Overview of the PCDD/Fs degradation potential and formation risk in the application of advanced oxidation processes (AOPs) to wastewater treatment

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A B S T R A C T

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are a family of unintentionally produced persistent organic pollutants (POPs) that have received considerable public and scientific attention due to the toxicity of some of their congeners, more specifically those with chlorine substitution in the 2,3,7,8 positions. The environmental management and control of PCDD/Fs is addressed at a global level through the Stockholm Convention that establishes that POPs should be destroyed or irreversibly transformed in order to reduce or eliminate their release to the environment. Several technologies, including advanced oxidation processes (AOPs) such as photolysis, photocatalysis and Fenton oxidation, have been considered as effective methods for destroying PCDD/Fs in polluted waters. Nevertheless, during the remediation of wastewaters it is critical that the treatment technologies applied do not lead to the formation of by-products that are themselves POPs, especially if PCDD/Fs precursors or chlorine are present in the reaction medium. Despite the high effectiveness of AOPs in the oxidation of major contaminants, scarce references deal with the monitoring of PCDD/Fs in the course of the oxidation process, revealing that a detailed assessment of non-combustion technologies with respect to PCDD/Fs formation is still lacking. This study reports a review of the state of the art related to the potential remediation and/or formation of PCDD/Fs as a result of the application of AOPs for the treatment of polluted waters, warning on the correct selection of the operating conditions.

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HIGHLIGHTS

• AOPs effectiveness in the degradation of PCDD/Fs containing wastewaters is reviewed.
• Photolysis based processes have been mostly applied for PCDD/Fs destruction.
• The formation of PCDD/Fs during the advanced oxidation of wastewaters is analyzed.
• Different AOPs led to PCDD/Fs formation in presence of their precursors.
• Low oxidant doses and chloride ions were key variables in PCDD/Fs formation.

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1. Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are a family of unintentionally produced persistent organic pollutants (POPs) characterized by their resistance due to the resistance to biological and chemical degradation, lipophilic nature that causes their biomagnification along food chains and various degrees of inherent toxicity (Fiedler, 2003; Van den Berg et al., 2006). Short term exposure to high levels of PCDD/Fs causes liver damage and chloracne (Marinković et al., 2010). Long term exposure is related with endocrinological, immunological, neurological, developmental, and reproductive effects (Srogi, 2008; Marinković et al., 2010). The U.S. EPA has regulated 2,3,7,8-TCDD as a carcinoagent based on the positive animal data and the compatible epidemiological findings of occupational exposure (Watanabe et al., 1998; U.S. EPA, 2000).

PCDD/Fs have never been produced intentionally but are released to the environment as unwanted byproducts from chemical-industrial processes like the production and use of chlorinated organic chemicals, and thermal or combustion sources where it is worth to mention the incineration of various types of wastes (Fiedler, 2003; Kulkarni et al., 2008). Since PCDD/Fs are persistent in the environment, and once emitted to the receiving environment atmospheric transport moves them away from their emission sources, they are able to remain in the environment for long times (Altarawneh et al., 2009; Lee et al., 2009). As a result, they can be transferred to other matrices called reservoirs which are considered a secondary source of PCDD/Fs. Reservoirs in the environment include landfills and waste dumps, contaminated soils and contaminated sediments (Weber et al., 2008, 2011; Götz et al., 2013). In addition, the formation of PCDD/Fs as a result of the biochemical treatment of precursors such as chlorophenols (CPs) (Oberg and Rappe, 1992) and during sewage sludge treatment (Oberg et al., 1993) has been reported. Besides, PCDD/Fs can be produced under certain natural conditions such as forest fires, volcanic eruptions and enzymatic or photolytic reactions of natural substrates.

PCDD/Fs can be formed by two fundamental pathways; on the one hand, they can be formed via the degradation of carbon species in the presence of a chlorine source and at temperatures in the range 200–600 °C, the so called “de novo synthesis” (Addink and Olie, 1995). On the other hand, PCDD/Fs can be formed via precursor compounds, which include compounds such as CPs, chlorobenzenes (CBzs), chlorinated diphenylethers (CDEs) and polychlorinated biphenyls (PCBs) (Weber, 2007). Among them, it is though that the most important and direct precursors are monocyclic aromatic compounds such as CPs and CBzs (Altarawneh et al., 2009). Two potent PCDD/Fs precursors are pentachlorophenol (PCP), used as fungicidal and bactericidal agent in wood and leather treatment, and polychlorinated phenoxy phenols (PCPPs), such as triclosan, which can be found as impurities in PCP (Holt et al., 2008). PCDD/Fs formation in the presence of their precursors is generally favored under alkaline conditions, heat (150–600 °C), with even ambient temperatures in the presence of catalysts, e.g. copper, iron, aluminum salts, or radicals, as well as during irradiation with UV light (Holt et al., 2012).

PCDD/Fs are ubiquitous contaminants in the environment and have been found throughout the world in all primary (air, soil, ambient water, sediment) and secondary (food including fish and shellfish, meat, dairy products, and consumer goods) media (Mukerjee, 1998). The environmental management and control of PCDD/Fs is addressed at a global level through the Stockholm Convention, which states for unintentionally POPs that measures have to be taken to reduce their total releases derived from anthropogenic sources, considering if possible their total elimination (Stockholm Convention, 2001). Several methods have been considered in the development of an efficient approach for destroying PCDD/Fs such as photoysis (Dung and O’Keefe, 1994), photocatalysis (Choi et al., 2000), ozonolysis (Vollmuth and Niessner, 1997), Fenton based oxidation (Katsumata et al., 2006), supercritical water treatment (Sako and Sugeta, 2000), radiolysis (Hilarides and Gray, 1994) and biodegradation (Field and Sierra-Alvarez, 2008).

