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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.

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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.

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* 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).

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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 ($OH^{\cdot}$), superoxide ($\cdot O_2^-$), ozonide $\cdot O_3^-$, photoproduced 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–$10^9\ M^{-1}\ s^{-1}$ [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 ($\cdot O$) (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