Review

Organic pollutants removal in wastewater by heterogeneous photocatalytic ozonation

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HIGHLIGHTS

- Current catalysts in photocatalytic ozonation are dissected.
- Strategies for fabricating novel TiO\(_2\)-based photocatalysts are summarized.
- The operation parameters in photocatalytic ozonation are reviewed.
- Reaction mechanism and generation paths of hydroxyl radicals are discussed.
- Future developing trends are proposed for photocatalytic ozonation.

GRAPHICAL ABSTRACT

Organics oxidation mechanism and the generation pathways of hydroxyl radicals in heterogeneous photocatalytic ozonation.

ABSTRACT

Heterogeneous photocatalysis and ozonation are robust advanced oxidation processes for eliminating organic contaminants in wastewater. The combination of these two methods is carried out in order to enhance the overall mineralization of refractory organics. An apparent synergism between heterogeneous photocatalysis and ozonation has been demonstrated in many literatures, which gives rise to an improvement of total organic carbon removal. The present overview dissects the heterogeneous catalysts and the influences of different operational parameters, followed by the discussion on the kinetics, mechanism, economic feasibility and future trends of this integrated technology. The enhanced oxidation rate mainly results from a large amount of hydroxyl radicals generated from a synergistically induced decomposition of dissolved ozone, besides superoxide ion radicals and the photo-induced holes. Six reaction pathways possibly exist for the generation of hydroxyl radicals in the reaction mechanism of heterogeneous photocatalytic ozonation.

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1. Introduction

Industrial activity releases about 300–400 million tons of heavy metals, solvents, toxic sludge and other waste into the global waters each year, posing a great threat to human beings (Palaniappan et al., 2010). Owing to an increasing concern about the refractory organics in wastewater, water quality control and regulations against hazardous pollutants have become more and more stringent in many countries (Pera-Titus et al., 2004). Moreover, new recalcitrant organic pollutants are continuously emerging and discharged into environment (Thomas, 2002), and some burgeoning organics have been found in drinking water (Benotti et al., 2009). As a result, the development of new eco-friendly methods to obliterate these contaminants becomes an imperative task.

Advanced oxidation processes (AOPs), arising in 1970s, are highly competitive technologies for the destruction of a wide range of recalcitrant organic pollutants resistant to conventional approaches. They successfully function in the advanced treatment of low concentrated effluents, and can also be used as pretreatment to enhance the biodegradability of wastewater. Organic contaminants are mainly decomposed by hydroxyl radicals (HO\(^{\cdot}\)) in the AOPs, a highly reactive agent that non-selectively destroy almost all organics in water (Staehelin and Hoigné, 1982; Glaze and Kang, 1989; Oyama, 2000; Kasprzyk-Hordern et al., 2003; Pera-Titus et al., 2004; Wang and Xu, 2012). The in situ generation of HO\(^{\cdot}\) can be facilitated by using luminous, chemical and other forms of energy (Augugliaro et al., 2006). To enhance the overall performance, various AOPs are combined in the wastewater treatment, which usually cause interesting synergies (Augugliaro et al., 2006; Shemer et al., 2006; Huang et al., 2008; Oller et al., 2011; Wei et al., 2011; Zeng et al., 2013).

Heterogeneous photocatalysis and ozonation have proved to be efficient tools for eliminating organic contaminants in wastewater (Gaya and Abdullah, 2008; Nawrocki and Kasprzyk-Hordern, 2010). Photocatalysis has shown to be adequate for the destruction of a wide variety of compounds, but the mineralization is slowly attained due to its low oxidation rate and the process is advantageous only for very dilute solutions (Hoffmann et al., 1995; Augugliaro et al., 2006). Ozone is a robust oxidizing agent (\(E^{\circ} = 2.08\) eV) compared with other agents, such as \(H_2O_2\) (\(E^{\circ} = 1.78\) eV), and can react with several classes of organic compounds through direct or indirect reactions (Oyama, 2000; Zhao et al., 2008, 2009; Cao et al., 2014; Xing et al., 2014a; Huang et al., 2015). Ozonation is more powerful than photocatalysis in organics degradation and more ascendant in treating highly concentrated samples (Agustina et al., 2005; Augugliaro et al., 2006). However, the main drawback of these routes is that they lead to a very limited mineralization of organic pollutants, therefore it is necessary to modified the approach when the complete removal of the compounds and their degradation intermediates is required. To further enhance the mineralization, a combination of heterogeneous photocatalysis with ozone is expected to decompose organic substances more quickly and thoroughly, as shown in Fig. 1. This combination has revealed dramatically synergistic effect that can increase the treating efficiency and shorten the reaction time, as well as the overall costs (Kopf et al., 2000; Wang et al., 2002b; Augugliaro et al., 2006; Wang and Xu, 2012). Consequently, the simultaneous application of heterogeneous photocatalysis and ozonation has great potential in pollutant abatement and wastewater treatment.

Though homogeneous photocatalytic ozonation can also enhance the efficiency in reducing chemical oxidation demand (COD), biochemical oxidation demand (BOD) and total kjeldahl nitrogen (TKN) in effluents (Kern et al., 2013), metal ions would also stay in the solution and thereby giving rise to a second pollution. An additional removal of homogeneous catalyst is then required, which makes the process more complex and expensive. Hence, only heterogeneous photocatalytic ozonation will be discussed in this paper, which is more promising and robust as a new water treatment technology.

In the last decade, photocatalytic ozonation has drawn accelerated attention since its first appearance. The citation in the related area keeps constant growing, as elucidated in Fig. 2. However, to the best of our knowledge, very few reviews on this issue were devoted over all journals, except for the only one published in 2005 (Agustina et al., 2005). The scope of the present paper is to comprehensively address the heterogeneous photocatalytic ozonation of wastewater based on the recently published work. Table 1 summarizes the target pollutants, light sources, catalysts, reaction intermediates, reaction dynamics and main results in these papers. On this basis, the authors shed light on the heterogeneous catalysts and the influences of various operational parameters, further with intensive investigation on the kinetics, reaction mechanism and...
economic feasibility of photocatalytic ozonation. Finally the future perspectives in this rapidly developing field are presented.

2. Catalyst

For heterogeneous catalytic ozonation, the most extensively used catalysts typically include transition metal oxides (MnO2, TiO2, Al2O3, FeOOH, and CeO2), metals (Cu, Ru, Pt and Co) on supports (SiO2, Al2O3, TiO2, CeO2 and activated carbon), zeolites modified with metals, activated carbon, modified activated carbon and natural minerals (Nawrocki and Kasprzyk-Hordern, 2010). In terms of catalysts applied in photocatalytic ozonation, photocatalytic activity functions dominantly in boosting the overall catalytic efficiency compared with ozonation activity. Theoretically, photocatalysts, the photo-reactive materials, have great potential in converting photon energy into chemical energy to decompose organic contaminants, which all can be practically utilized in photocatalytic ozonation.

2.1. Photocatalysts

Heterogeneous photocatalysis uses semiconductor materials to convert photon energy into chemical energy to destroy organic pollutants. The fundamental mechanism are well established and briefly summarized as the following procedures. Semiconductor particles absorb photon of energy equal to or greater than its band gap and electrons get excited from the valence band (VB) to the conduction band (CB), thus leaving electron deficiencies or holes in the VB. This contributes to the generation of electron-hole pairs to transfer into the particle surface, in turn to trigger a series of oxidation/reduction reactions of the adsorbed substrates. In aqueous solution, the dissolved oxygen can scavenge the surface electrons generating superoxide ion (O2−) or hydroperoxyl radicals (HO2•):

\[
e^- + O_2 \rightarrow O_2^-
\]

\[
O_2^- + H^+ \rightarrow HO_2
\]

The formed HO2 can lead to the formation of H2O2 and HO•:

\[
HO_2^- + e^- \rightarrow HO_2
\]

\[
HO_2 + H^+ \rightarrow H_2O \rightarrow 2HO^-
\]

Through this way, the recombination of electron-hole recombination gets effectively inhibited and the lifetime of positive holes is prolonged. The generated radicals (mainly including HO• and O2−)
Table 1
Summary of organic pollutants removal by heterogeneous photocatalytic ozonation.