In spite of their low water solubility, PCDD/Fs have been found in the aquatic environment, where they enter mainly from atmospheric deposition, the use of agricultural chemicals and as direct discharges from industrial sources and sewage treatment plants among others (Kim et al., 2002). Therefore, effective and simple wastewater treatments for the removal of PCDD/Fs from contaminated water is required urgently for proper environmental management (Katsumata et al., 2006; Lee et al., 2009). Advanced oxidation processes (AOPs) are oxidative methods based on the generation of intermediate radicals, mainly hydroxyl radicals (OH), that have been successfully applied in wastewater treatment to degrade many organic compounds (Pera-Titus et al., 2004). The destruction of PCDD/Fs as a result of the application of several AOPs to the treatment of polluted waters has been reported in the literature. Although some AOPs such as supercritical water oxidation have proved to have good potential remediation (Zhao et al., 2014), more research is needed in order to make the process more realistic in terms of energy consumption and investment (Gogate and Pandit, 2004; Kulkarni et al., 2008). Therefore, this study focuses in AOPs that have been studied more in depth, especially in wastewater remediation such as photoysis, photocatalysis and Fenton oxidation among others. In particular, photocatalysis, which is probably the major degrading mechanism from the total environment (Kietavisong et al., 1990), has been one of the most applied AOPs for PCDD/Fs remediation showing good results (Friesen et al., 1990, 1996).

Nevertheless, the partial oxidation of organic contaminants during the remediation of wastewaters may produce transformation products being more toxic than their parent compounds (Fatta-Kassinos et al., 2011; Homem and Santos, 2011). Therefore, one important criterion to take into account in the assessment of treatment technologies is the potential formation of POPs and other toxic by-products, concretely if the highly toxic PCDD/Fs
Table 1
Summary on the application of AOPs for PCDD/Fs degradation.

