A review of synergistic effect of photocatalysis and ozonation on wastewater treatment

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Abstract

For the treatment of wastewater that contain recalcitrant organic compounds, such as organo-halogens, organic pesticides, surfactants, and colouring matters, wastewater engineers are now required to develop advanced treatment processes. A promising way to perform the mineralization of this type of substance is the application of an advanced oxidation process (AOP).

Photocatalytic oxidation and ozonation appear to be the most popular treatment technologies compared with other advanced oxidation processes (AOPs) as shown by the large amount of information available in the literature. The principal mechanism of AOPs function is the generation of highly reactive free radicals. Consequently, combination of two or more AOPs expectedly enhances free radical generation, which eventually leads to higher oxidation rates.

The use of combine photocatalysis and ozonation is an attractive route because of the enhancement of the performance for both agents by means of the hydroxyl radical generation, a powerful oxidant agent that can oxidize completely the organic matter present in the aqueous system. The scope of this paper is to review recently published work in the field of integrated photocatalysis and ozonation on wastewater treatment.

In this review the chemical effects of various variables on the rate of degradation of different pollutants are discussed. The mechanism and kinetics has also been reported.

It can be concluded that photocatalytic oxidation in the presence of ozone is a process that is qualitatively and quantitatively different from the well-known photocatalytic oxidation with oxygen and the ozonation without photocatalyst. The reason for the higher oxidation rate is probably a photocatalytic induced decay of ozone, initiated by the combination of titanium dioxide and UV-A radiation.

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Keywords: Synergistic effect; Photocatalysis ozonation; Wastewater treatment

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A combination of several treatment methods, such as O₃/VUV, may be more dangerous as a result of ozonation [1–4] but a by ozonation or photolysis alone and the treated wastewater. For example, a certain organic compound can hardly be degraded high treatment efficiency compared with individual treatment. In general, a combination of several methods gives processes. In particular, for the textile effluent, the decolourization was almost complete with the combined method. The advantages of the highest removal of the organic effluent (see Figs. 1 and 2). The scope of this paper is to review recently published work in the field of integrated photocatalysis and ozonation on wastewater treatment. The summary of compounds degraded by various researchers using photocatalytic ozonation including information about the UV source used, intermediates detected and results is presented in Table 1. All results using different organic effluents always showed that the application of photocatalytic ozonation gave the minimum total degradation time and produced the highest removal of the organic effluent (see Figs. 1 and 2). In particular, for the textile effluent, the decolorization was almost complete with the combined method. The advantages of photocatalysis giving decrease in TOC, and the advantages of ozonation giving no increase of high intermediate concentrations, were combined here.

1. Introduction

For the treatment of wastewater that contain trace recalcitrant organic compounds, such as organo-halogens, organic pesticides, surfactants, and colouring matters, environmental engineers are now required to develop more advanced treatment processes. In general, a combination of several methods gives high treatment efficiency compared with individual treatment. For example, a certain organic compound can hardly be degraded by ozonation or photolysis alone and the treated wastewater may be more dangerous as a result of ozonation [1–4] but a combination of several treatment methods, such as O₃/VUV (ozone/ultraviolet), O₃/H₂O₂/UV (ozone/hydrogen peroxide/ultraviolet), and UV/H₂O₂ (ultraviolet/hydrogen peroxide), improves the removal of pollutants from the wastewater [5–7].

On the other hand, photocatalysis has a great potential for the removal of organic pollutants from wastewater [8] although it is still not in practical use because of its low oxidation rate. Therefore, a combination of photocatalysis together with ozone, which is a strong oxidizer, is reasonable for the treatment of difficult to degrade organic compounds since the organic compounds are then expected to decompose more quickly and thoroughly in the presence of ozone, to carbon dioxide, water, or inorganic ions. Sanchez et al. [9] combined these two methods for the removal of aniline from water and found that the decomposition rate of aniline is larger than when individually treated by either of the two methods. Wang et al. in 2002 studied the decomposition of formic acid in an aqueous solution using photocatalysis, ozonation, and their combination. As a result, the decomposition rate of formic acid by the combination of photocatalysis and ozonation was found to be higher than the sum of the decomposition rates when formic acid was individually decomposed by a combination of the two methods, which indicates the presence of a synergistic effect of photocatalysis and ozonation [10].

Fig. 1. Degradation of various organic compound (textile effluent in 1 h, aniline in 2 h and 2,4-dichlorophenoxyacetic acid in 6 h) using photocatalysis, ozonation, and combined photocatalysis ozonation (15,9,25).