<table>
<thead>
<tr>
<th>Target pollutant</th>
<th>Light source</th>
<th>Catalyst</th>
<th>Intermediates</th>
<th>Reaction order</th>
<th>Measurement index</th>
<th>Main results</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td><strong>Pharmaceutical compounds</strong></td>
<td></td>
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<tr>
<td>Diclofenac</td>
<td>UVA/a high pressure mercury lamp</td>
<td>Degussa P25</td>
<td>Oxalic acid, maleic acid, malonic acid, formic acid, acetic acid</td>
<td>A first order kinetics</td>
<td>[Substrate]_l, [Intermediates]_l, TOC, [H,O,O], [O], [O], ozone consumption, ecotoxicity</td>
<td>Photocatalytic ozonation showed the lowest ozone consumption and ecotoxicity compared to the other ozonation systems tested</td>
<td>Aguinaco et al. (2012)</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>UVA/a high pressure mercury lamp</td>
<td>Degussa P25</td>
<td>Maleic acid, fumaric acid, oxalic acid, formic acid, malonic acid</td>
<td></td>
<td></td>
<td>A kinetic model for aqueous diclofenac photocatalytic ozonation was proposed and experimentally tested</td>
<td>Beltrán et al. (2010)</td>
</tr>
<tr>
<td>Diclofenac and Sulfamethoxazole (SMX)</td>
<td>UVA/four 15 W black light lamps</td>
<td>Degussa P25</td>
<td></td>
<td></td>
<td></td>
<td>Calculated results indicated the synergic effect of ozone and photocatalytic oxidation</td>
<td>Beltrán et al. (2012)</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>Solar light/ a 1500 W air cooled xenon arc lamp</td>
<td>Titania coated magnetic activated carbon (TiFeC)</td>
<td></td>
<td>A pseudo-first order kinetics</td>
<td>[Substrate]_l, iron and titanium cations leached l, TOC, [H,O,O], [O], ozone consumed</td>
<td>Complete metoprolol removal and more than 60% TOC conversion were achieved after 3 h</td>
<td>Rey et al. (2012)</td>
</tr>
<tr>
<td>Atenolol, hydrochlorothiazide, oxoflacin, and trimethoprin</td>
<td>UVA/a 15 W black light lamp</td>
<td>Degussa P25</td>
<td></td>
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<td></td>
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<tr>
<td>Testosterone, bisphenol A, and acetaminophen</td>
<td>UVA/two black light lamps</td>
<td>Degussa P25</td>
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<tr>
<td>Chlortetracycline</td>
<td>UV/a 125 W high pressure UV lamp</td>
<td>Degussa P25</td>
<td></td>
<td>A pseudo-first order kinetics</td>
<td>[Substrate]_l, TOC, total phenolic content (TPC), [H,O,O], [O],</td>
<td>Photocatalytic ozonation was the most efficient process for TCP and TOC removals with the highest ozone consumption efficiency</td>
<td>Rodríguez et al. (2013)</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>UV/a 700 W high pressure mercury lamp</td>
<td>Degussa P25</td>
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<tr>
<td><strong>Acid compounds</strong></td>
<td></td>
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<tr>
<td>Formic acid</td>
<td>UVA/a 6 W blacklight blue fluorescent lamp</td>
<td>TiO_2 film on a Pyrex glass tube</td>
<td>None</td>
<td></td>
<td>[Substrate]_l, TOC, [O]</td>
<td>The synergetic effect of photocatalysis and ozonation was due to the promoted production of hydroxyl radicals by ozone over TiO_2</td>
<td>Wang et al. (2002b)</td>
</tr>
<tr>
<td>Humic acid</td>
<td>UV/a 37 W low pressure mercury vapor lamp</td>
<td>Al and Fe co-doped TiO_2 nanotubes</td>
<td>None</td>
<td></td>
<td>[Substrate]_l, TOC, [O]</td>
<td>O_3, UVA/Pilkington Active™ showed excellent potential for ozonation removal due to the enhanced photogeneration of hydroxyl radicals</td>
<td>Yuan et al. (2013)</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>UVA/a 30 W UV lamp</td>
<td>TiO_2 on Pilkington Active™ glass sheets</td>
<td>None</td>
<td></td>
<td>[Substrate]_l, TOC, ozone consumption level</td>
<td>O_3/UVA/Pilkington Active™ showed excellent potential for ozonation removal due to the enhanced photogeneration of hydroxyl radicals</td>
<td>Mehrjouei et al. (2011)</td>
</tr>
<tr>
<td>Gallic acid</td>
<td>UVA/a 700 W high pressure mercury lamp</td>
<td>Degussa P25</td>
<td>Oxalic acid, formic acid, pyruvic acid, maleic acid, and malonic acid</td>
<td></td>
<td></td>
<td>Photocatalytic ozonation led to total mineralization of the organic matter in less than 90 min</td>
<td>Beltrán et al. (2006)</td>
</tr>
<tr>
<td>2,4-Dichlorophenoxyacetic acid</td>
<td>UV/a 10 W UV tube lamp</td>
<td>TiO_2 fiber</td>
<td>Oxalic acid, maleic acid, glyoxylic acid, fumaric acid, formic acid</td>
<td></td>
<td></td>
<td>O_3/UVA/TiO_2 fiber was promising to mineralize recalcitrant organic contaminants in water at low concentrations</td>
<td>Raj et al. (2008)</td>
</tr>
<tr>
<td>2,4-Dichlorophenoxyacetic acid</td>
<td>UVA/a 6 W Philips blacklight fluorescent</td>
<td>Degussa P25</td>
<td></td>
<td></td>
<td></td>
<td>The rapidness of substrate dehalogenation was examined in the O_3/UVA/TiO_2 process</td>
<td>Piera et al. (2000)</td>
</tr>
<tr>
<td>Target pollutant</td>
<td>Light source</td>
<td>Catalyst</td>
<td>Intermediates</td>
<td>Reaction order</td>
<td>Measurement index</td>
<td>Main results</td>
<td>Reference</td>
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<tr>
<td>1-Amino-4-bromoanthraquinone-2-sulfonylic acid</td>
<td>UV/α 39 W UV lamp</td>
<td>TiO2 thin film on a glass</td>
<td></td>
<td></td>
<td>[Br(^-)], [SO(_4)(^2-)], TOC, COD</td>
<td>O(_3)/UV/TiO2 process more significantly improved the mineralization rate with over 90% TOC removal efficiency</td>
<td>Wang et al. (2013a)</td>
</tr>
<tr>
<td>Monochloroacetic acid and pyridine</td>
<td>UV/α UV lamp</td>
<td>Degussa P25</td>
<td>Formaldehyde, formic acid (for acetic acid); formaldehyde, acetic acid, formic acid, acetaldehyde (for propionic acid)</td>
<td>A formal zero order kinetics</td>
<td>[Substrates](_i), [CH(_3)COOH], [CH(_2)OH], [CH(_3)CO(_2)H]</td>
<td>The photocatalytic ozonation of monochloroacetic acid and pyridine led to 6 and 24 times higher degradation rates than without TiO2 and 4 and 18 times higher rates than without ozone</td>
<td>Kopf et al. (2000)</td>
</tr>
<tr>
<td>Formic acid, acetic acid and propionic acid</td>
<td>UVA/six 6 W medium pressure mercury vapor lamps</td>
<td>Degussa P25</td>
<td>Formaldehyde, formic acid, acetic acid, formic acid, acetaldehyde (for propionic acid)</td>
<td>A formal zero order kinetics</td>
<td>[Substrates](_i), [CH(_3)COOH], [CH(_2)OH], [CH(_3)CO(_2)H]</td>
<td>The combined system proved most effective in the oxidation of carboxylic acids</td>
<td>Ilisz et al. (2004)</td>
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<tr>
<td>Phenols and alcohols</td>
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<tr>
<td>Phenol</td>
<td>UV/α 15 W UV lamp</td>
<td>Activated carbon supported TiO2</td>
<td></td>
<td></td>
<td>[Substrate], relative light intensity</td>
<td>The O(_3)/UV/TiO2 degradation rate constant for phenol was found to be 3.7 times than that of O(_2)/UV/TiO2 system</td>
<td>Dong et al. (2010)</td>
</tr>
<tr>
<td>Phenol</td>
<td>UV/α general electric UV mercury lamp</td>
<td>Mn/TiO2</td>
<td>Pyruvic acid, maleic acid</td>
<td>A pseudo-first order kinetics</td>
<td>[Substrate], [Intermediates], TOC, [O(_3)]</td>
<td>All the irradiated systems showed an increase in the phenol degradation, being CO(_2) and small organic acids as the final products</td>
<td>Villaseñor et al. (2002)</td>
</tr>
<tr>
<td>Phenol</td>
<td>Visible light/α 300 W xenon lamp</td>
<td>WO(_3) powder</td>
<td></td>
<td></td>
<td>[Substrate], TOC, [O(_3)]</td>
<td>The O(_3)/vis/WO(_3) treatment exhibited a much higher TOC removal than ozonation alone</td>
<td>Nishimoto et al. (2010)</td>
</tr>
<tr>
<td>Phenol</td>
<td>Visible light/α 300 W xenon lamp with a cutoff filter</td>
<td>WO(_3) powder</td>
<td></td>
<td></td>
<td>[Substrate], TOC, [O(_3)]</td>
<td>The synergistic effect of photocatalysis and ozonation was important for complete TOC removal</td>
<td>Manno et al. (2011)</td>
</tr>
<tr>
<td>Catechol</td>
<td>UV/α 15 W low pressure UV lamp</td>
<td>Carbon-black-modified TiO2 thin films on Al sheet</td>
<td>Ortho/para bisphenols, 6-heptene acid and n-heptanal</td>
<td>A first order kinetics of three stages</td>
<td>TOC, [O(_3)], [O(_3)]</td>
<td>The rate constants were 2.56–5.36 times higher than the maximal rate constants of O(_2)/UV/TiO2 and 4.68–9.8 times higher than the maximal rate constants of TiO2/UV</td>
<td>Li et al. (2003)</td>
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<tr>
<td>4-Cumylphenol</td>
<td>UV</td>
<td>Al supported TiO2 film</td>
<td></td>
<td></td>
<td>[Substrate], COD</td>
<td>The photocatalytic ozonation had the advantages of optimal mineralization, simplicity and an absence of suspended solids or sludges</td>
<td>Ardizzone et al. (2011)</td>
</tr>
<tr>
<td>Phenol, p-chlorophenol (CP) and p-nitrophenol (NP)</td>
<td>U/V/α 70 W high pressure mercury lamp</td>
<td>Degussa P25</td>
<td>Hydroquinone, resorcinol, benzoquinone, catechol, oxalic acid, maleic acid, fumaric acid, glyoxylic acid, Formaldehyde</td>
<td>A first order kinetics</td>
<td>[Substrates](_i), [Intermediate]s, TOC, [O(_3)]</td>
<td>Photocatalytic ozonation led to lower degradation times for COD and TOC removal with the mineralization percentage nearly 100, 90, 75% in phenol, CP and NP</td>
<td>Beltrán et al. (2005)</td>
</tr>
<tr>
<td>Methanol</td>
<td>U/V/α two black light blue lamps</td>
<td>Degussa P25</td>
<td></td>
<td></td>
<td>[Substrates](_i), [Intermediate]s, [H(_2)O(_2)], [H(_2)O], [O(_3)], [O(_3)]</td>
<td>Strong synergic effect between O(_3) and UVA/TiO(_2) led to higher quantum yield of photo-generated oxidizing species in O(_3)/UVA/TiO(_2)</td>
<td>Mena et al. (2012)</td>
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<tr>
<td>Dyes</td>
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<tr>
<td>Orange II</td>
<td>Visible light/α 55 W xenon lamp</td>
<td>Au/Br(_2)O(_3) and Au/Br(_2)O(_3) nanorods</td>
<td></td>
<td></td>
<td>[Substrate], [O(_3)]</td>
<td>Photocatalytic ozonation using Au/Br(_2)O(_3) nanorods led a fourfold increase in the rate compared to that in the absence of Au/Br(_2)O(_3)</td>
<td>Anandan et al. (2010)</td>
</tr>
<tr>
<td>Reactive Red 194</td>
<td>U/V/α mercury vapor UVA lamp</td>
<td>Anatase TiO(_2) (99.7% purity)</td>
<td>2-Propanoyl benzoic acid, 2-dodecanone, 8-methyl-6-nonanamide, 1,2-benzenedi carboxylic</td>
<td>A first order kinetics</td>
<td>[Substrate], [O(_3)]</td>
<td>The most efficient method for deaeromatization and mineralization was the O(_3)/UVA/TiO(_2) among the applied AOPs</td>
<td>Yildirim et al. (2011)</td>
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(continued on next page)
### Table 1 (continued)