<table>
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<th>References</th>
<th>Main operating conditions</th>
<th>Matrix</th>
<th>Summary of main results</th>
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<tbody>
<tr>
<td>Dulin et al. (1986)</td>
<td>Photolysis: solar and UV (313 nm) [2,3,7,8-TCDD]₀ = 116.23 μg L⁻¹ (hexane); 108.2 μg L⁻¹ (water–AcN) [2,3,7-TrCDD]₀ = 49.17 μg L⁻¹ (hexane)</td>
<td>Water-acetonitrile (AcN) (90:10)</td>
<td>UV – Water–acetonitrile solution: – 62% conversion of TCDD after 24 h – Hexane solution: – 66% conversion of TCDD after 4 h – 61% conversion of 2,3,7-TrCDD after 70 h Solar irradiation – Water–acetonitrile solution: – 49% conversion of TCDD after 26 h</td>
</tr>
<tr>
<td>Sixten et al. (1990)</td>
<td>Photolysis: solar [1,2,3,4,7,8-HpCDD]₀ = 2.1 μg L⁻¹ (water–AcN)</td>
<td>Natural water</td>
<td>Natural waters – 1,2,3,4,7-PeCDF: 98% conversion after 5.25 d. Half live of 0.94 d – 1,2,3,4,6,7,8-HpCDD: 94.4% conversion after 10.21 d. Half live of 2.5 d</td>
</tr>
<tr>
<td>Dung and O’Keeffe (1994)</td>
<td>Photolysis: solar and UV (300 nm) [PCDFs]₀ = 1 mg L⁻¹</td>
<td>Hexane</td>
<td>Photodegradation was inversely related to the degree of chlorination – Rate constants increased as the chlorination level of PCDD/Fs – Photocatalytic process – The rate of the single catalyst system was higher than that of the coupled catalyst system – Photodegradation was enhanced by initiating indirect photo-reactions with organic contaminants – Photocatalysis – Degradation rates decreased with increasing degree of chlorination – Rates in natural water were higher than in distilled water – Cleavage of C–O bond was found as alternative pathway in water – UV</td>
</tr>
<tr>
<td>Friesen et al. (1996)</td>
<td>Photolysis: solar [2,3,7,8-TCDF]₀ = 2.3 μg L⁻¹ (Natural water), 2.1 μg L⁻¹ (water–AcN) [2,3,4,6,7,8-HpCDF]₀ = 1.8 μg L⁻¹ (Natural water), 2.7 μg L⁻¹ (water–AcN)</td>
<td>Water–AcN (2:3, v/v)</td>
<td>UV – Rate constants of 2,7-DCDF, 2,3,7,8-TCDF and 1,2,7,8-TCDF were in the order: natural water &gt; pure water &gt; hexane &gt; methanol &gt; 60% AcN–water – 56% conversion of 2,3,7,8-TCDF after 6 h – 56% conversion of 2,3,7,8-TCDF after 6 h – Photodegradation was enhanced by initiating indirect photo-reactions with organic contaminants – Photodegradation was inversely related to the degree of chlorination – Reductive dechlorination was the dominant pathway in organic solvents – Cleavage of C–O bond was found as alternative pathway in water</td>
</tr>
<tr>
<td>Kim and O’Keeffe (2000)</td>
<td>Photolysis: solar and UV (300 nm) [PCDD/Fs]₀ = 30 μg</td>
<td>Water</td>
<td>Natural waters – Water–AcN: rate constants increased with the degree of chlorination – Half-lives of 6.3 d for 2,3,7,8-TCDF and 46.2 d for 2,3,4,7,8-PeCDF – Natural water: rate constants increased with the degree of chlorination – Half-lives of 1.2 d for 2,3,7,8-TCDF and 0.19 d for 2,3,4,7,8-PeCDF – 89% conversion of 2,3,4,7,8-PeCDF after 6 h – 56% conversion of 2,3,7,8-TCDF after 6 h – Photodegradation was enhanced by initiating indirect photo-reactions with organic contaminants</td>
</tr>
<tr>
<td>Wu and Ng (2008)</td>
<td>Photolysis: UV (300–400 nm; 6.33 mW cm⁻²) Photocatalysis: coupled ZnO/SnO₂ catalyst [PCDF/Fs]₀ = 50 ng</td>
<td>Synthetic standard solution containing 2,3,7,8-PCDD/Fs</td>
<td>UV: degradation rates decreased with increasing degree of chlorination. PCDDs rate constants were higher than those from UV light due to the fact that light intensity in UV experiments was 10 times bigger. Rate constants of congeners 1,2,7,8-TCDD and OCDF were higher than the corresponding for 1,2,3,4,6,7,8-HpCDF</td>
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<td>Koester and Hites (1992)</td>
<td>Photolysis: UV (17.4 Wm⁻²) [PCDF/Fs]₀ = 100 ng</td>
<td>Silica gel</td>
<td>Photolysis – Rate constants increased as the chlorination level of PCDD/Fs increased – PCDF/Fs were higher than those for PCDDs</td>
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<td></td>
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<td>Fly ash</td>
<td>Photocatalysis – Degradation rates decreased as the chlorination level of PCDD/Fs increased – The rate of the coupled catalyst system was higher than that of the single catalyst system – The rate of direct photolysis was lower than the rate of the photocatalytic process</td>
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<td>Silica gel – PCDF/Fs half-lives were in the range 3–270 h and increased with increasing levels of chlorination. Rate constants of PCDFs were higher than those for PCDDs</td>
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<td>Fly ash – No PCDD/Fs photodegradation was depicted after 200 h – the organic material and the particle’s surface inhibited the photodegradation</td>
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<td>Table 1 (continued)</td>
<td>References</td>
<td>Main operating conditions</td>
<td>Matrix</td>
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<td>Niu et al. (2003)</td>
<td>Photolysis: solar</td>
<td>TiO₂ film on a glass plate</td>
<td>• Rate constants decreased with the degree of chlorination and were lower than those in natural waters and organic solvents. Rate constants of PCDFs were higher than those of PCDDs. • Degradation rates of PCDD/Fs on spruce needles were faster than on fly ashes and in air.</td>
</tr>
<tr>
<td>Kreatiwong et al. (1990)</td>
<td>Photolysis: UV (310 nm) Isooctane solution: [2,3,7,8-TCCDD]o = 1 mg L⁻¹ [2,3,7-tri(CDD)]o = 0.4 mg L⁻¹ Soil: [2,3,7,8-TCCDD]o = 0.2 mg Kg⁻¹ (OCDD) = 10 mg Kg⁻¹</td>
<td>Isooctane solution</td>
<td>• Isooctane solution – 90% of degradation for 2,3,7,8-TCDD after 21 min – Lateral chlorines, positions 2,3,7,8, were preferentially lost – Soil • 45% of degradation for 2,3,7,8-TCDD after 15 d – Longitudinal chlorines, positions 1,4,6,9, were preferentially lost.</td>
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<tr>
<td>Muto et al. (2001)</td>
<td>Photocatalysis: UV (400W; TiO₂) [PCDDs]o = 2.1 mg L⁻¹ [PCDFs]o = 0.25 mg L⁻¹</td>
<td>AcN–water solution</td>
<td>• PCDD/Fs photodegraded more than 70% after 24 h (half lives in the range 7.92 × 10⁻²–0.1 d). The degradation rate increased as the chlorination level of PCDD/Fs increased • Dechlorination efficiencies of 76% for PCDDs and 100% for PCDFs after 24 h were achieved</td>
</tr>
<tr>
<td>Choi et al. (2000)</td>
<td>Photolysis: UV (254 nm and &gt;300 nm) and solar Photocatalysis: UV (254 nm; TiO₂) and solar</td>
<td>TiO₂ film on a glass plate</td>
<td>• UV irradiation – Direct photolysis (λ &gt; 254 nm): PCDDs were degraded around 38.5% after 15 h – Direct photolysis (λ &gt; 300 nm): no PCDDs degradation – Photocatalysis: 85% conversion of PCDDs within 15 h of irradiation • Sunlight irradiation – Direct photolysis (λ &gt; 300 nm): no PCDDs degradation – Photocatalysis: similar PCDDs degradation than with direct photolysis. The PCDDs degradation rates decreased with chlorine and increased with light intensity and TiO₂ coating mass up to 2 mW cm⁻² (300 &lt; λ &lt; 400 nm) and 200 µg cm⁻¹ TiO₂ coated mass.</td>
</tr>
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<td>Wu et al. (2004)</td>
<td>Photocatalysis: UV (300–450 nm; 6.33 mW cm⁻²; TiO₂, ZnO and SnO₂ catalysts) [1,2,3,6,7,8-HxCDD; OCl] = 50 ng</td>
<td>TiO₂, ZnO and SnO₂ film coated on a quartz plate</td>
<td>• The degradation rate decreased as the number of chlorines increased • The immobilized catalyst provided two orders of magnitude higher reaction rates than direct photolysis. Rate constants followed next order: UV/TiO₂ &gt; UV/ZnO &gt; UV/SnO₂ &gt; UV &gt; sunlight</td>
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<tr>
<td>Wu et al. (2005)</td>
<td>Photocatalysis: UV (300–400 nm) Photocatalysis: UV (300–400 nm; TiO₂) [2,3,7,8-TCCDD; 1,2,3,6,7,8-HxCDD]o = 50–2000 ng</td>
<td>2,3,7,8 TCDD and 1,2,3,6,7,8-HxCDD immobilized on TiO₂/solid phase</td>
<td>• Photocatalytic process: 81.57% conversion of 1,2,3,6,7,8-HxCDD. Formation of 2,3,7,8-substituted congeners by-products. • Photocatalytic process: 85% conversion of 1,2,3,6,7,8-HxCDD and 2,3,7,8-TCCDD. No 2,3,7,8-substituted congeners were detected. The degradation rate decreased as the chlorination level of PCDD/Fs increased</td>
</tr>
<tr>
<td>Vollmuth and Niessner (1997)</td>
<td>UV (254 nm)/O₂ (960 mg h⁻¹) [PCP]o = 5 mg L⁻¹</td>
<td>Aqueous solution containing technical PCP (PCDD/Fs as impurities of PCP)</td>
<td>• Degradation of high chlorinated PCDD/Fs was shown • Increasing in low chlorinated PCDD/Fs concentration during the first 2 min, being degraded afterwards</td>
</tr>
<tr>
<td>Wenzel et al. (1999)</td>
<td>UV (80 mW cm⁻²)/O₂ (100 g m⁻³) [PCDFs]o = 2.8–6758 ng L⁻¹</td>
<td>• Aqueous solution containing technical PCP (PCDD/Fs as impurities of PCP) • Landfill leachate</td>
<td>• 100% removal of chlorinated phenols and PAHs, 23–96% for PCBs and at least 74% for PCDD/Fs</td>
</tr>
<tr>
<td>Katsumata et al. (2007)</td>
<td>Ultrasonic/UV/Fe⁷⁺: ultrasonic power = 0–150 W UV = 0–2 mW cm⁻² Fe⁷⁺ = 0–11.2 mg L⁻¹ [2,3,7,8-TCCDD]o = 20 ng L⁻¹</td>
<td>Aqueous solutions</td>
<td>• 2,3,7,8-TCDD degradation percentage after 30 min: – Ultrasonic/UV/Fe⁷⁺: 100% – Ultrasonic: 93% – UV/Fe⁷⁺: 87% – UV: 16% • The rate constant in ultrasonic/UV/Fe⁷⁺ system was four times greater than that in the ultrasonic system</td>
</tr>
<tr>
<td>Katsumata et al. (2006)</td>
<td>Photo-Fenton: Fe⁷⁺ = 0–5.6 mg L⁻¹ H₂O₂ = 0–34 mg L⁻¹ UV &lt; 300 nm [PCDDs]o = 10 ng L⁻¹</td>
<td>Aqueous solutions</td>
<td>• After 20 min: complete degradation of 2,3,7,8-TCCDD • After 120 min: Penta- to Hexa-CDD were completely degraded • After 300 min: not complete degradation of HpCDD and OCDD • Degradation rates decreased as the number of chlorines increased</td>
</tr>
<tr>
<td>Lee et al. (2009)</td>
<td>Fenton: Fe⁷⁺ = 5 mg L⁻¹ (Fisher iron); Fe⁷⁺ = 5.2 mg L⁻¹ (steel dust iron); H₂O₂ = 3 mg L⁻¹ [PCDDs]o = 250 ng L⁻¹</td>
<td>Aqueous solutions</td>
<td>• Removal of 2,3,7,8-TCCDD with both catalyst. • OCCD removal only with Fisher iron • Accumulation of 1,2,3,7,8-PeCDD in the system</td>
</tr>
</tbody>
</table>
| Tuhkanen (2001) | Ozonolysis: Fenton: Fe⁷⁺ = 46 g Kg⁻¹ H₂O₂ = 34 mL (30%) [PCDD/Fs]o = 200–300 ng Kg⁻¹ 1-TEQ | Aqueous solutions | • Ozonolysis – The PCDD/Fs removal percentage was between 10% and 75% – The PCDDs degradation was higher than that for PCDFs – The degradation was higher for high chlorinated PCDD/Fs congeners • Fenton – The PCDD/Fs removal percentage was between 0 and 58% – The PCDDs degradation was higher than that for PCDFs (continued on next page)
are formed and under which operation conditions their formation is relevant (Weber, 2007). Whereas the evaluation of PCDD/Fs emissions together with their formation mechanisms in combustion processes have been studied in depth, a detailed assessment of PCDD/F formation in non-combustion technologies is more limited (Weber, 2007). Although scarce, there are some works where PCDD/Fs formation for a number of advanced oxidation technologies has been reported if their precursors are present (Vollmuth et al., 1994; Holt et al., 2012; Vallejo et al., 2013b). Nevertheless, deep knowledge regarding the formation of PCDD/Fs during the application of AOPs for the abatement of chlorinated organic compounds considered as potential PCDD/Fs precursors is still lacking to date.