Fig. 2. Degradation of nitrogen containing organic compounds by photocatalysis, ozonation and combined photocatalysis ozonation (30).
Table 1
Summary of compounds degraded by various researchers using photocatalytic ozonation including information about the UV used, intermediates detected and results and comments

<table>
<thead>
<tr>
<th>Compound degraded/source of effluent</th>
<th>Source of light</th>
<th>Intermediates detected</th>
<th>Results and comments</th>
<th>Parameter monitored</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acid compounds</strong></td>
<td></td>
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<tr>
<td>Acetic acid</td>
<td>Six 6 W medium pressure Hg vapor lamp</td>
<td>Formic acid, formaldehyde</td>
<td>The acetic acid degradation rate was seven times higher in the combined systems than that using photocatalysis alone</td>
<td>DOC and acetic acid degradation</td>
<td>[58]</td>
</tr>
<tr>
<td>Formic acid</td>
<td>6 W black light blue fluorescent lamp</td>
<td>Not analysed</td>
<td>The kinetic constant for the combination methods is more than the sum of both the kinetic constants for photocatalysis and ozonation taken separately</td>
<td>Decomposition of formic acid</td>
<td>[10]</td>
</tr>
<tr>
<td>Formic acid</td>
<td>Six 6 W medium pressure Hg vapor lamp</td>
<td>None</td>
<td>The degradation rate of formic acid using combined method was nearly five times higher than those using photocatalysis alone</td>
<td>DOC and formic acid degradation</td>
<td>[58]</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>Six 6 W medium pressure Hg vapor lamp</td>
<td>Acetic acid, formic acid, acetaldehyde, formaldehyde</td>
<td>The degradation rate of propionic acid using photocatalysis ozonation system was almost 10 times higher than that in the photocatalysis system</td>
<td>DOC and propionic acid degradation</td>
<td>[58]</td>
</tr>
<tr>
<td>Monochloroacetic acid and pyridine</td>
<td>UV lamp</td>
<td>Not analysed</td>
<td>When using the combined method, the degradation rate of monochloroacetic acid and pyridine led to 4 and 24 times higher degradation rate, respectively</td>
<td>Degradation of monochloroacetic acid and pyridine</td>
<td>[32]</td>
</tr>
<tr>
<td>2,4-Dichlorophenoxyacetic acid</td>
<td>20 W black light</td>
<td>2,4-Dichlorophenol chlorohydroquinone 1,2,4-trichlorobenzene</td>
<td>Combined method for 4 h resulted in 2/3 of TOC removal leading to about the same level for photocatalysis alone after 20 h</td>
<td>TOC removal</td>
<td>[44]</td>
</tr>
<tr>
<td>Sulfosalicylic acid</td>
<td>14 W 254 nm lamp (water)</td>
<td>Not analysed</td>
<td>The degradation efficiency at all pH values has the same order: O3/V−O/TiO2 &gt; O3/TiO2/UV &gt; O3/UV</td>
<td>COD removal rate</td>
<td>[51]</td>
</tr>
<tr>
<td>Humic acids</td>
<td>125 W black white fluorescent lamp</td>
<td>Not analysed</td>
<td>The degradation of humic acids in a sequential system including preozonation and photocatalysis were found to be efficient in organic matter and colour removal</td>
<td>Organic matter reduction and colour reduction</td>
<td>[38]</td>
</tr>
<tr>
<td><strong>Nitrogen compounds</strong></td>
<td></td>
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<tr>
<td>Aniline</td>
<td>125 W medium pressure Hg lamp</td>
<td>Not analysed</td>
<td>The degradation rate of aniline by the combination of photocatalysis and ozonation is larger than when individually treated</td>
<td>TOC removal</td>
<td>[9]</td>
</tr>
<tr>
<td>Free cyanide ions</td>
<td>6 W black light lamp</td>
<td>Cyanate, nitrate and carbonate ions</td>
<td>The degradation time of cyanide is almost complete in 90, 60, and 18 min run time when using photocatalysis, ozonation, and photocatalysis ozonation, respectively</td>
<td>Degradation of cyanide</td>
<td>[37]</td>
</tr>
<tr>
<td>Nitrogen containing organic compound</td>
<td>450 W xenon short arc lamp</td>
<td>Ammonia, nitrite nitrate, ethyamine</td>
<td>A considerable increase in the degradation efficiency of the N-compounds is reached by a combination of photocatalysis and ozonation</td>
<td>TOC removal</td>
<td>[57]</td>
</tr>
<tr>
<td><strong>Alcohols</strong></td>
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<td></td>
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<tr>
<td>Phenol, p-chlorophenol (CP), p-nitrophenol (NP)</td>
<td>700 W high pressure Hg lamp</td>
<td>Hydroquinone, resorcinol, catechol, oxalic acid fumaric acid, glyoxylic acid, phenol</td>
<td>Photocatalytic ozonation led to lower degradation times for COD and TOC removal. The percentage of mineralization was nearly 100, 90 and 75% in phenol, CP and NP</td>
<td>COD and TOC removal degradation of catechol</td>
<td>[40]</td>
</tr>
</tbody>
</table>
### Table 1 (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source of light</th>
<th>Intermediates detected</th>
<th>Results and comments</th>
<th>Parameter monitored</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catechol</td>
<td>15 W low pressure UV lamp</td>
<td>Not analysed</td>
<td>The combined photocatalysis ozonation process (TiO2/UV/O3) considerably increased TOC removal rate compared to TiO2/UV, O3, and O3/UV process.</td>
<td>TOC removal</td>
<td>[43]</td>
</tr>
<tr>
<td>Other organic compounds</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Textile effluent</td>
<td>125 W high pressure Hg lamp</td>
<td>Not analysed</td>
<td>The decolorization was almost complete and the highest TOC reduction was achieved when using photocatalysis ozonation methods.</td>
<td>TOC removal</td>
<td>[29]</td>
</tr>
<tr>
<td>Pesticides</td>
<td>6 W black light lamp</td>
<td>Not analysed</td>
<td>Photocatalytic ozonation process led to rapid decrease of the concentration of the biorecalcitrant pesticides and to a strong TOC reduction.</td>
<td>TOC reduction</td>
<td>[36]</td>
</tr>
<tr>
<td>4-Chlorobenzaldehyde</td>
<td>10 W low pressure Hg lamp</td>
<td>Not analysed</td>
<td>The highest efficiency for the substrate degradation was obtained by simultaneous ozonation and photocatalysis.</td>
<td>Degradation of substrate</td>
<td>[41]</td>
</tr>
<tr>
<td>Acetic acid, monochloro acetic acid and dimethyl-2,2,2-trichloro-1-hydroxyethylphosphat (DEP).</td>
<td>6 W low pressure Hg lamp</td>
<td>Formic acid, acetic acid, glycolic acid</td>
<td>The most rapid degradation of the intermediate compounds by the combined method explains the greatest TOC elimination rate produced by this combination.</td>
<td>Degradation of acetic acid monochloro acetic acid, DEP</td>
<td>[60]</td>
</tr>
<tr>
<td>Dihydrat phthalate</td>
<td>15 W low pressure UV lamp</td>
<td>Not analysed</td>
<td>The mineralization rate constant of dihydroxy phthalate with TiO2/UV/O3 is 1.2–1.8 times higher than that of O3/UV with the same ozone concentration.</td>
<td>TOC removal</td>
<td>[42]</td>
</tr>
<tr>
<td>Oxalate ion</td>
<td>700 W medium pressure Hg lamp</td>
<td>Not analysed</td>
<td>The highest decrease of oxalate concentration takes place in the photocatalysis ozonation system.</td>
<td>Degradation of oxalate concentration</td>
<td>[39]</td>
</tr>
<tr>
<td>Post harvest fungal spoilage of kiwi fruit</td>
<td>6 W UV lamp</td>
<td>Not analysed</td>
<td>The most rapid degradation of the intermediate compounds by the combined method explains the greatest TOC elimination rate produced by this combination.</td>
<td>Fungicide decomposition</td>
<td>[61]</td>
</tr>
<tr>
<td>Organic pollutants in raw water (phthalate esters (PAEs) and persistent organic pollutants (POPs))</td>
<td>15 W low pressure UV lamp</td>
<td>Not analysed</td>
<td>The combined photocatalysis ozonation process (TiO2/UV/O3) considerably increased TOC removal rate compared to TiO2/UV, O3, and O3/UV process.</td>
<td>DOC removal PAEs and POPs removal</td>
<td>[62]</td>
</tr>
</tbody>
</table>

