] V. Augugliaro, M. Litter, L. Palmisano, J. Soria, The combination of heterogeneous photocatalysis with chemical and physical operations: a tool for improving the photoprocess performance, *J. Photochem. Photobiol. C* 7 (2006) 127–144.
- [42] F.J. Rivas, F.J. Beltran, O. Gimeno, M. Carbajo, Fluorene oxidation by coupling of ozone, radiation, and semiconductors: a mathematical approach to the kinetics, *Ind. Eng. Chem. Res.* 45 (2006) 166–174.
- [43] P. Pichat, L. Cermentati, A. Albini, D. Mas, H. Delprat, C. Guillard, Degradation processes of organic compounds over UV-irradiated TiO_2 . Effect of ozone, *Res. Chem. Intermed.* 26 (2000) 161–170.
- [44] M.M. Sein, M. Zedda, J. Tuerk, T.C. Schmidt, A. Golloch, C. von Sonntag, Oxidation of diclofenac with ozone in aqueous solution, *Environ. Sci. Technol.* 42 (2008) 6656–6662.
- [45] M. Klare, G. Waldner, R. Bauer, H. Jacobs, J.A.C. Broekaert, Degradation of nitrogen containing organic compounds by combined photocatalysis and ozonation, *Chemosphere* 38 (1999) 2013–2027.
- [46] F. Beduk, M.E. Aydin, S. Ozkan, Degradation of malathion and parathion by ozonation, photolytic ozonation and heterogeneous catalytic ozonation processes, *Clean: Soil, Air, Water* 40 (2012) 179–187.
- [47] U. Cernigoi, U.L. Stangar, P. Trebbe, Degradation of neonicotinoid insecticides by different advanced oxidation processes and studying the effect of ozone on TiO_2 photocatalysis, *Appl. Catal. B* 75 (2007) 229–238.
- [48] J. Villaseñor, P. Reyes, G. Pecchi, Catalytic and photocatalytic ozonation of phenol on MnO_2 supported catalysts, *Catal. Today* 76 (2002) 121–131.
- [49] I.A. Balcioğlu, N. Getoff, M. Bekbölet, A comparative study for the synergistic effect of ozone on the g-irradiated and photocatalytic reaction of 4-chlorobenzaldehyde, *J. Photochem. Photobiol. A* 135 (2000) 229–233.
- [50] F.J. Beltran, F.J. Rivas, O. Gimeno, Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water, *J. Chem. Technol. Biotechnol.* 80 (2005) 973–984.
- [51] A. Rey, D.H. Quinones, P.M. Alvarez, F.J. Beltran, P.K. Plucinski, Simulated solar-light assisted photocatalytic ozonation of metoprolol over titania-coated magnetic activated carbon, *Appl. Catal. B* 111–112 (2012) 246–253.
- [52] T. Oyama, T. Otsu, Y. Hindano, T. Koike, N. Serpone, H. Hidaka, Enhanced remediation of simulated wastewaters contaminated with 2-chlorophenol and other aquatic pollutants by TiO_2 -photoassisted ozonation in a sunlight-driven pilot-plant scale photoreactor, *Sol. Energy* 85 (2011) 938–944.
- [53] L. Li, W. Zhu, P. Zhang, Z. Chen, W. Han, Photocatalytic oxidation and ozonation of catechol over carbon-black-modified nano- TiO_2 thin films supported on Al sheet, *Water Res.* 37 (2003) 3646–3651.
- [54] M. Addamo, V. Augugliaro, E. Garcia-Lopez, V. Loddo, G. Marci, L. Palmisano, Oxidation of oxalate ion in aqueous suspensions of TiO_2 by photocatalysis and ozonation, *Catal. Today* 107–108 (2005) 612–618.
- [55] M. Mehrjouei, S. Müller, D. Möller, Energy consumption of three different advanced oxidation methods for water treatment: a cost-effectiveness study, *J. Cleaner Prod.* 65 (2014) 178–183.
- [56] T. Ochiai, H. Nanba, T. Nakagawa, K. Masuko, K. Nakata, T. Murakami, R. Nakano, M. Hara, Y. Koide, T. Suzuki, M. Ikekita, Y. Morito, A. Fujishima, Development of an O_3 -assisted photocatalytic water-purification unit by using a TiO_2 modified titanium mesh filter, *Catal. Sci. Technol.* 2 (2012) 76–78.
- [57] S. Ardizzone, G. Cappelletti, D. Meroni, F. Spadavecchia, Tailored TiO_2 layers for the photocatalytic ozonation of cumylphenol, a refractory pollutant exerting hormonal activity, *Chem. Commun.* 47 (2011) 2640–2642.
- [58] L. Zou, B. Zhu, The synergistic effect of ozonation and photocatalysis on color removal from reused water, *J. Photochem. Photobiol. A* 196 (2008) 24–32.
- [59] M.D. Hernandez-Alonso, J.M. Coronado, J. Soria, J.C. Conesa, V. Loddo, M. Addamo, V. Augugliaro, EPR and kinetic investigation of free cyanide oxidation by photocatalysis and ozonation, *Res. Chem. Intermed.* 33 (2007) 205–224.