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<th>Target pollutant</th>
<th>Light source</th>
<th>Catalyst</th>
<th>Intermediates</th>
<th>Reaction order</th>
<th>Measurement index</th>
<th>Main results</th>
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<tbody>
<tr>
<td>Reactive Red 198 and Direct Green 6 UV/a 9 W UV-C lamp</td>
<td>Nickel-zinc ferrite magnetic nanoparticle Multiwalled carbon nanotube</td>
<td>Formate, acetate and oxalate anions</td>
<td>*</td>
<td>[Intermediates], [Substrates], [nitrate, sulfate and chloride]</td>
<td>Photocatalytic ozonation using nickel-zinc ferrite nanoparticle was a very effective method for dye degradation</td>
<td>Mahmoodi et al. (2012)</td>
<td></td>
</tr>
<tr>
<td>Reactive Red 198 and Direct Green 6 UV/a 9 W UV-C lamp</td>
<td>Formate, acetate and oxalate anions</td>
<td>*</td>
<td>[Intermediates], [Substrates]</td>
<td>Photocatalytic ozonation using multiwalled carbon nanotube was a very effective method for dye degradation</td>
<td>Mahmoodi et al. (2013)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive Red 198 and Reactive Red 120 UV/a 9 W UV-C lamp</td>
<td>Copper ferrite nanoparticle</td>
<td>Formate, acetate and oxalate anions</td>
<td>A first order kinetics</td>
<td>[Substrates], [Intermediates], [nitrate, sulfate and chloride], UV_{254}</td>
<td>Photocatalytic ozonation using copper ferrite nanoparticle was able to decolorize and treat the colored textile wastewater without using high pressure of oxygen or heating</td>
<td>Mahmoodi et al. (2011)</td>
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<td><strong>Pesticides</strong></td>
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<tr>
<td>Carbaryl</td>
<td>UV/a 125 W medium pressure mercury lamp</td>
<td>Degussa P25</td>
<td></td>
<td>*</td>
<td>[Substrate], TOC, COD, BOD</td>
<td>A synergistic effect of COD reduction, TOC removal, increase of BOD, and COD was noticed except at alkaline pH due to faster self-decay of ozone</td>
<td>Rajeswari and Kanmani (2009a)</td>
</tr>
<tr>
<td>Carbendazim</td>
<td>UV/a 15 W medium pressure mercury lamp</td>
<td>Degussa P25</td>
<td></td>
<td>*</td>
<td>[Substrate], COD, BOD</td>
<td>The degradation rate constant of carbendazim with UV/O_3/TiO_2 was 1.5 times higher than that of ozonation and 2.3 times higher than that of UV/TiO_2</td>
<td>Rajeswari and Kanmani (2009b)</td>
</tr>
<tr>
<td>Alachlor, atrazine, chlorfenivative, diuron, isoproturon and pentachlorophenol</td>
<td>UV/a 6 W black light lamp</td>
<td>Degussa P25</td>
<td></td>
<td>*</td>
<td>[Substrates], TOC</td>
<td>The photocatalytic ozonation led to a strong TOC reduction for the pesticide aqueous solutions, except for atrazine</td>
<td>Farré et al. (2005)</td>
</tr>
<tr>
<td><strong>Other organic compounds</strong></td>
<td></td>
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</tr>
<tr>
<td>Acetic acid, monochloroacetic acid and dimethyl-2,2,2-trichloro-1-hydroxyethylphosphonate (DEP)</td>
<td>UV/a 6 W low pressure mercury lamp</td>
<td>TP-2 TiO_2-coated tube</td>
<td></td>
<td>*</td>
<td>[Substrates], [Intermediates], TOC</td>
<td>The effect of the photocatalytic ozonation was larger on the degradation of hydrophobic compounds than aromatic compounds</td>
<td>Tanaka et al. (1996)</td>
</tr>
<tr>
<td>Aniline</td>
<td>UV/a 125 W medium pressure mercury lamp</td>
<td>Degussa P25</td>
<td></td>
<td>*</td>
<td>[Substrate], TOC, [O_3]</td>
<td>The generation of hydroxyl radicals was the reason for the synergism of ozonation and heterogeneous photocatalysis</td>
<td>Sánchez et al. (1998)</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>UV/a 15 W low pressure UV lamp</td>
<td>Carbon black modified nano-TiO_2 film TiO_2</td>
<td></td>
<td>A pseudo-zero order kinetics</td>
<td>[Substrates], TOC</td>
<td>The mineralization rate constants of dibutyl phthalate with O_3/UV/TiO_2 were 1.2-1.8 (3.5) times higher than that of O_3/UV (UV/TiO_2)</td>
<td>Li et al. (2005)</td>
</tr>
<tr>
<td>Dimethyl phthalate</td>
<td>UV/a 15 W UV lamp</td>
<td>TiO_2</td>
<td></td>
<td>A first order kinetics</td>
<td>[Substrates], TOC</td>
<td>The rate constants in O_3/UV/TiO_2 was 2.5(5.2) times more than that in O_3/UV (O_3/UV) process</td>
<td>Jing et al. (2011)</td>
</tr>
<tr>
<td><strong>Real effluents</strong></td>
<td></td>
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<tr>
<td>Textile effluent</td>
<td>UV/a 150 W high pressure mercury lamp</td>
<td>Degussa P25</td>
<td></td>
<td>*</td>
<td>Decolorization, UV_{315}, TOC</td>
<td>The photocatalytic ozonation process led to almost complete decolorization and higher than 60% TOC reduction</td>
<td>Moraes et al. (2000)</td>
</tr>
<tr>
<td>Winery wastewaters</td>
<td>UV/a 700 W high pressure mercury lamp</td>
<td>Degussa P25</td>
<td></td>
<td>*</td>
<td>TOC, COD, [O_3], [O_3]</td>
<td>O_3/UV/Vis/TiO_2 led to the total mineralization of the COD removed with the existence of a synergistic effect</td>
<td>Gimeno et al. (2007a)</td>
</tr>
<tr>
<td>Postharvest fungal spoilage of kiwifruit</td>
<td>UV/a 15 W low pressure UV lamp TiO_2 on alumina balls</td>
<td></td>
<td></td>
<td>*</td>
<td>[flusilazol], TiO_2</td>
<td>Photocatalytic ozonation can be a very attractive method for postharvest disease control of kiwifruit</td>
<td>Hur et al. (2005)</td>
</tr>
</tbody>
</table>