### 2. Photocatalysis and ozonation

According to their recent paper, Serpone and Emiline [11] defined that photocatalysis, in its most simplistic description, is the acceleration of a photo-reaction by action of a catalyst. An earlier IUPAC document defined it as a catalytic reaction involving light absorption by a catalyst or a substrate. Photocatalytic degradation has proven to be a promising technology for degrading various organic compounds including refractory chlorinated aromatics [12–16] and more than 1700 references have been collected on this discipline [17]. Compared with other conventional chemical oxidation methods, photocatalysis may be more effective because semiconductors are inexpensive and capable of mineralizing various refractory compounds [18]. Due to its capability of generating OH radicals, which is a powerful oxidant species, photocatalysis can be considered as an advanced oxidation process (AOP). However, photochemical AOPs are light induced reactions, mainly oxidations that rely on the generation of hydroxyl radicals by the combination with added oxidants or semiconductors. The degradation efficiency of photochemical AOPs is greatly enhanced using either homogeneous or heterogeneous photocatalysis [19]. Heterogeneous processes employ semiconductors slurries (e.g. TiO2/UV, ZnO/UV) for catalysis, whereas homogeneous photochemistry (e.g. H2O2/UV, Fe3+/UV) is used in a single-phase system.
Photocatalytic reactions occur when charge separation are induced in large bandgap semiconductor by excitation with ultra bandgap radiations [20]. In this way, the absorption of light by the photocatalyst greater than its bandgap energy excites an electron from the valence band of the irradiated particle to its conduction band, producing a positively charged hole in the valence band and an electron in the conduction band [21] as shown in Fig. 3. The hole in the valence band may react with water absorbed at the surface to form hydroxyl radicals and on the other hand, the conduction band electron can reduce absorbed oxygen to form peroxide radical anion that can further disproportionate to form OH• through various pathways [22]. During the photocatalytic process, other oxygen containing radicals are also formed including superoxided radical anion and the hydroperoxide radical [23]. In addition, the band electron may also react directly with the contaminant via reductive processes [24]. It is not clear under which experimental conditions, one reaction pathway is more important than the other.