- [60] F.J. Beltran, O. Gimeno, F.J. Rivas, M. Carbajo, Photocatalytic ozonation of gallic acid in water, *J. Chem. Technol. Biotechnol.* 81 (2006) 1787–1796.
- [61] J.S. Hur, S.O. Oh, K.M. Lim, J.S. Jung, J.W. Kim, Y.J. Koh, Novel effects of TiO_2 photocatalytic ozonation on control of postharvest fungal spoilage of kiwifruit, *Postharvest Biol. Technol.* 35 (2005) 109–113.
- [62] S. Wang, F. Shiraiishi, K. Nakano, A synergistic effect of photocatalysis and ozonation on decomposition of formic acid in an aqueous solution, *Chem. Eng. J.* 87 (2002) 261–271.
- [63] R. Rajeswari, S. Kanmani, Degradation of pesticide by photocatalytic ozonation process and study of synergistic effect by comparison with photocatalysis and UV/ozonation processes, *J. Adv. Oxid. Technol.* 12 (2009) 208–214.
- [64] L. Li, W. Zhu, P. Zhang, Q. Zhang, Z. Zhang, $\text{TiO}_2/\text{UV}/\text{O}_3$ -BAC processes for removing refractory and hazardous pollutants in raw water, *J. Hazard. Mater.* B128 (2006) 145–149.
- [65] S. Anandan, G.L. Lee, P.K. Chen, C. Fan, J.J. Wu, Removal of orange II dye in water by visible light assisted photocatalytic ozonation using Bi_2O_3 and $\text{Au}/\text{Bi}_2\text{O}_3$ nanorods, *Ind. Eng. Chem. Res.* 49 (2010) 9729–9737.
- [66] T. Müller, Z. Sun, M.P.G. Kumar, K. Itoh, M. Murabayashi, The combination of photocatalysis and ozonolysis as a new approach for cleaning 2,4-dichlorophenoxyacetic acid polluted water, *Chemosphere* 36 (1998) 2043–2055.
- [67] E.P. Melian, O.G. Diaz, J.M.D. Rodriguez, J. Arana, J.P. Pena, Adsorption and photocatalytic degradation of 2,4-dichlorophenol in TiO_2 suspensions; effect of hydrogen peroxide, sodium peroxodisulphate and ozone, *Appl. Catal. A* 455 (2013) 227–233.
- [68] F.J. Beltran, A. Aguinaco, J.F. Garcia-Araya, A. Oropesa, Ozone and photocatalytic processes to remove the antibiotic sulfamethoxazole from water, *Water Res.* 42 (2008) 3799–3808.
- [69] E. Gilbert, Influence of ozone on the photocatalytic oxidation of organic compounds, *Ozone Sci. Eng.* 24 (2002) 75–82.
- [70] T. Ochiai, K. Masuko, S. Tago, R. Nakano, Y. Niitsu, G. Kobayashi, K. Horio, K. Nakata, T. Murakami, M. Hara, Y. Nojima, M. Kurano, I. Serizawa, T. Suzuki, M. Ikekita, Y. Morito, A. Fujishima, Development of a hybrid environmental purification unit by using of excimer VUV lamps with TiO_2 coated titanium mesh filter, *Chem. Eng. J.* 218 (2013) 327–332.
- [71] J. Arana, J.A. Herrera Melian, J.M. Dona Rodriguez, O. Gonzalez Diaz, A. Viera, J. Perez Pena, P.M. Marrero Sosa, V. Espino Jimenez, TiO_2 -photocatalysis as a tertiary treatment of naturally treated wastewater, *Catal. Today* 76 (2002) 279–289.
- [72] R.R. Giri, H. Ozaki, T. Ishida, R. Takanami, S. Taniguchi, Synergy of ozonation and photocatalysis to mineralize low concentration 2,4-dichlorophenoxyacetic acid in aqueous solution, *Chemosphere* 66 (2007) 1610–1617.
- [73] D. Wu, H. You, R. Zhang, C. Chen, D.J. Lee, Inactivation of *Amphidinium* sp. in ballast waters using UV/Ag- TiO_2 + O_3 advanced oxidation treatment, *Bioresour. Technol.* 102 (2011) 9838–9842.
- [74] S. Gomes de Moraes, R.S. Freire, N. Duran, Degradation and toxicity reduction of textile effluent by combined photocatalytic and ozonation processes, *Chemosphere* 40 (2000) 369–373.
- [75] H. Wada, T. Murayama, Y. Kuroda, Recycling of cyanide wastewater applying combined UV-ozone oxidation with a titanium dioxide catalyst and ion exchange resin method, *Bull. Chem. Soc. Jpn.* 75 (2002) 1399–1405.
- [76] M. Mehrjouei, S. Müller, D. Möller, Design and characterization of a multi-phase annular falling-film reactor for water treatment, *J. Environ. Manage.* 120 (2013) 68–74.