* Not referred.
in solution are very efficient non-selective oxidizers, which result in the oxidation and eventual mineralization of organic compounds.

Photocatalysts typically include TiO2 (Gaya and Abdullah, 2008; Wang and Jing, 2014), ZnO (Kaur and Singhal, 2014; Xu et al., 2014a), WO3 (He et al., 2014; Katsumata et al., 2014), CdSe (Elmalem et al., 2008; Li et al., 2014), CdS (Chronopoulos et al., 2014; Lang et al., 2014), α-Fe2O3 (Sun et al., 2014; Wei et al., 2014), SnO2 (Wang et al., 2002a; Jana et al., 2014) and Ag3PO4 (Bi et al., 2011; Zhang et al., 2014a). Among these semiconductor materials, TiO2 is the most extensively and intensively studied one due to its high photoconductivity, chemical stability, low toxicity, low costs and wide commercial availability. Many efforts have been devoted to design and fabricate nano-sized or film-state photocatalysts with improved photocatalytic efficiency. As the prime part, TiO2 have long been a mainstay among researches. Generally, three strategies have been devoted for preparing improved UV or visible-light photoactive titania. Fig. 3 presents the SEM or TEM images of the modified titania as photocatalysts based on the three strategies. One direction is to increase exposed photo-reactive sites by size and morphology control. Many structures, such as quantum dots (QDs) (Phillips et al., 2013; Pan et al., 2014b), nanosheets (Pan et al., 2013; Zhao et al., 2014), nanotubes (Ali et al., 2014; Xing et al., 2014b), nanowires (Wu et al., 2012; Zhao et al., 2013), mesoporous hollow shells (Joo et al., 2013; Moon et al., 2014) are reported. Another approach aims at enhancing the charge separation or broadening the absorption spectra by metal or non-metal doping or compounding with charge transfer materials. The noble (Zielinska-Jurek and Zaleska, 2014; Zhang et al., 2014b), transition metals (Feng et al., 2012; Wang and Jing, 2014) and non-metals (Lin et al., 2014; Wang et al., 2014; Wu and Ju, 2014) deposited or doped TiO2, TiO2–carbon nanotube (Xia et al., 2007; Woan et al., 2009) and TiO2–graphene composites (Liu et al., 2010; Lee et al., 2012; Yang et al., 2013) have been largely investigated. The third method, to build Anatase–Rutile (A–R) phase junction of TiO2, is less studied but cannot be ignored. The mixed-phase samples of anatase and rutile directly contribute to charge carrier separation in photocatalytic reactions, and therefore outperform the individual polymorphs with greatly enhanced quantum yield and photocatalytic activity (Zhang et al., 2008; Scanlon et al., 2013; Liu et al., 2014). Although TiO2 thin films generally exhibit lower photocatalytic activity than the corresponding powder materials due to their smaller specific surface area, its easily separation for recycle makes a big significance in applications. Researchers extensively use the referred paths to modify titana films. Doped, deposited or compounded mesoporous thin films (Xiang et al., 2013; Wang et al., 2013c; Cheng et al., 2014; Elgh and Palmqvist, 2014; Fakhouri et al., 2014) are the most acclaimed. Varied methods are reported for the realization of the preparation strategies. Among these, sol–gel and hydrothermal treatments have been most largely investigated. The advantage of sol–gel method derives from its ability to synthesize nanosized titania with high purity at relatively low temperature. And hydrothermal approach especially works in the fabrication of shape and controlled TiO2 with high crystallinity.

Visible-light photocatalysis is extensively considered as sustainable AOP by harnessing solar energy, making it economically feasible and environmentally benign. The key to achieve this goal lies in the fabrication of highly visible–photoactive materials with narrowed but suitable band gap. The band gap of photocatalysts determines the VB and CB potentials, and also the absorption spectra range. Wide band gap semiconductor photocatalysts, such as TiO2, can only absorb UV light, which only take 4% of the whole solar spectra. In order to increase visible light absorption, researchers generally use the above-summarized strategies to fabricate highly visible-responsive materials with narrowed band gap. Although photocatalysis under visible light draws a flooded research attention, more considerations are suggested to be paid on the utilization pathway of solar energy and the design of efficient solar photocatalysis reactors.

### 2.2. Catalysts applied in photocatalytic ozonation

Despite various types of semiconductor materials with varied morphologies and compounded components, very limited photocatalysts are served in photocatalytic ozonation. Table 2 summarizes all the heterogeneous catalysts in photocatalytic ozonation. Among these, TiO2 and TiO2-based materials with both photocatalytic and ozonation activity are the most widely implemented. The catalysts can be typically divided into two kinds, the UV driven and visible light driven ones. Moreover, the UV driven catalysts can be suspended or immobilized, TiO2-based or non-TiO2-based materials.