It is generally accepted that the substrate adsorption in the surface of semiconductors plays an important role in photocatalytic oxidation [25]. Titanium dioxide (TiO2) is a semiconductor that absorbs light at λ < 385 nm with the corresponding promotion of an electron from the valence band to the conduction band. This excitation process leaves behind a positively charged vacancy called a hole (h+). The hole by itself is either a very powerful oxidizing agent or it may generate hydroxyl radicals in presence of water and molecular oxygen [26,27]. Unlike other semiconductors, TiO2 photocatalysts can function using sunlight as the energy source. Titanium dioxide is extensively used as photocatalyst due to its high chemical stability, optical and electronic properties [28].

Photocatalysis is a potential new method capable of eliminating relatively recalcitrant organic compounds [26,29]. This methodology is based on the production of electron-hole pairs by illumination with light of suitable energy, of a semiconductor powder such as TiO2 dispersed in an aqueous medium. These charges migrate to the particle surface and react with adsorbed species of suitable redox potential. In aerated media, adsorbed molecular oxygen accepts photogenerated electrons, while water molecules can react with photogenerated holes to produce hydroxyl radicals.

However, although photocatalysis has shown to be adequate for the destruction of a wide variety of compounds, in some cases the complete mineralization is slowly attained and the efficiency of the processes, in terms of energy consumption, is only advantageous for very dilute effluents [26]. To overcome this difficulty some additives such as H2O2, Fe2+, Fe3+, S2O82−, Ag+, etc., with different chemical roles have been added to the photocatalytic systems [9].

Furthermore, ozone can also be used for degradation of organic pollutants in water. Ozone is a powerful oxidant (electrochemical oxidation potential of 2.07 V versus 2.8 V for hydroxyl radical), which is generally produced by an electric discharge method in the presence of air or oxygen. Two reactions of ozone with dissolved organic substance can be distinguished in water: a highly selective attack of molecular ozone takes place on the organic molecules at low pH, whereas free radicals from ozone decomposition can also react non-selectively with the organic compounds [30]. Additional free hydroxyl radicals can be produced in the aqueous media from ozone by pH modification or can be introduced by combining ozone either with hydrogen peroxide or UV-irradiation from a high pressure mercury lamp [31].

On the other hand, the use of ozone for the destruction of organics in water is also a well-known water treatment technique. Unlike photocatalysis, ozonation, due to its capability for selective destruction of recalcitrant organics, is used as a pre-treatment step before ordinary biological techniques, thus being more efficient for highly contaminated wastewater. The simultaneous application of ozonation and photocatalysis has the capability for efficient treatment of organically contaminated waters over a wide range of concentrations [9]. A schematic diagram of a laboratory-scale set-up for photocatalysis ozonation is illustrated in Fig. 4.

3. Mechanism and kinetics

Photocatalytic oxidation and ozonation appear to be the most promising pre-treatment technologies compared with other advanced oxidation processes (AOPs) as shown by the large amount of information available in the literature. The principal mechanism of AOPs function is the generation of highly reactive free radicals.
Consequently, a combination of two or more AOPs enhances free radical generation, which eventually leads to higher oxidation rates.