In this manuscript, the progress based on already reported scientific literature regarding the capacity for PCDD/Fs remediation of different AOPs during the treatment of aqueous samples containing these compounds is reviewed in the first part. Moreover, an overview of the state of the art related to the potential formation of PCDD/Fs as consequence of the advanced oxidation of aqueous solutions containing PCDD/Fs precursors is offered in the second section. The cases described throughout the text are summarized at the end of the document in Tables 1 and 2.

2. Advanced oxidation technologies used for the destruction of PCDD/Fs

Several AOPs have been considered in the development of an efficient and economically feasible approach for destroying PCDD/Fs such as photolysis (Dung and O’Keefe, 1994), photocatalysis (Choi et al., 2000) and ozonolysis (Vollmuth and Niessen, 1997). Below an overview regarding the PCDD/Fs destruction capacity of different AOPs when were applied for their abatement, mainly in aqueous samples, is shown.

### 2.1. Photolysis

Photolytical processes have been considered as an efficient technique for the elimination of PCDD/Fs (Colombini et al., 1996; Choi et al., 2000; Niu et al., 2003; Wu et al., 2005; Wu and Ng, 2008). Sunlight photolysis is probably the major degrading mechanism for removal of chlorinated dioxins from the total environment (Friesen et al., 1990; Kieatiwong et al., 1990) since the absorption spectra of many PCDD/Fs congeners overlap the solar spectrum incident on the earth’s surface (Koester and Hites, 1992; Kim and O’Keefe, 2000).

PCDD/Fs can react photochemically by reaching an excited state through the direct absorption of light (direct photolysis) or by reactive oxygen species such as OH· formed from water and other dissolved organic molecules (DOM), Fig. 1 (Kim and O’Keefe, 2000). Generally degradation via OH· addition is the most important mechanism for photolysis and photocatalysis of POPs (Wu and Ng, 2008).

There are several studies that report the photolytic treatment of PCDD/Fs in aqueous and organic solutions. In this way, Dulin et al. (1996) performed the photolysis of 2,3,7,8-TCDD and 2,3,7-TrCDD using hexane and a mixture of water–acetonitrile (AcN) (90:10) as solvents under sunlight and UV irradiation (313 nm). With water–AcN solutions, they found TCDD conversion percentages of 62% and 49% after 24 h of treatment, with rate constants of 1.26 and 0.60 d⁻¹ under UV and sunlight respectively. In hexane solution, 65% of TCDD conversion was achieved after 4 h of irradiation with a rate constant value of 6.58 d⁻¹ under UV light. Finally, in the same solution, 61% of the congener 2,3,7-TrCDD was converted after 70 h of UV irradiation with a rate constant value of 17.54 d⁻¹.

Friesen et al. (1990) investigated the sunlight photodegradation of 1,2,3,4,7-PeCDD and 1,2,3,4,6,7-HpCDD in natural waters and distilled water–AcN solutions (2:3, v/v). They found photolysis rates 15 times slower in water–AcN solutions than in natural water. Such result indicated that chemicals in natural waters catalyzed the photolysis of PCDD/Fs by direct photosensitization or by indirect photoreactions. The involvement of sensitized photolysis was observed by the same authors, Friesen et al. (1996), in a different work where they studied the photolysis of two PCDF congeners, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF, in water–AcN solutions (2:10, v/v) and natural water under midsummer sunlight conditions. They found that the rate constant increased with the degree of chlorination.