A commercial TiO2 Degussa P25 (80% anatase and 20% rutile) was used in most of experimental investigations. Its average particle size is 30 nm with specific area 50 m² g⁻¹. It is commercially produced by flame hydrolysis of TiCl4 at temperatures higher than 1200 °C in the presence of hydrogen and oxygen (Akpan and Hameed, 2009). Kopf et al. (2000) found the addition of Degussa P25 into photocatalytic ozonation led to 6 and 24 times higher degradation rates of monochloroacetic acid and pyridine, respectively. This decent performance may result from the reduced recombination rate of electron-hole pairs in the anatase phase, as the UV-induced electrons created in the anatase phase transfers to the less active rutile phase (Schindler and Kunst, 1990). Besides commercial supply, Jing et al. (2011) synthesized a TiO2 with crystallize size of 8.4 nm by a hydrothermal method. It showed a good anatase phase, greater surface area, stronger absorption to UV light and lower agglomeration compared with TiO2 prepared by a classic sol–gel method (sol–gel TiO2). Its photocatalytic activity at maximum was 2.5 times higher than that of sol–gel TiO2 in degrading dimethyl phthalate (Jing et al., 2011). Al and Fe co-doped TiO2 nanotubes with hollow, open-ended structures were successfully prepared by a hydrothermal method as well (Yuan et al., 2013). It had a large specific surface area and low band gap energy. The 1.0% co-doped (Al/Fe: 0.25/0.75) TiO2 had a band gap of 3.06 eV and showed the highest catalytic activity in decomposing humid acid in drinking water. The enhanced performance was attributed to the promoting effect of doping Al³⁺ and Fe³⁺ in the generation of hydroxyl radicals. TiO2–graphene nano composites have also been used in the photocatalytic process under UV with enhanced TOC removal in wastewater treatment, and they are also very sensitive to visible light (Wang et al., 2012; Zhao et al., 2012; Ullah et al., 2013; Wang et al., 2013b). This is possibly because the photo-excited electrons transferred from TiO2 to graphene to hinder electron-hole recombination, and thereby enhanced oxidative reactivity of the process. It is expected that TiO2–graphene nano composites can also function as an efficient catalyst in photocatalytic ozonation.

In terms of non-TiO2-based catalyst, Mahmoodi (2011), Mahmoodi et al. (2012), and Mahmoodi (2013) tested three different catalysts including nickel–zinc ferrite magnetic nanoparticle (NZFMN), Copper ferrite nanoparticle (CFN) and multiwalled carbon nanotube (MWCNT) for dye degradation by photocatalytic ozonation. They proved to be potential candidates for developing high-performance photocatalyst materials without using high pressure of ozone or heating.

With regard to the suspended semiconductor catalyst, it needs to be separated before cycling use. Moreover, the extinction of UV light due to the scattering by the catalyst particles would lead to reduced photon absorption. Based on this, immobilized catalyst is reasonably adopted to avoid this shortage. Tanaka et al. (1996)
was among the first to use a TiO$_2$-coated tube installed in a round glass bottle as the reactor. Mehrjouei et al. (2011) immobilized TiO$_2$ on a well-known commercial product Pilkington Active™, and this catalyst showed excellent potential for the removal of oxalic acid in water. Furthermore, a novel carbon black modified nano-TiO$_2$ film (CB-TiO$_2$) was devised by a sol–gel method and implemented in photocatalytic ozonation to mineralize dibutyl phthalate in water (Li et al., 2005). Carbon black modification made the TiO$_2$ film more porous with looser structure, smaller crystal size and longer excitation wavelength. Consequently, it led to 1.4 times higher photocatalytic activity than that of non-modified TiO$_2$ films in degrading dibutyl phthalate. It should be mentioned that although the immobilization of TiO$_2$ avoided the shortcoming of catalyst recycling, immobilized catalyst was not as efficient as the suspended form due to the mass transfer limitation in the reaction system.

As a new generation of photocatalyst, visible-light-induced materials have also been implemented in photocatalytic ozonation. Rey et al. (2012) and Quiñones et al. (2014) deposited anatase TiO$_2$ particles on a commercial magnetic meso-to-microporous activated carbon support (TiFeC) by a sol–gel method. TiFeC was not as effective as Degussa P25, but the easily magnetical separation, excellent stability (low Fe and Ti losses) and reusability made it an interesting alternative material for solar photocatalytic ozonation. A commercially-available WO$_3$ powder was highly responsive to visible range and thereby tested by Nishimoto...
et al. in photocatalytic ozonation of phenol under visible-light illumination (Nishimoto et al., 2010; Mano et al., 2011). It consisted of a mixture of well-crystalized monoclinic and triclinic phases with diameters ranging from 0.2 to 2 μm and a surface area of 3.6 m² g⁻¹. It was demonstrated to be an more active visible light responsive photocatalyst superior to the commercial N–TiO₂ powder in the presence of ozone (Nishimoto et al., 2010). Besides, Bi₂O₃ nanorods were synthesized using microwave-assisted approach and found to be more valid compared to the Bi₂O₃ particles prepared by a conventional thermal method (Anandan et al., 2010). Au nanoparticles deposited Bi₂O₃ nanorods (Au/Bi₂O₃) created a fourfold increase in the degradation rate of Orange II compared to that without Au/Bi₂O₃ catalyst. Au nanoparticles acted as electron traps to impede electron-hole recombination, therefore more free radicals were produced consequently to improve the overall mineralization performance. Furthermore, the mechanical strength of devices was also enhanced through the deposition of nanomaterial (Anandan et al., 2010).

As with solar photocatalysis, solar photocatalytic ozonation attracts significant attention. The utilization of solar light could decrease electrical energy consumption and abolish the costs on light source, which makes the technology more cost-effective and competitive. It may be considered as one of the most promising approaches among AOPs with an industrialized feasibility. Furthermore, it triggers the significance in designing more reliable photocatalysts which can be highly responsive to solar light, visible light or the both. However, there are still many challenges that are not yet to be solved in terms of the visible light induced photocatalyst itself. Difficulties mainly include the enhancement of solar light conversion and the suppression of the recombination of photogenerated electron-hole couples. Practically, it is more worthy of intensive probing how to effectively focus the changeable sunlight to build a stable reaction system.

3. Effect of operational parameters

Photocatalytic ozonation experiments were typically carried out in a batch (Kopf et al., 2000; Beltrán et al., 2005; Li et al., 2005) or semi-batch mode (Beltrán et al., 2010; Rey et al., 2012; Quiñones et al., 2014) using a cylindrical (Kopf et al., 2000; Moraes et al., 2000; Li et al., 2005; Quiñones et al., 2014) or tubular glass reactor (Li et al., 2003; Beltrán et al., 2005, 2010; Jing et al., 2011), equipped with magnetic stirring, thermostatic water bath, gas inlet, gas outlet and liquid sampling ports. The reactor was commonly placed in a black box under illumination by an immersed (Li et al., 2003; Jing et al., 2011; Khan et al., 2013) or outside-in light source (Ning et al., 2013; Xie et al., 2013). Fig. 4 gives schematic illustration of these two modes respectively. For an immersed light source, the lamp was usually surrounded by a quartz thimble, the irradiating light contacted more sufficiently with the solution with less extinction than the outside-in manner. Nevertheless, the immersed lamp was susceptible to damage during operation, and more expenses would be required for the quartz thimble. Various kinds of lamps were employed in photocatalytic ozonation according to Table 1. Mercury lamp was the most widely implemented among all types, and cooled xenon lamp and black-light lamp were also commonly used.

3.1. pH

The pH of solution plays viable roles in the photocatalytic process as it determines the surface charge of the photocatalyst (Haque and Muneer, 2007), size of aggregates it forms (Zhang et al., 2012) and generation of oxidizing species (Qamar et al., 2006). The commonly applied Degussa P25 was reported to have a point of zero charge (pzc) at pH 6.9 (Kosmulski, 2006). Taking TiO₂ for example, firstly, pH is related to the ionization state of the catalyst surface according to the following reactions (Eqs. (5) and (6)), as well as those of the reactant substrates and products.

\[
\text{TiOH} + \text{H}^+ \rightarrow \text{TiOH}_2^+ \quad (5)
\]

\[
\text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O} \quad (6)
\]

The titania surface will remain positively charged in acidic medium (pH < 6.9) and negatively charged in alkaline medium (pH > 6.9). Other materials with different pH₅₀⁺ certainly have disparate surface charge at the same pH, and thereby behave different
adSORption performance. for the weakly acidic contaminants, the photocatalytic degradation rate increases at lower pH due to an increase in the adsorption. Some organic pollutants undergo hydrolysis at alkaline pH, which is one of the reasons for the improved photocatalytic degradation at alkaline pH (Bhatkhade et al., 2002).

Secondly, it is notable that TiO2 nanoparticles tend to aggregate in acidic solution (Zhang et al., 2012), Leading to a decrease in substrate adsorption and photon absorption. Therefore, pH can directly influence the adsorption of substrates onto the catalyst surfaces as well as photon absorption, a significant step in photocatalytic degradation. Thirdly, the pH of solution affects the formation of reactive oxidizing species. The positive holes are considered as the main oxidizing species at a low pH, whereas hydroxyl radicals are deemed to the predominant active species under neutral or alkaline conditions (Tunesi and Anderson, 1991).