Sanchez et al. [9] in their investigation, found that although the strategy of ozonation pre-treatment followed by photocatalysis would be a satisfactory route for aniline degradation, the simultaneous ozonation and photocatalysis methodology resulted in much higher total organic carbon (TOC) removal which, in spite of more energy and material demanding, could be preferred from an application point of view (see Table 1). In fact, besides the direct ozonation of the intermediate compounds, in the presence of TiO$_2$ under illumination, ozone can generate OH$^*$ radicals through the formation of an ozone radical (O$_3^*$) in the adsorption layer:

$$\text{TiO}_2 + hv \rightarrow e^- + h^+ \quad (1)$$
$$O_3 + e^- \rightarrow O_3^* \quad (2)$$

The generated O$_3^*$ species rapidly reacts with H$^+$ in the solution to give HO$_2^*$ radical, which evolves to give O$_2$ and OH$^*$ as shown in Eqs. (3) and (4) below:

$$O_3^* + H^+ \rightarrow HO_2^* \quad (3)$$
$$HO_2^* \rightarrow O_2 + OH^* \quad (4)$$

In photocatalysis, the hydroxyl radical is generally considered to be mainly responsible for the organic attack. It must be considered that the OH$^*$ radical can react with O$_2$

$$OH^* + O_3 \rightarrow O_2 + HO_2^* \quad (5)$$

in competition with aniline and the corresponding organic intermediates. Further, the O$_2^*$ species participates in a closed loop reaction scheme, which leads to a continuous consumption of ozone. In the absence of O$_3$, dissolved O$_2$ itself can accept TiO$_2$ conduction band electron and generate O$_2^*$ -

$$O_2 + e^- \rightarrow O_2^* \quad (6)$$

Which in turn can be protonated to form HO$_2^*$. In contrast with HO$_2^*$ (see Eq. (3)), this species cannot give OH$^*$ radicals in a single step and an alternative reaction pathway has been proposed to account for OH radical’s generation from HO$_2^*$:

$$2HO_2^* \rightarrow H_2O_2 + O_2 \quad (8)$$
$$H_2O_2 + O_2^* \rightarrow OH^* + HO^* + O_2 \quad (9)$$

This mechanism requires a total of three electrons for the generation of a single OH$^*$ species, which is a less favoured situation if compared with the one electron needed through the O$_3^*$ reaction pathway [9].

To get more information about the photocatalytic ozonation processes, Kopf et al. [32] measured the ozone decomposition by illumination in aqueous TiO$_2$ suspension in the absence of organic compounds. The solutions (pH 3) were saturated with ozone. After stopping the gas supply illumination was started.

It is obvious that the decomposition is accelerated by the application of titanium dioxide and appropriate light. The reaction depends on light intensity. If the light intensity is decreased, the ozone decomposition is also decreased. These results show that a real photocatalytic reaction occurs in the suspension, not the radiation alone but the combination of radiation and photocatalyst initiates a decomposition reaction of ozone. Another investigation by Kopf et al. [32] indicated that oxygen should have an influence on the photocatalytic ozonation. Besides other reaction paths, such as direct ozone attack (Eq. (29)), or direct electron transfer from TiO$_2$ to the ozone molecule (Eqs. (1)-(4)), a further possible reaction path is proposed [32].

Charge separation:

$$\text{TiO}_2 + hv \rightarrow e^- + h^+ \quad (10)$$

Charge transfer of positive charge:

$$h^+ + H_2O \rightarrow OH^* + H^+ \quad (11)$$

Electron transfer and further reactions:

$$e^- + O_2 \rightarrow O_2^* \quad (12)$$
$$O_2^* + H^+ \rightarrow HO_2^* \quad (13)$$
$$O_3 + O_2^* \rightarrow O_3^* + O_2 \quad (14)$$
$$O_2^* + H^+ \rightarrow HO_2^* \quad (15)$$
$$HO_2^* \rightarrow OH^* + O_2 \quad (16)$$

Oxidation of the organic compound R-H:

$$OH^* + R-H \rightarrow R^* + H_2O \quad (17)$$
$$\text{or}$$
$$OH^* + R \rightarrow R^* + OH \quad (18)$$

In reactions (13)-(16) the ozone decomposition according to the mechanism of Weiss [33] with the extension of Buhler et al. is described [34].

The difference between photocatalytic ozone decomposition and ozone decomposition in aqueous solution is the initiation of the reaction. The starting radical is formed photochemically by an electron transfer from titanium dioxide to oxygen and not, like in the Weiss mechanism, by the reaction of OH$^*$ with ozone. In both cases primarily O$_2^*$ is formed. O$_2^*$ reacts with ozone forming the ozonide ion (14). After protonation OH$^*$ radicals are formed ((15) and (16)). The formation of OH$^*$ radicals in acidic solutions via direct electron transfer from the catalyst to the ozone molecule or via O$_2^*$ explains the degradation of organic compounds by photocatalytic ozonation which react very slowly with the ozone molecule or with HO$_2^*$, one of the primary oxidising species in photocatalytic processes [32].