On the other hand, Dung and O’Keefe (1994) studied the photodegradation of 2,7-DCDF, 2,3,7,8-TCDF and 1,2,7,8-TCDF in aqueous solutions and/or organic solvents by UV (300 nm) and sunlight irradiations. In a later research, Kim and O’Keefe (2000) completed the previous work through the photodegradation of PCDD/Fs in pure water and organic solvent/water mixture under the same conditions. Using UV irradiation, rate constants of PCDFs isomers were found to be higher than PCDDs in water solutions and vice versa in organic mixtures, since PCDFs are more polarized than PCDDs and then they should be more reactive in pure water than in less polar solutions. Results showed that photodegradation was inversely related to the degree of chlorination, thus the degradation rates decreased as the chlorine substituents increased, contrary to what was shown by Friesen et al. (1996). It could be explained due to the fact that the presence of bulky chlorine substituents on the aromatic ring sterically hinders the attack of OH·, and the decrease in the electron density with the number of chlorines decreased the reaction rate of electrophilic addition of OH· (Choi et al., 2000). Under sunlight conditions and working with natural waters, the authors found that PCDD/Fs half-lives were longer than those from UV light because the light intensity in UV experiments was 10 times higher than with sunlight in the region where PCDD/Fs absorb (300–318 nm). In general, the photodegradation was higher in natural water than in pure water.
Table 2
Summary of the formation of PCDD/Fs during the advanced oxidation treatment of wastewaters.

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<th>AOP Matrix</th>
<th>Summary of main results</th>
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<td>Photolysis based processes</td>
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<tr>
<td>Vollmuth et al. (1994)</td>
<td>Photolysis: UV (254 nm) [PCP]₀ = 1 mg L⁻¹ (purified); 0.092 mg L⁻¹ (technical)</td>
<td>• Synthetic waters containing purified and technical PCP and seepage water from a landfill</td>
</tr>
<tr>
<td>Vollmuth and Niesner (1995)</td>
<td>Photolysis: UV (254 nm)/O₂ (960 mg h⁻¹)</td>
<td>• Seepage water from a landfill</td>
</tr>
<tr>
<td>Hong et al. (2000)</td>
<td>Photolysis: UV [PCP]₀ = 5 mg L⁻¹ Photolysis: UV (λ &gt; 370 nm, 1800 μW cm⁻²) Fe³⁺ = 560 mg L⁻¹ HA = 50 mg L⁻¹</td>
<td>• Reagent water containing PCP</td>
</tr>
<tr>
<td>Fukushima et al. (2000)</td>
<td>Photolysis: solar [PCN]₀ = 30 g [2,4-D]₀ = 24 g</td>
<td>• Aqueous solution containing PCP, Fe³⁺ and HA</td>
</tr>
<tr>
<td>Holt et al. (2012)</td>
<td>Photolysis: solar</td>
<td>• Liquid formulation: 2,4-dichlorophenoxyacetic acid</td>
</tr>
<tr>
<td>Mezcua et al. (2005)</td>
<td>Photolysis: UV (254-236 nm) Photocatalysis: UV (254 nm)/TiO₂</td>
<td>• Solid formulation: pentachloronitrobenzene</td>
</tr>
<tr>
<td>Yu et al. (2006)</td>
<td>Photocatalysis: UV (254 nm)/TiO₂</td>
<td>• Reagent water and wastewater from an urban wastewater treatment plant spiked with TCS</td>
</tr>
<tr>
<td>Aranami and Readman (2007)</td>
<td>Photolysis: artificial white light</td>
<td>• Pure water, fresh water and sea water spiked with TCS</td>
</tr>
<tr>
<td>Lores et al. (2005)</td>
<td>Photocatalysis: UV (254 nm) [Tricosan]₀ = 1 mg L⁻¹</td>
<td>• SPME fiber coating and pure water spiked with TCS</td>
</tr>
<tr>
<td>Sanchez-Prado et al. (2006)</td>
<td>Photocatalysis: UV (254 nm; 550 W m⁻²) and simulated sunlight irradiation</td>
<td>• Wastewater from a sewage treatment plant</td>
</tr>
<tr>
<td>Sankoda et al. (2011)</td>
<td>Photocatalysis: UV (TiO₂)</td>
<td>• SPME fiber coating from wastewater extraction</td>
</tr>
<tr>
<td>Fenton based processes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fukushima and Takumi (2001)</td>
<td>Photo-Fenton: UV (λ &lt; 370 nm) Fe³⁺ = 5.6 mg L⁻¹ HA = 50 mg L⁻¹</td>
<td>• Reagent water containing TCS</td>
</tr>
<tr>
<td>Poerschmann et al. (2009)</td>
<td>Fenton: H₂O₂ = 1.1375.9 mg L⁻¹ Fe³⁺ = 61.6 mg L⁻¹ [2-CPP]₀ = 500 mg L⁻¹</td>
<td>• Formation of 2,8-DCDD: [2,8-DCDD]max = 0.25 μg L⁻¹ after 120 min</td>
</tr>
<tr>
<td>Munoz et al. (2011)</td>
<td>Fenton-like: H₂O₂ = 299.2 mg L⁻¹ Fe³⁺ = 10 mg L⁻¹ [4-CPP; 3-CP; 2-CPP]₀ = 2000 mg L⁻¹</td>
<td>• H₂O₂/Fe³⁺ system: OCDD was formed at pH 5 (Not observed at pH 3)</td>
</tr>
<tr>
<td>Muñoz et al. (2012)</td>
<td>Fenton-like: H₂O₂ = 20% of the stoichiometric value Fe³⁺ = 10 mg L⁻¹ [2,4,5-TCP]₀ = 2000 mg L⁻¹ [2,6-DTCP]₀ = 900 mg L⁻¹ [2,4,4-TCP]₀ = 500 mg L⁻¹</td>
<td>• H₂O₂/Fe³⁺/HA system: not formation of OCDD was observed</td>
</tr>
<tr>
<td></td>
<td>Fenton-like: H₂O₂ = 20% of the stoichiometric value Fe³⁺ = 10 mg L⁻¹ [2,4,DCP; 3,5- DCP]₀ = 2000 mg L⁻¹</td>
<td>• Formation of chlorinated benzenediols (≤ 71 μg L⁻¹), hydroxylated chlorobiphenyls (≤ 53 mg L⁻¹), hydroxylated chloro- diphenyl ethers (≤ 7.1 mg L⁻¹) and hydroxylated chlorinated benzeno- furans (≤ 11 mg L⁻¹)</td>
</tr>
<tr>
<td></td>
<td>Fenton-like: H₂O₂ = 20% of the stoichiometric value Fe³⁺ = 10 mg L⁻¹ [2,4,5TCP]₀ = 500 mg L⁻¹ [2,4,6-TCP]₀ = 100 mg L⁻¹</td>
<td>• Formation of chlorinated diphenyl ethers, biphenyls and dibenzofurans working with substoichiometric H₂O₂ doses and low iron quantities. Under these conditions, the toxicity of the sample increased related to the untreated solution</td>
</tr>
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(continued on next page)
adsorbed on silica gel and fly ashes by UV light (Niu et al., 2003), who reported sunlight photodegradation of increasing levels of chlorination. The same behavior was observed degraded faster than PCDDs and their half-lives increased with inhibited the photodegradation of PCDD/Fs. Generally, PCDF organic material on fly ashes, as well as the particles surface itself, exposure to light. The authors concluded that the presence of ica gel, degradation rates followed first order kinetics with easy Hites (1992) investigated the photodegradation of PCDD/Fs instead of enhancing the photolysis by indirect photoreactions. It could be explained by the presence of additional co-extracted organic compounds, which can retard the direct photolysis rate instead of enhancing the photolysis by indirect photo-reactions.