For ozonation, ozone can degrade organic pollutants through direct attack or indirect reaction with free radicals, which is strongly pH dependent. In the absence of UV light, ozone can react directly with organic compounds through selective reactions of electrophilic substitution and diatomic cycloaddition. This occurs at acidic or neutral conditions and contributes to the formation of carboxylic acid as the end products that can hardly be further mineralized. Ozone decomposed faster in water at higher pH, resulting in fast and non-selective reactions of radicals with organic compounds (Oyama, 2000). As opposed to ozonation alone, catalytic ozonation allows for efficient generation of hydroxyl radicals at a low pH value (Nawrocki and Kasprzyk-Hordern, 2010). Therefore, it can be deduced that pH of the solution plays a crucial role in determining the efficiency of photocatalytic ozonation since it can alter the reaction pathways as well as kinetics.

Generally, low pH favored the degradation of the dyes and oxalic acid. Chlorotetracycline, methanol, carbaryl and carbendazim were more effortlessly decomposed under an approximately neutral solution. Mena et al. (Mena et al., 2012) discovered that the mineralization rate of methanol remarkably increased when pH varied from 7 to 3. Methanol was selected as the target pollutant because it almost does not react directly with ozone, but is a well-known scavenger of hydroxyl radicals and positive holes. Lower dissolved ozone concentration was detected at pH 7 (1 × 10^{-6} M) compared to that at pH 3 (6.1 × 10^{-6} M), indicating a higher consumption of ozone at neutral pH probably due to its faster decomposition. Therefore, the positive effect of increasing pH on the photocatalytic ozonation reaction was on account of the formation of higher concentration of oxidizing species that favored the ozone decomposition in water (Mena et al., 2012). However, Mahmoodi (2011), Mahmoodi et al. (2012), and Mahmoodi (2013) found that dye degradation decreased with increasing pH when photocatalytic ozonation was applied. Both direct electrophilic attack and indirect oxidation through hydroxyl radicals occurred and contributed to the decomposition of dyes at a low pH in photocatalytic ozonation. The electrostatic interaction depended on the charge of both the MWCNT surface and the dye, which could be influenced by the pH of solution. The surface of MWCNT is positively charged at acidic pH, thus the electrostatic interactions between MWCNT surface and dye would be enhanced during O3/UV/MWCNT. Hence, lower pH favored the dye adsorption on MWCNT surface, and thereby increased the dye decomposition by photocatalytic ozonation (Mahmoodi, 2013).

An increased removal of oxalic acid by lowering pH was also observed by Mehrjouei et al. (2011). An unexpected result at pH 3 revealed a greater removal than that at pH 2.1 in the first 20 min, but the total removal was higher at pH 2.1, assuming that effective generation of hydroxyl radicals was limited in the more acidic solution.

The influence of pH may be attributed to the different kinds of catalyst and different nature of the target compounds, since electrostatic interaction and surface adsorption greatly depend on the charge properties of both the catalyst surface and substance, which are considerably influenced by the pH of solution. Therefore, it is necessary to study the nature of the substrates and catalytic mechanism before determining the probable pH to destroy them.

3.2. Reaction temperature

The experiments were commonly carried out at room temperature in the published papers. Generally, an elevated temperature contributed to a continuous increase of degradation efficiency within a certain range, beyond which the decomposing rate would decrease.

Temperature influences the photocatalytic ozonation in several ways, some of which showed opposite effects to the other. On one hand, an increment of temperature lead to less adsorption of pollutants at a constant pressure, thus resulting in a decreased degra-
dation of adsorbed compounds over the catalyst surface. The ozone solubility in water reduces when temperature increases, causing a shortage in ozone molecular to handle the photocatalytic ozonation process. And the recombination of charge carriers could be enhanced by elevating the solution temperature, which also has a negative effect on the degradation efficiency. On the other hand, increasing temperature should improve all chemical reaction rates involved in the oxidizing system, including ozone decomposition and formation of active species. Therefore, it reveals the optimal temperature for the combined system when the positive impact predominates in those negative effects.

Few researchers tested the influence of solution temperature on photocatalytic ozonation. Mehrjouei et al. (2011) examined the effect of temperatures in the range of 10–70 °C on the degradation of oxalic acid. The increasing temperature from 10 to 55 °C consequently enhanced the degradation rate of oxalic acid, while even higher temperatures of up to 70 °C had a negative effect and reduced the degradation rate. The mineralization speeded up from 10 to 55 °C owing to the accelerated rate of ozone decomposition to generate hydroxyl radicals under the given condition. However, a lack of ozone molecules available to handle the oxidation process probably hindered the degradation efficiency at 70 °C. Mano et al. (2011) discovered that the TOC removal was continuously accelerated with temperature increasing from 15 to 45 °C with WO3 catalyst under visible light irradiation. An increment of reaction temperature substantially led to more active species generated from the synergism of photolysis and ozonation, as well as from self-decomposition of dissolved ozone (Mano et al., 2011). Therefore, photocatalytic ozonation could effectively utilize solar light, including available infrared light as an energy source to heat the wastewater, and UV–Visible light as irradiation source to initiate photocatalytic reactions. We can conclude that the effect of temperature is relatively limited, which means an adjustment of temperature is normally not required in photocatalytic ozonation.

3.3. Light intensity

The overall quanta of light absorbed by any photocatalyst or substrate are given by the quantum yield of the reaction according to Eq. (7):

\[
\phi_{\text{overall}} = \frac{\text{reacted molecules}}{\text{absorbed photons}} = \frac{r_j}{I_c} \quad (7)
\]

where \(r_j\) is the reaction rate, and \(I_c\) represents the absorption rate of radiant energy, which is generally lower than that impinging on the reacting system due to inevitable light reflection, scattering and energy loss as heat in the photo-process. In addition, the recombination of photo-generated electrons and positive holes is considered as another important factor limiting the photonic efficiency. It has been demonstrated that ozone is a more efficient electron scavenger than oxygen, and the photocatalytic reactions can be accelerated with the addition of ozone.

The absorbed light intensity is usually calculated by the radical transfer equation to the reaction system (Alfano et al., 1997; Brucato et al., 2006; Toepfer et al., 2006) or experimentally determined by the light transmission through the photocatalyst suspension (Loddo et al., 2006). Mena et al. (2012) indirectly calculated the adsorbed light intensity in photocatalytic ozonation of methanol over Degussa P25. It was always higher than 90% of that impinging the reactor with 0.5 g L\(^{-1}\) catalyst at various pH. The quantum yield for photo-generated species during photocatalytic ozonation at pH 3 was calculated to be 0.80 mol Einstein\(^{-1}\), while that in photocatalytic process was 0.34 mol Einstein\(^{-1}\). At pH 7, the enhancement of quantum yield dramatically increased from 0.29 mol Einstein\(^{-1}\) in photocatalytic process to 3.27 mol Einstein\(^{-1}\) in photocatalytic ozonation. A great synergism exists between ozonation and photocatalysis due to the inhibited recombination of electron–hole couples through the reaction of dissolved ozone and hydrogen peroxide with photo-excited electrons.

The reaction rate in photocatalysis largely depends on the absorbed photon flux of the photocatalyst, revealing an increase in the degradation rate with higher light intensity during photocatalytic reactions (Karunakaran and Senthivelan, 2005; Qamar et al., 2006). Therefore, light intensity should have a positive effect on the overall efficiency of heterogeneous photocatalytic ozonation for more generation of active species under stronger illumination. Exactly as examined by Piera et al. (2000), the TOC removal in O\(_3\)/UVA/TiO\(_2\) process followed a half order dependence with light intensity. Whereas, increasing light intensity would cause higher operation costs as well. Hence, the oxidation efficiency and electrical input should be both considered to determine the optimum light intensity. It should be mentioned that the nature or form of the light does not influence the reaction pathway, which indicates the band-gap sensitization mechanism does not matter in photocatalytic ozonation reactions (Gaya and Abdullah, 2008).

3.4. Ozone dosage

Ozone dosage within a certain concentration exerts a positive effect on the photocatalytic ozonation. Generally, an increment of ozone dosage led to higher oxidation rates and mineralization efficiency within certain limits, but a further increase of ozone dosage does not have any significant effect.