- [77] M. Mehrjouei, S. Müller, D. Möller, Decomposition kinetics of MTBE, ETBE and, TAE in water and wastewater using catalytic and photocatalytic ozonation, *J. Mol. Catal. A* 386 (2014) 61–68.
- [78] P. Lukes, M. Clupek, P. Sunka, F. Peterka, T. Sano, N. Negishi, S. Matsuzawa, K. Takeuchi, Degradation of phenol by underwater pulsed corona discharge in combination with TiO_2 photocatalysis, *Res. Chem. Intermed.* 31 (2005) 285–294.
- [79] X.L. Hao, M.H. Zhou, L.C. Lei, Non-thermal plasma-induced photocatalytic degradation of 4-chlorophenol in water, *J. Hazard. Mater.* 141 (2007) 475–482.
- [80] Y. Zhang, J. Lu, X. Wang, Q. Xin, Y. Cong, Q. Wang, C. Li, Phenol degradation by TiO_2 photocatalysts combined with different pulsed discharge systems, *J. Colloid Interface Sci.* 409 (2013) 104–111.
- [81] Y.S. Mok, J.O. Jo, J.C. Whitehead, Degradation of an azo dye Orange II using a gas phase dielectric barrier discharge reactor submerged in water, *Chem. Eng. J.* 142 (2008) 56–64.
- [82] M. Mehrjouei, S. Müller, D. Möller, Removal of fuel oxygenates from water using advanced oxidation technologies by means of falling film reactor, *J. Chem. Eng.* 211–212 (2012) 353–359.
- [83] F.J. Beltran, A. Aguinaco, J.F. Garcia-Araya, Mechanism and kinetics of sulfamethoxazole photocatalytic ozonation in water, *Water Res.* 43 (2009) 1359–1369.
- [84] Y. Jing, L. Li, Q. Zhang, P. Lu, P. Liu, X. Lu, Photocatalytic ozonation of dimethyl phthalate with TiO_2 prepared by a hydrothermal method, *J. Hazard. Mater.* 189 (2011) 40–47.
- [85] M. Mehrjouei, S. Müller, D. Möller, Catalytic and photocatalytic ozonation of tert-butyl alcohol in water by means of falling film reactor: kinetic and cost-effectiveness study, *J. Chem. Eng.* 248 (2014) 184–190.

- [86] M.D. Hernandez-Alonso, J.M. Coronado, A.J. Maira, J. Soria, V. Loddo, V. Augugliaro, Ozone enhanced activity of aqueous titanium dioxide suspensions for photocatalytic oxidation of free cyanide ions, *Appl. Catal. B* 39 (2002) 257–267.
- [87] K. Tanaka, K. Abe, T. Hisanaga, Photocatalytic water treatment on immobilized TiO₂ combined with ozonation, *J. Photochem. Photobiol. A* 101 (1996) 85–87.
- [88] S.P. Tong, D.M. Xie, H. Wei, W.P. Liu, Degradation of sulfosalicylic acid by O₃/UV O₃/TiO₂/UV, and O₃/V-O/TiO₂: a comparative study, *Ozone Sci. Eng.* 27 (2005) 233–238.
- [89] L. Murruni, G. Leyva, M. Litter, Photocatalytic removal of Pb (II) over TiO₂ and Pt–TiO₂ powders, *Catal. Today* 129 (2007) 127–135.
- [90] S. Nishimoto, T. Mano, Y. Kameshima, M. Miyake, Photocatalytic water treatment over WO₃ under visible light irradiation combined with ozonation, *Chem. Phys. Lett.* 500 (2010) 86–89.
- [91] W. Chu, W.K. Choy, T.Y. So, The effect of solution pH and peroxide in the TiO₂-induced photocatalysis of chlorinated aniline, *J. Hazard. Mater.* 141 (2007) 86–91.
- [92] F.J. Beltran, J.F. Garcia-Araya, B. Acedo, Advanced oxidation of atrazine in water. I. Ozonation, *Water Res.* 28 (1994) 2153–2164.
- [93] E.M. Rodriguez, G. Fernandez, P.M. Alvarez, F.J. Beltran, TiO₂ and Fe (III) photocatalytic ozonation processes of a mixture of emergent contaminants of water, *Water Res.* 46 (2012) 152–166.
- [94] R. Rajeswari, S. Kanmani, Comparative study on photocatalytic oxidation and photolytic ozonation for the degradation of pesticide wastewaters, *Desalin. Water Treat.* 19 (2010) 301–306.
- [95] L. Rivas, I.R. Bellobono, F. Ascari, Photomineralization of n-alkanoic acids in aqueous solution by photocatalytic membranes: influence of radiation power, *Chemosphere* 37 (1998) 1033–1044.
- [96] T. Oppenländer, *Photochemical Purification of Water and Air*, Wiley VCH, Weinheim, 2003.
- [97] P. Zhang, L. Jian, Ozone-enhanced photocatalytic degradation of natural organic matter in water, *Water Sci. Technol.* 6 (2006) 53–61.