Works related to the photolysis of PCDD/Fs adsorbed on solid surfaces have been also reported in the literature. Koester and Hites (1992) investigated the photodegradation of PCDD/Fs adsorbed on silica gel and fly ashes by UV light (≈300 nm). On silica gel, degradation rates followed first order kinetics with easy removal due to their white color and reflective surface, whereas on fly ash PCDD/Fs were not photo-degraded even after 200 h of exposure to light. The authors concluded that the presence of organic material on fly ashes, as well as the particles surface itself, inhibited the photodegradation of PCDD/Fs. Generally, PCDF degraded faster than PCDDs and their half-lives increased with increasing levels of chlorination. The same behavior was observed by Niu et al. (2003), who reported sunlight photodegradation of PCDD/Fs adsorbed on spruce needles. Rate constants were lower than in natural waters or organic solvents and faster than on fly ashes and air (Podoll et al., 1986; Koester and Hites, 1992).

Wu and Ng (2008) reported the direct photolysis of PCDD/Fs using a synthetic standard solution and an ash-extracted solution from the bag filter of an electric arc furnace. In general, they showed that PCDDs were more resistant to photodegradation than PCDFs. In addition, half-lives decreased as the chlorination level of PCDD/Fs increased in agreement with Friesen et al. (1996), highlighting the fact that the photolysis of low chlorinated PCDD/Fs could be inhibited since they could be formed and accumulated via dechlorination of high chlorinated PCDD/Fs. Furthermore, the rate of PCDD/Fs photolysis in the ash-extracted was lower than in the standard solution. It could be explained by the presence of additional co-extracted organic compounds, which can retard the direct photolysis rate instead of enhancing the photolysis by indirect photo-reactions.

Since sunlight photolysis is considered one of the major mechanisms for the degradation of PCDD/Fs from the total environment, it has led to a large number of works dealing with their photochemical remediation. Nevertheless, most of them have been carried out on a laboratory scale and with standard solutions. Therefore, more research related to their application for real wastewaters remediation is still needed before their application at larger scale.

2.2. Photocatalysis

Photocatalysis is highly promising because it can operate at ambient temperature and pressure with low energy photons, does not require expensive catalysts, and can use natural sunlight
Photocatalytic treatment method is based on the formation of electrons in the conduction band and positive holes \((h^+\)) in the valence band when the photocatalyst is subjected to radiation. The positive hole oxidizes either the pollutant directly or water to produce \(\text{OH}^\cdot\), whereas the electron in the conduction band reduces the oxygen adsorbed on the photocatalyst. Fig. 2 (Ahmed et al., 2011). Suppressing the recombination of electron–hole pairs is an important consideration in enhancing photocatalysis. This can be achieved by the addition of \(\text{H}_2\text{O}_2\), which as well as oxygen, can scavenge the excited electrons and be reduced to \(\text{OH}^\cdot\) (Yu et al., 2006).

Muto et al. (2001) reported the photocatalytic degradation of PCDD/Fs in an acetonitrile–water solution using a TiO\(_2\) thin film. PCDD/Fs were photodegraded more than 70% after 24 h of irradiation. Degradation of low chlorinated PCDD/Fs was slower than that of high chlorinated ones, as shown by Friesen et al. (1996) and Wu and Ng (2008), and possibly explained by the sequential photodechlorination of highly chlorinated congeners. Rate constants were in the order of 6.91–8.78 \(\text{d}^{-1}\) and half-lives of 7.92 · 10\(^{-2}\)–0.1 d assuming pseudo first-order reactions for low levels of PCDD/Fs.

Choi et al. (2000) studied the photocatalytic degradation of several PCDDs congeners on TiO\(_2\) films under UV or solar irradiation. Under UV irradiation, in the absence of TiO\(_2\), direct photolysis was noticeable at \(\lambda \approx 254\) nm (\(\approx 38.3\%\) degradation), whereas it was negligible at \(\lambda > 300\) nm. In presence of TiO\(_2\) catalyst, the photocatalytic degradation resulted in 85% conversion within 15 h of irradiation. With sunlight illumination, no direct photolytic degradation was observed, whereas the use of the catalyst depicted overall degradation efficiencies similar to the UV lamp. The PCDDs degradation rates, described by first-order kinetics, decreased with increasing chlorine atoms number and increased with light intensity and TiO\(_2\) coating mass.