Furthermore, Wang et al. [10] indicated in their investigation that a synergistic effect occurred when the photocatalytic ozonation treatments are carried out simultaneously. Two possible mechanisms are considered for the synergistic effect. Firstly, it is considered that in the photocatalytic reactor, the dissolved
ozone was easy to get electrons produced on the surface of titanium dioxide according to the mechanism:

\[ \text{O}_3(\text{ads}) + e^- \rightarrow \text{O}_3(\text{ads}) \quad (19) \]

The recombination of electrons and positive holes could be interfered by the reaction between ozone and electrons on the surface of titanium dioxide. Consequently, a larger number of radicals are produced, thereby accelerating the photocatalytic reaction. Secondly, it is considered that a larger number of hydroxyl peroxide and hydroxyl radicals were produced from the dissolved ozone as a result of UV-irradiation [35]. In the ozonation under UV-irradiation, the hydroxyl radical is produced according to the following mechanism [10]:

\[ \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (20) \]

\[ \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^\cdot \quad (21) \]

\[ \text{H}_2\text{O}_2 \rightleftharpoons \text{HO}_2^- + \text{H}^+ \quad (22) \]

\[ \text{O}_3 + \text{HO}_2^- \rightarrow \text{O}_3^- + \text{HO}_2^* \quad (23) \]

\[ \text{HO}_2^* \rightarrow \text{O}_2 + \text{H}^+ \quad (24) \]

\[ \text{O}_3^- + \text{H}^+ \rightarrow \text{O}_3^- + \text{O}_2 \quad (25) \]

\[ \text{O}_3^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \text{OH}^\cdot \quad (26) \]

Recently, Farre et al. [36] suggested that for the photocatalytic ozonation system, the reaction also proceeded by radical attack to organic molecule. However, the OH radical is produced by (i) reaction of adsorbed H_2O molecule with photogenerated holes at the illuminated TiO_2 particle:

\[ \text{TiO}_2 + h\nu \rightarrow \text{h}^+ + \text{e}^- \quad (27) \]

\[ \text{H}_2\text{O} + \text{h}^+ \rightarrow \text{OH}^\cdot + \text{H}^+ \quad (28) \]

and (ii) by reaction of adsorbed O_3 and photogenerated electrons at the TiO_2 particles, namely reaction (1)–(4) above by Sanchez et al. [9]. The presence of dissolved ozone in the irradiated TiO_2 aqueous suspension increases the OH radical production and decreases the electron-hole recombination, increasing the efficiency of the photocatalytic process.

To date, a kinetic model based on Langmuir-Hinshelwood (L-H) equations adequately describes the reactivity results and provides the values of kinetic constant and equilibrium adsorption constant in the degradation of organic compound using photocatalytic ozonation methods [9,10,37-39].

Farre et al. found that the degradation processes follow zero order kinetics when photocatalytic ozonation is applied [36]. On the other hand, Beltran et al. [40] discovered that phenol removal obeyed first order kinetics. Other researchers, Balcioglu et al. [41] reported in their investigation which also employed the combined method, the decomposition modes follow pseudo-first order kinetics. And Li et al. [42] described in their experiments on photocatalysis ozonation process, the mineralization of dibutyl phthalate follows pseudo-zero order kinetics, as reported by Li et al. [43].

4. Intermediates detected

Intermediates are formed during the process of degradation. Table 1 shows that most of the researchers did not analyse for intermediates and focused mainly on the degradation rate of organics. Some of them analysed TOC with only a few mentioning the intermediates formed.

Regarding the intermediates, Muller et al. [44] got quite different results in the photocatalysis, ozonolysis and the combination of both methods in the treatment of 2,4-dichlorophenoxyacetic acid (2,4-D). They could identify 2,4-dichlorophenol (2,4-DCP), chlorohydroquinone (CHQ) and 1,2,4-trichlorobenzene (THB). While CHQ and THB are minor intermediates, 2,4-DCP is the main and long living intermediate in all three methods. In photocatalysis, the 2,4-DCP disappeared after a total running time of about 40 h. In ozonolysis, 2,4-DCP formed only in negligible amounts. In the combination approach, the maximum concentration of 2,4-DCP was only about 10% of the maximal level in photocatalysis and it vanished within 10–12 h, which is in about the same amount of time with the degradation of 2,4-dichlorophenoxyacetic acids.

Beltran et al. [40] reported the intermediates found in photocatalytic ozonation of phenols. Intermediate compounds formed can be classified into three categories. These categories are polyphenols (mainly hidroquinone), unsaturated carboxylic acids (mainly fumaric acid) and saturated carboxylic acids (mainly oxalic acid). Oxalic acid was the main end product that remained in water, especially during the oxidation of p-nitrophenol. Also, nitrogen as nitrate from p-nitrophenol and chloride from p-chlorophenol were detected in solution.

Other researchers did not analyse the intermediates without giving any particular reasons. However, the researchers used the advantage of ozonolysis, which results in no build up of high intermediates concentration.