Beltrán et al. (2009) studied the influence of ozone dosage on the removal of sulfamethoxazole in photocatalytic ozonation. An unremitting increase of oxidation rate was observed when improving ozone dosing quantity from 10 to 20 mg L\(^{-1}\). It did not make sense to continuously augment this parameter since the corresponding acceleration of degradation rate was negligible. This phenomenon was attributed to complex Langmuir kinetics for the adsorption and reaction of substrates over the catalyst surface, which was also reported by Mena et al. (2012). Moreover, the increment of ozone dosage would require extra energy consumption and thereby increase the operational costs.

The effect of ozone dosage was also examined by Li et al. (2005) in photocatalytic ozonation of dibutyl phthalate with a carbon black modified nano-TiO\(_2\) film. The addition of ozone significantly enhanced the mineralization of pollutants prior to heterogeneous photocatalysis alone. The TOC removal rate was over 75% at 30 min with 25 mg h\(^{-1}\) of ozone, while it was only 73% when ozone dosage increased to 50 mg h\(^{-1}\) in the absence of the catalyst. On this basis, a synergetic effect among the O\(_3\)/UV, UV/TiO\(_2\), and O\(_3\)/TiO\(_2\) processes was concluded. The surface of the semiconductor catalyst was readily hydroxylated when contacting with water. Meanwhile, electron–hole pairs were generated over the catalyst surface owing to UV radiation. The oxidation potential of the hydroxylated TiO\(_2\) must lie above the VB of the semiconductor catalyst, thus thermodynamically possibly resulting in the formation of hydroxyl radicals through the oxidation of surface-bound OH\(^-\) and H\(_2\)O by the photo-exited positive holes. In consequence, the removal of dibutyl phthalate got accelerated.

3.5. Catalyst dosage

The impact of catalyst dosage on photocatalytic ozonation of various organic pollutants has been investigated by many researchers. An increment of catalyst dosage normally benefits to the degradation rate and removal efficiency of organic pollutants, but a continuous increase of catalyst dosage may exert an inhibiting effect due to the light transmission obstacles.
Aguinaco et al. (2012) discovered that the presence of TiO₂ did not affect the removal rate of diclofenac (DCF) in photocatalytic ozonation at all. DCF was completely degraded in about 5.5 min, which was attributed to the direct reaction between ozone and DCF (Aguinaco et al., 2012). Furthermore, negligible differences in the TOC removal efficiency were observed when the catalyst dosage was between 0.5 and 2.5 g L⁻¹. The same optimum catalyst dosage range was also detected by Gimeno et al. (2007b). The suppressive effect at higher catalyst dosage originates from the particle interference on the transmission of light to reach the core of catalyst suspension.

Mahmoodi (2011) tested the influence of catalyst dosage on the decomposition of dyes over CFN. The degradation rate of dyes slightly increased when the dosage of CFN varied from 0.01 to 0.03 g L⁻¹, but a further increase of CFN dosage up to 0.04 g L⁻¹ does not make any further improvement. This influence is in agreement with catalytic oxidation processes that always have a critical catalyst dosage, above which the apparent reaction rate is inhibited due to light penetration problems.

4. Kinetics

The Langmuir–Hinshelwood (L–H) model has been used to formulate the rate equations for the values of kinetic constant and equilibrium adsorption constant in the mineralization of organic pollutants by photocatalytic ozonation (Jing et al., 2011). The following equation is adopted in L–H model to determine the reaction rate (r), where r represents the reaction rate (mg L⁻¹ min⁻¹), C the concentration of the substrate, k the reaction rate constant (mg L⁻¹ min⁻¹), K the Langmuir adsorption coefficient of the substrate (mg⁻¹ L¹).

\[ r = -\frac{dC}{dt} = k \frac{KC}{1 + KC} \]  
(8)

The decomposition rate followed a pseudo-first order kinetics in most of the published literatures, but a pseudo-zero order reaction kinetics, first order kinetics or zero order kinetics were also reported (Table 1). Rey et al. (2012) and Quiñones et al. (2014) discovered that the pollutant depletion followed a pseudo-first order kinetics when photocatalysis and ozonation was combined. Li et al. (2003) reported that the TOC removal in photolytic ozonation obeyed a pseudo-zero order kinetics dependent upon ozone concentration. The mineralization of dibutyl phthalate also obey a pseudo-zero order kinetics, as reported by Li et al. (2005). Other researchers, Aguinaco et al. (2012) found the substrate and TOC decomposition modes both submitted to a first order kinetics in the combined method. In the meanwhile, Mano et al. (2011) concluded the TOC removal complied with a first order kinetics of three stages. In addition, as described by Ilisz et al. (2004), the mineralization of aliphatic carboxylic acids in the photocatalytic ozonation followed a formal zero kinetics.

5. Mechanism

Heterogeneous photocatalytic ozonation is a very complex gas-liquid reaction system that involves chemical, catalytic, and photocatalytic reactions, with a vast number of variables to investigate. A dramatic synergism exists between heterogeneous photocatalysis and ozonation as demonstrated by a large amount of literatures according to Table 1. The primary mechanism of AOPs lies in the promoting generation of highly active free radicals. Consistently, the simultaneous application of photocatalysis and ozonation synergistically enhances free radicals formation, and consequently results in higher mineralization efficiency.

When ozone is bubbled into a photocatalytic system, in addition to the homogeneous pathways of direct ozonation, the role of ozone as an electron trap must be considered. Ozone can interact with TiO₂ surface in different ways (Bulavin et al., 1995), mainly including: (i) physical adsorption; (ii) formation in weak hydrogen bonds with hydroxyl groups of the catalyst, and (iii) dissociative adsorption on strong surface Lewis acid sites contributing to the decomposition of ozone molecule with generation of an oxygen molecule and an oxygen atom still attached to the surface.

In the presence of ozone and light illumination, adsorbed ozone can generate hydroxyl radicals through the formation of an ozone radical (O₃⁻) in the adsorption layer (Tanaka et al., 1996):

\[ \text{TiO}_2 + h\nu \rightarrow e^- + h^+ \]  
(9)

\[ O_3(\text{ads}) + e^- \rightarrow O_3^- \]  
(10)

The generated ozone radical (O₃⁻) rapidly react with H⁺ in the solution to give HO₃ radical, which then decompose into O₂ and HO⁻ as shown in the equations below:

\[ O_3^- + H^+ \rightarrow HO_3 \]  
(11)

\[ HO_3 \rightarrow O_2 + HO^- \]  
(12)

And the absorbed oxygen in the form of superoxide ion (O₂⁻) promotes the decomposition of ozone into free radicals in water (Naydenov and Mehandjiev, 1993; Beltrán et al., 2002; Jing et al., 2011):

\[ O_2 + H_2O \xrightarrow{TiO_2} e^- + O_2^- + H^+ \]  
(13)

\[ O_3 + O_2^- \rightarrow O_3^- + O_2 \]  
(14)

\[ O_3^- + H^+ \rightarrow HO^- + O_2 \]  
(15)

Kopf et al. (2000) measured the ozone decay under illumination in TiO₂ suspension in the absence of organic compounds to get more information about the photocatalytic ozonation mechanism. It was found that a real photocatalytic reaction occurred in the suspension, not under the light irradiation alone but a combination of light irradiation and photocatalyst to initiate the decomposition of ozone. Furthermore, the author discovered that probably the oxygen molecule firstly reacted with the photo-generated electron, and the electron subsequently transferred to the ozone molecule. In addition to other reaction pathways, such as direct ozone attack, or direct electron transfer from TiO₂ to the ozone molecule, a further reaction route was proposed below (Kopf et al., 2000).