In other work, Wu et al. (2004) evaluated the photodegradation of 1,2,3,6,7,8-HxCDD and OCDD under UV light (300–450 nm) using three different catalysts, TiO\(_2\), ZnO and SnO\(_2\), immobilized on quartz. The same authors, Wu et al. (2005), in a later research, investigated the degradation of 2,3,7,8-TCDD and 1,2,3,6,7,8-HxCDD by direct photolysis and photocatalysis on TiO\(_2\) film with UV light. In addition, Wu and Ng (2008) evaluated the photocatalytic degradation of 1,2,3,6,7,8-HxCDD and OCDD using a coupled catalyst of ZnO and SnO\(_2\). In all studies the degradation rate was higher than the direct photolysis, and decreased as the chlorination level of the congeners increased, implying that higher chlorinated PCDD/Fs are less susceptible to photodegradation accordingly to what was previously reported (Kim and O’Keefe, 2000; Choi et al., 2000). In the work of Wu et al. (2005), 2,3,7,8-PCDD/Fs were not detected as photocatalytic byproducts, thus another pathway involving C–O cleavage might be more important than reductive dechlorination during this process. However, two of these congeners, 2,3,7,8-TCDD and 1,2,3,7,8-PCD, formed by reductive dechlorination of longitudinal chlorine atoms, were detected during the direct photolysis process of 1,2,3,6,7,8-HxCDD.

2.3. Photolysis/ozonolysis

O\(_3\) is widely used in water treatment as disinfectant and oxidant. The transformation of organic compounds with O\(_3\) can occur via direct reaction or with \(\text{OH}^\cdot\) that result from O\(_3\) decay in water (von Gunten, 2003a). The use of O\(_3\) in conjunction with UV light as a method to remove organic material from wastewaters has been technically developed. Fig. 3 (Legrini et al., 1993).

Vollmuth and Niessner (1997) studied the behavior of PCDD/F during the treatment of an aqueous solution of technical PCP by UV/O\(_3\). The combination of both processes achieved an OCDD reduction of 95% after 1 h of treatment, being more effective than the application of both technologies individually. As result of the treatment, the concentration of high chlorinated congeners decreased with time, and consequently low chlorinated congeners followed a typical accumulation–destruction pattern.

Wenzel et al. (1999) treated a leachate from a waste landfill containing toxic compounds such as CPs, PAHs, PCBs and PCDD/Fs using UV/O\(_3\). The oxidation treatment turned out to be effective reaching degradation ratios of 100% for CPs and PAHs, 23–96% for PCBs and at least 74% for PCDD/Fs. Nevertheless, an increase in the concentration of adsorbable organic halogens was detected. Indicating the formation of halogenated by-products.

2.4. Sonolysis

The sonochemical process for the degradation of organic compounds involves the reaction with \(\text{OH}^\cdot\) combined with a thermal reaction. \(\text{OH}^\cdot\) are produced by the sonolysis of water as the solvent inside the collapsing cavitation bubbles under extremely high temperature and pressure. Organic compounds can react with \(\text{OH}^\cdot\) or be decomposed pyrolytically due to high local temperature and pressure in the vicinity of the collapsing bubbles (Katsumata et al., 2007).

Katsumata et al. (2007) investigated the degradation of 2,3,7,8-TCDD in water by sonolysis combined with UV irradiation and Fe\(^{3+}\). Using sonolysis, the degradation of 2,3,7,8-TCDD was improved by increasing both the ultrasonic power, due to the radical reaction enhancement, and the temperature. The combination of sonolysis with Fe\(^{3+}\) and UV irradiation amplified their individual action. On this way, after 30 min, 93% of 2,3,7,8-TCDD was degraded by sonolysis, whereas 16% with UV, 87% with UV/Fe\(^{3+}\) and 100% with the ultrasonic/UV/Fe\(^{3+}\) system. The authors established that the degradation pathway of 2,3,7,8-TCDD would be mainly an oxidative reaction by \(\text{OH}^\cdot\) radical attack, since they did not observe either less chlorinated PCDD formed from C–Cl bond cleavage or addition and rearrangement of chlorine atoms.

2.5. Fenton oxidation

Fenton’s reagent (\(\text{H}_2\text{O}_2\) oxidation in the presence of Fe\(^{3+}\)) has been proposed as a very effective oxidizing agent for chlorinated organic compounds (Kao and Wu, 2000). The generally accepted mechanism of the Fenton process proposes that \(\text{OH}^\cdot\) are formed according to reaction 1 and the catalyst, Fe\(^{2+}\), is regenerated through reaction 2 (Bautista et al., 2008):

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{Fe}^{3+} & \rightarrow \text{Fe}^{2+} + \text{OH}^\cdot + \text{OH}^- \\
\text{H}_2\text{O}_2 + \text{Fe}^{3+} & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2
\end{align*}
\]

Katsumata et al. (2006) investigated the degradation of PCDDs in aqueous solutions by Fe\(^{3+}/\text{H}_2\text{O}_2/\text{UV}\) treatment. Under optimal Fe\(^{3+}\) and \(\text{H}_2\text{O}_2\) concentrations, they achieved the complete degradation of 2,3,7,8-TCDD after 20 min. Furthermore, 2,3,7,8-chlorinated congeners from Fe– to HxCDD were completely degraded within 120 min, whereas the complete degradation of Hp– and OCDD was not achieved within 300 min of treatment. As it was reported in other works (Kim and O’Keefe, 2000; Choi et al., 2000), degradation rates decreased as the chlorine substituents increased.
Lee et al. (2009) utilized both steel dust, a steel industry byproduct, as heterogeneous catalyst and Fisher iron as homogenous catalyst for the Fenton oxidation of PCDDs in aqueous solutions. They achieved under optimal operating conditions a great efficiency in the removal of 2,3,7,8-TCDD with both Fisher and steel dust iron, whereas OCCD showed promising results only for Fisher iron. However, they mentioned that the toxic 1,2,3,7,8-PCDD might accumulate in the system.

On solid phase, Tuhkanen (2001) reported the degradation of PCDD/Fs and PCBs by Fenton and ozonolysis in ash/soil material originated from an old landfill site containing bottom ash from a waste incineration plant. The ozonolysis removed PCDD/Fs in the range 10–75%, being this reduction higher for PCDDs and among them for high chlorinated congeners. For Fenton treatment, the percentage of PCDD/Fs removal was within 0–58%, and as in the previous case, it was higher for PCDDs. In other work, Kao and Wu (2000) studied the Fenton treatment of TCDD in soils in order to improve their biodegradability. The transformation of TCDD from the soil particles was demonstrated to be through either oxidation or desorption, achieving 99% of TCDD removal. As a result, less chlorinated PCDDs isomers (dechlorination products) were produced and sequentially degraded leading mainly to aromatic hydrocarbons (cleavage products).