5. Effect of ozone dosage

Li et al. [42] accounted the effect of ozone dosage in their research on photocatalytic ozonation of dibutyl phthalate over TiO_2 film. The addition of ozone considerably improved TOC removal compared to photocatalysis and ozonolysis near UV (UVO_3). After 30 min, TOC removal rate was over 75% when ozone dosage was over 25 mg/h, while only 73% using UVO_3 when ozone dosage was 50 mg/h. These results showed the synergistic effect of UVO_3, TiO_2/UV and TiO_2/O_3 [45-47]. When the semiconductor is in contact with water, the surface of TiO_2 is readily hydroxylated. Under near-UV illumination, electron-hole pairs are formed in the semiconductor, the oxidation potential of hydroxylated TiO_2 must lie above the position of the semiconductor valence band, and the oxidation of surface-bound OH^- and H_2O by TiO_2 valence band holes to form OH is thermodynamically possible and expected [48]. Thus the mineralization of dibutyl phthalate was accelerated.

Effect of ozone dosage was also examined by Li et al. [48] in their study on removing organic pollutants in secondary effluents using photocatalysis ozonation and subsequent biological activated carbon. They found that DOC removal efficiency
increased with ozone dosage. The total DOC removal efficiency increasing C=O double bonds, specific functional groups (e.g. OH, CH₂, OCH₃) and atoms carrying negative charge (N, P, O, S)

O₃ + R → Rox

where R is the organic solutes and Rox is the oxidised organic products. Compounds susceptible to ozonolysis are those containing C=O double bonds, specific functional groups (e.g. OH, CH₂, OCH₃) and atoms carrying negative charge (N, P, O, S).

At high pH value, ozone decomposes to non-selective hydroxyl radicals, which, in turn, attack the organic pollutants:

O₃ + OH⁻ → HO₂⁻ + O₂ + HO₂⁻ (29)

OH⁻ + R⁺ → R'ox

where R'ox is the oxidised organic products for radical-type reactions.

Therefore, the pH of the effluent is a major factor determining the efficiency of ozonation since it can alter degradation pathways as well as kinetics. Ozonation is usually coupled with another oxidant such as hydrogen peroxide or UV-irradiation to enhance the formation of hydroxyl radicals in aqueous phase.

Many researches found that increasing pH will accelerate ozone decomposition to generate OH radicals, which destroys the organic compounds more effectively than ozone does.

For the photocatalytic process, generally pH has a varied effect on the process and it is expected that increase or decrease in the pH should affect the rate of degradation as adsorption varies with pH. In the case of substances which are weakly acidic, the photocatalytic degradation increases at lower pH because of an increase in the adsorption. Some substances undergo hydrolysis at alkaline pH, which is one of the reasons for the increase in the photocatalytic degradation at alkaline pH values. At alkaline pH values, the concentration of OH⁻ radicals is relatively higher and this may also be another reason for the increase in the photocatalytic degradation rate. It can be concluded that the effect of pH is negligible so pH adjustment is not required in the photocatalytic degradation.

For the photocatalysis and ozonolysis, Muller et al. 44] found that neither the preference for low pH values of the photocatalysis nor that for high pH values for the ozonolysis could be better than the degradation rate obtained by simultaneous application of both methods at neutral pH values. The kinetic results showed that degradation at pH 7 using the combination approach is more than 1.5 times faster than the best result of ozonolysis at pH 11, and more than three times faster than the fastest degradation applying photocatalysis using the unbuffered set-up (pH 3.4–3.5).

Tong et al. 51] reported that the pH values for the degradation of sulfosalicylic acid solution by photocatalysis ozonation decreased firstly within a period of time and increased subsequently with the mineralization of intermediates. They found that the pH value in the system increased an initial pH of 2.2–2.8 for ozonation of 45 min.

7. Effect of pH

Ozone has many desirable oxidizing properties for use in wastewater treatment. Unlike other oxidants, there are two mechanisms through which ozone can degrade organic pollutants, namely (i) direct electrophilic attack (Eq. 29) and (ii) indirect attack through the formation of hydroxyl radicals (Eqs. (30)–(31)).[49] Direct attack by molecular ozone (commonly known as ozonolysis) occurs at acidic or neutral conditions and is a selective reaction resulting in the formation of carboxylic acids as end products that cannot be oxidized further by molecular ozone.

O₃ + OH⁻ → HO₂⁻ + O₂ + HO₂⁻ (29)

OH⁻ + R⁺ → R'ox (31)

where R'ox is the oxidised organic products for radical-type reactions.
into the rutile phase. Its specific area is 50 m² g⁻¹ with average particle size of 30 nm. The PC500-Millennium photocatalyst is made of only one crystallographic phase, anatase, with a specific area of 300 m² g⁻¹ which is much higher than P25 but with lower particle size of 5–10 nm. The mixed anatase/rutile P-25 Degussa is reported as the most efficient in their experimental condition. Crystalline phase contact between anatase and rutile in P-25 Degussa, as well as the crystallite size, was suggested to explain its efficiency [56]. Therefore Degussa P-25 is the most suitable photocatalyst. All the investigations reported here used Degussa P-25 TiO₂ for their study [9,29,36–40,57,58].