Charge formation:

\[ \text{TiO}_2 + h\nu \rightarrow e^- + h^+ \]  
(9)

Charge transfer of VB hole to give a hydroxyl radical:

\[ h^+ + H_2O \rightarrow HO^- + H^+ \]  
(16)

\[ h^+ + OH^- \rightarrow HO^- \]  
(17)

\[ h^+ + -OH \rightarrow HO^- \]  
(18)

Electron transfer:

\[ e^- + O_2 \rightarrow O_2^- \]  
(1)

Further reactions:

\[ O_3^- + H^+ \rightarrow HO_3 \]  
(2)

\[ O_3^- + O_2^- \rightarrow O_5^- + O_2 \]  
(19)

\[ O_5^- + H^+ \rightarrow HO_3 \]  
(20)
\[ \text{HO}_3 \rightarrow \text{HO}^+ + \text{O}_2 \]  
\[ \text{Oxidation of organic compound } \text{R–H}: \]  
\[ \text{HO}^+ + \text{R–H} \rightarrow \text{R}^+ + \text{H}_2\text{O} \]  
or  
\[ \text{HO}^+ + \text{R} \rightarrow \text{R}^- + \text{OH} \]  
(23)

The difference between photocatalytic ozonation and catalytic ozonation in the aqueous solution lies in the initiation of the chain reactions. The photochemical reaction is triggered by an electron transfer from titanium dioxide to oxygen or ozone, whereas catalytic ozonation mechanism usually begins with the reaction of hydroxyl anion with ozone (Nawrocki and Kasprzyk-Hordern, 2010). In both processes, superoxide ion (\( \text{O}_2^- \)) is primarily formed, and subsequently reacts with ozone to give ozonide ion (\( \text{O}_3^- \)) consequently resulting in the formation of hydroxyl radical (Kopf et al., 2000). And the lesser extent superoxide anion (\( \text{O}_2^- \)) can also act as an oxidant, ultimately leading to mineralization of organic compounds as the equation below (Jing et al., 2011):

\[ \text{O}_2^- + \text{S} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  
(24)

If the irradiation wavelengths lower than 300 nm are employed, especially at 254 nm where ozone has a higher absorption coefficient (\( \varepsilon_{254} = 3300 \text{ M}^{-1} \text{ cm}^{-1} \)) than \( \text{H}_2\text{O}_2 \) (\( \varepsilon_{254} = 18.6 \text{ M}^{-1} \text{ cm}^{-1} \)), photolysis of ozone takes place, generating additional hydroxyl radicals and other oxidants, with subsequent increment of the oxidation efficiency:

\[ \text{O}_3 \rightarrow \text{O}_2^- + \text{O}_2 \]  
(30)

\[ \text{O}_3 \rightarrow \text{HO}^- + \text{O}_2 \]  
(33)

So that the recombination of the positive hole and negative electron pairs was hindered, ultimately a large number of radicals formed, thereby accelerating the oxidation process.

To sum up, direct ozonation can decompose unsaturated organic pollutants to form recalcitrant intermediates. Further mineralization of TOC is achieved through oxidation by hydroxyl radicals, photo-excited holes and superoxide ion radicals, as illustrated in Fig. 5. The enhanced generation of free radicals results from complementary and synergistic mechanisms of photocatalysis and ozonation. Six reaction pathways possibly exist during the generation of hydroxyl radicals in the proposed reaction mechanism: (i) direct electron transfer from \( \text{TiO}_2 \) to the oxygen molecule to generate hydroxyl radicals through the formation of an ozonide radical (Eqs. (9)–(12)); (ii) electron transfer from \( \text{TiO}_2 \) to the oxygen molecule with formation of superoxide anion radical, which then reacts with ozone to give hydroxyl radicals through the formation of an ozonide radical (Eqs. (9), (1), (2) and (19)–(21)); (iii) photo-generated positive holes oxidizing the adsorbed \( \text{H}_2\text{O}_2 \) to generate hydroxyl radicals (Eqs. (9) and (16)–(18)); (iv) direct photolysis of ozone to produce hydroxyl radicals in the case of irradiation with light wavelength lower than 300 nm (Eqs. (25) and (26)); (v) production of hydrogen peroxide as intermediates under UV-irradiation in the presence of ozone, then hydroxyl radicals formed under UV-irradiation in the presence of ozone (Eqs. (27)–(33)); (vi) a recombination of photo-generated electron-hole pairs inhibited by the reaction of ozone and electrons on the surface of titanium dioxide, consequently a large amount of radicals produced (Eq. (34)).

![Schematic illustration of proposed reaction mechanism in photocatalytic ozonation.](image-url)
6. Miscellaneous

6.1. Economic feasibility

In a view of a wastewater treatment technique, it is necessary to assess the economic feasibility of heterogeneous photocatalytic ozonation. Actually, the complementary mechanisms of each process can result in momentous savings in both capital and operation and maintenance (O&M) costs when they are designed to meet the desired water quality goals. The use of ozone to reduce the color and increase the UV transmittance would result in cost savings of a UV system (Burns et al., 2008). Furthermore, the dosages of UV and ozone could be substantially decreased in this combined technology to attain the required mineralization levels, making the operational costs even lower. This is achieved through the design of a smaller O3/UV system to handle the polluted water (Magbanua et al., 2006). According to Kopf et al. (2000), photocatalytic ozonation had a much lower specific energy consumption than the photocatalysis (UV/TiO2) and ozonation (without photocatalyst) for the same DOC decrease. The specific energy consumption (kW h g-1 DOC-reduction) in decomposing monochloroacetic acid and pyridine was only 5% and 15% of that in ozonation, and 9% and 28% of that in photocatalysis, respectively. Mena et al. (2012) also gave a simplified economic estimation on the heterogeneous photocatalytic ozonation. The calculated operation costs in the combined process were always lower than that in photocatalytic experiments or ozonation alone, due to highly reduced reaction time. Therefore, heterogeneous photocatalytic ozonation may be a cost-effective alternative for pollutant abatement and wastewater treatment. It makes an impressive difference on certain occasions, especially for the low discharged industrial wastewater with recalcitrant organics very difficult to deal with.

The overall expenses mainly concentrated on the actual operational costs of UV system. UV equipment has lower capital cost but is considerably more expensive over long period time than ozone system. As far as UV tubes are concerned, they can effectively work for 7 years or even longer. Nevertheless, the commercial UV lamps have very limited life expectancies, and they normally cannot effectively produce UV irradiation after 1 year of service. As a result, the maintenance and replacement of the photocatalysis instrument would cause a sustained economic input, which accounts for the major proportion of the O&M costs. Therefore, it is imperative to strengthen the research and development (R&D) to produce efficient UV sources with longer lifetime. This can accordingly improve the core competence of this combining technique.

On the other hand, the cost of UV light could hopefully be reduced by implementing solar photocatalytic ozonation. It provides an economic feasibility on industrialization as long as to overcome technical challenges. To achieve this goal, more reliable visible light induced and solar induced photocatalysts are firstly needed.

6.2. Future trends

At the present stage of photocatalytic ozonation, future development trends in this area would include:

(i) Preparation of novel catalysts with high performance under UV to destroy the refractory organics to higher extents.
(ii) Reliable photocatalysts that can be activated by solar or visible light are needed.
(iii) Design of new reactor to overcome the mass transfer limitation for the immobilized photocatalyst.
(iv) Research and development of efficient UV lamps with longer lifetime.
(v) The investigation on the insightful mechanism by means of advanced instrumentation is requisite.

7. Conclusion

Heterogeneous photocatalytic ozonation appears to be the most robust and promising AOP available to destroy a great variety of recalcitrant organic contaminants in wastewater, with a dramatic synergism between photocatalysis and ozonation. The enhancement of higher oxidation rate results from a larger amount of active radicals formed. Hydroxyl radicals generate through a synergistically induced decay of dissolved ozone, initiated by a combination of photocatalyst and light irradiation obedient to six possible pathways.

Various parameters influence the efficiency of the complex gas-liquid process, pH, temperature, light intensity, ozone dosage and catalyst dosage, which closely relate to the type of substrates as well as the predominant reaction mechanism. It is necessary to study the nature of the substrate to be degraded, which will provide a clue to the adjustment of the operational parameters.

Heterogeneous catalysts are the key factor in photocatalytic ozonation, among which Degussa P25 is the most widely applied at present. Different kinds of photoactive catalysts are under development, but their performance still needs to be improved in order to lower the total cost of the process. Meanwhile, the development of highly efficient UV lamps with longer life time is critical to photocatalytic ozonation. The replacement of UV lamps accounts for a relatively big part of the operation cost.

The combination of solar light and ozone could be the ultimate object for the industrialized feasibility, catalysts with high activity under visible light and systematic optimization of operational parameters are completely necessary to achieve this goal.

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