The photocatalyst derives its activity from the fact that when photons of certain wavelength strike its surface, electrons are promoted from the valence band and transferred to the conduction band. This leaves positive holes in the valence band, which can react with the hydroxylated surface to produce OH radicals. This leaves positive holes in the valence band, which can react with the hydroxylated surface to produce OH radicals. The used photocatalyst differs in their crystal composition: BDH specimen is pure anatase while P-25 is mixture of anatase and rutile [59].

Hernandez-Alonso et al. [37] tested two photocatalysts with known activity for cyanide photodegradation using photocatalysis ozonation method. Two commercial TiO₂ samples were used, that is Degussa P-25 (80% anatase, 20% rutile) and BDH TiO₂ (100% anatase). The synergetic effect of ozone and TiO₂ under irradiation is present in both TiO₂ samples; however, it is more pertinent with the BDH specimen than with the P-25. The enhancement of reactivity in the presence of ozone with respect to oxygen is related to the ability of ozone of trapping electrons and, therefore, it also depends on the availability of electrons in the photocatalyst. The used photocatalyst differs in their crystal composition: BDH specimen is pure anatase while P-25 is mixture of anatase and rutile. The higher BDH photocactivity is probably related to the lower band gap energy of the anatase sample that facilitates the electron trapping by ozone.

8. Economics aspects

The economic aspects of the different methods must be considered in light of the energy consumption for all of them. Photocatalytic ozonation needs additional electrical energy for the ozone generator. Therefore energy consumption of the three processes was compared according to consumption of electrical power (kWh) of the laboratory device under the experimental conditions.

Kopf et al. [32] calculated the energy consumption for the UV-lamp and ozone generator in their investigation on the photocatalytic ozonation of monochloroacetic acid and pyridine. They found that the energy consumption of the UV lamp and ozone generator was 0.046 and 0.018 kWh in 60 min, respectively. The energy consumption for DOC (dissolved organic carbon) decrease was compared for three methods, i.e. TiO₂O₂ (photocatalysis), H₂O/O₃ (ozonation) and TiO₂/O₃ (photocatalytic ozonation) and is shown in Table 2. The photocatalytic ozonation method resulted in much lower specific energy consumption than the other two alternatives.

9. Conclusion

It was shown that the photocatalytic oxidation in the presence of ozone is a process, which is qualitatively and quantitatively different from either the well-known photocatalytic oxidation with oxygen or ozonation without photocatalyst.

Five possible mechanisms are considered for the synergistic effect: (i) direct electron transfer from TiO₂ to the ozone molecule which generate OH radicals through the formation of an oxide radical (Eqs. (1)–(4)), (ii) electron transfer from TiO₂ to the oxygen molecule to form O₂•− radical, then O₂•− radical reacts with ozone to give OH radicals through the formation of an oxide radical (Eqs. (10)–(16)), (iii) a recombination of electrons and positive holes interfered by the reaction between ozone and electrons on the surface of titanium oxide, so a large number of radicals produced, thereby accelerating the photocatalytic reaction (Eq. (19)), (iv) production of hydrogen peroxide and OH radicals increased by UV-irradiation of ozone (Eqs. (20)–(26)), and (v) OH radicals produced by the reaction of absorbed H₂O molecule with photogenerated holes at the illuminated TiO₂ particle (Eqs. (27) and (28)).

The main problem of AOPs lies in the high cost of reagents such as ozone, hydrogen peroxide or energy source such as ultraviolet light. For the photocatalytic ozonation methods the energy demand of the O₃/TiO₂/UV could be considerably decreased by the use of solar-irradiation and in situ electrochemical O₃ generation. However, the use of solar radiation as an energy source can reduce costs.

The synergistic effect summarized in Table 1 showed the advantages of the application of photocatalytic ozonation method. Photocatalytic ozonation could be an effective alternative way for oxidation and elimination of recalcitrant organic compounds under specific conditions for the treatment of industrial wastewater.

Table 2: Photocatalytic ozonation of monochloroacetic acid, specific energy consumption (kWh/g DOC-reduction)

<table>
<thead>
<tr>
<th></th>
<th>TiO₂/O₂</th>
<th>H₂O/O₃</th>
<th>TiO₂/O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochloroacetic acid</td>
<td>19</td>
<td>110</td>
<td>5.4</td>
</tr>
<tr>
<td>Pyridine</td>
<td>120</td>
<td>73</td>
<td>11</td>
</tr>
</tbody>
</table>

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