Mino et al. (2004) studied the degradation of 2,7-DiCDD by Fe$^{3+}$/H$_2$O$_2$ and Fe$^{2+}$/H$_2$O mixed reagents in model solutions of these reagents and in treated model soil. With the first matrix, Fenton reagent, Fe$^{3+}$/H$_2$O$_2$, did not show significant DCDD degradation activity, whereas Fe$^{2+}$/H$_2$O$_2$, mixed reagent depicted a strong DCDD degradation capacity. The authors found as optimal conditions a working pH of 2.5, a reaction temperature near to 70 °C and batch reagents addition. In the case of DCDD treated soil, strong Fe$^{2+}$/H$_2$O$_2$ activity was found at pH 2.5, 70 °C and addition of reagents every 10 min.

2.6. Electrochemical oxidation

During electrochemical oxidation, OH$^-$ are electrogenerated from water discharge on the anode surface (Fig. 4). Boron doped diamond (BDD) anodes are known to have a greater oxidative power with high O$_2$ overvoltage producing large amounts of OH$^-$ (Anglada et al., 2009).

Vallejo et al. (2013a) reported the degradation of PCDD/Fs during the electrochemical treatment of municipal landfill leachates using a BDD anode with a working current density of 900 A m$^{-2}$. They observed that after 3 h of treatment, when 90% of COD was depleted, the concentration of the major congeners 1,2,3,4,6,7,8-HpCDD and OCDD was reduced by 70% and the total COD was depleted, the concentration of the major congeners 1,2,3,4,6,7,8-HpCDD and OCDD was reduced by 70% and the total toxic equivalents (TEQ) value decreased by 58%.

2.7. General PCDD/Fs degradation pathway

The degradation of PCDD/Fs by means of the application of AOPs is based on the generation of extremely reactive oxidant species, mainly OH$. On the reaction of PCDD/Fs with OH$^-$ under moderate atmospheric conditions, OH$^-$ addition is more favorable than a substitution reaction because it has lower energy barriers (Lee et al., 2004). Therefore, it is expected that the oxidation pathway begins with the addition of OH$^-$ to the aromatic ring structure leading to a PCDD/F adduct radical (Choi et al., 2000). Theoretically, using density functional theory calculations, Lee et al. (2004) found that there was not dependency on the chlorination pattern of PCDD/Fs for the first OH$^-$ addition step. However, some works have reported that the preferred position of OH$^-$ addition depends on the number and position of chlorines. According to Choi et al. (2000), OH$^-$ addition takes place preferentially at an unsubstituted carbon, since the electron density of the aromatic ring decreases with increasing chlorine substituents and therefore, the reaction rate of electrophilic OH$^-$ addition decreases. On the other hand, according to Lee et al. (2004) and Sun et al. (2008), OH$^-$ is known to behave both as electrophilic and nucleophilic species and therefore the oxygen-bonded carbon, which has the most positive charge among all carbon sites in PCDD, is the most region selective for initial OH$^-$ addition. Further steps involve the cleavage of both C-O and C-CI bonds (Sun et al., 2008) followed by oxidative ring opening leading to small organic ions and inorganic species (Katsumata et al., 2006).

In addition to the oxidative pathway by the OH$^-$ radical attack, some authors have reported that a reductive mechanism could be possible in the photo(catalytic) system (Choi et al., 2008). The photolysis of PCDDs is strongly dependent on the nature of solvents or surrounding media (Choi et al., 2004). Working with organic solvents solutions, reductive dechlorination is known to take place in the photodegradation of PCDD/Fs compounds due to their hydrogen-donor properties (Dung and O’Keefe, 1994). Homolysis of C–Cl bond by reductive dechlorination was favored at lateral chlorine (2,3,7,8) positions, which have more electron affinity than longitudinal chlorine (1,4,6,9) positions (Friesen et al., 1990, 1996). In water, on the basis of its low hydrogen donor potency, photolysis rates of PCDD/Fs degradation were much higher than in organic solvents suggesting that reductive dechlorination was a minor pathway (Friesen et al., 1990, 1996; Kim and O’Keefe, 2000). In the case of working with solid phase, as with aqueous solutions, the cleavage of the aromatic ring may dominate the photoreaction pathway over reductive dechlorination (Wu et al., 2004, 2005).

3. PCDD/Fs formation during the application of AOPs to the treatment of chlorinated organic compounds

Although most studies focus on the capacity of AOPs for PCDD/Fs destruction during the treatment of aqueous samples, it must be noticed that some oxidation technologies could also result in the formation of toxic by-products, such as PCDD/Fs, if their precursors are present in the treatable waters and depending on the operational conditions. On this way, although scarce, there are some works that cope with the formation of PCDD/Fs during the application of AOPs to aqueous solutions containing mainly organic compounds that can serve as their precursors (Vollmuth et al., 1994; Buth et al., 2010; Holt et al., 2012) and complex matrices such as landfill leachates (Vollmuth and Niessner, 1995; Vallejo et al., 2013a). Further along, works dealing with the formation of PCDD/Fs within the advanced oxidation treatment of waters containing chlorinated organic compounds are reported.

3.1. Photolysis

Vollmuth et al. (1994) studied the formation of PCDD/Fs during the photolysis of synthetic waters and landfill seepage waters.
containing PCP. The irradiation of water containing purified PCP resulted in the formation of the congeners 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDD. Besides, the formation of non 2,3,7,8-substituted congeners was also observed. In addition, they observed that during the photolysis of technical PCP–Na, only 1,2,3,4,7,8-HxCDD and 1,2,3,4,6,7,8-HpCDD were formed, whereas the remaining PCDD/Fs congeners, which were impurities of the technical PCP–Na, were reduced between 80.6% and 100%. Finally, when they treated a landfill seepage water, they observed the formation of several 2,3,7,8-PCDD/F (1,2,3,4,6,7,8-HpCDD, 1,2,3,6,7,8-HxCDD and OCDF) while the OCDD content was reduced about 69.3%.

Landfill seepage waters were also used in a later work, Vollmuth and Niessner (1995), in order to study the degradation of some persistent compounds, among them PCDD/Fs, by using UV, O3, and UV/O3 treatments. The degradation of PCDD/Fs could not be detected, whereas on the contrary, an increase in the congeners concentrations was observed. The authors concluded that higher O3 and UV doses were needed for the degradation of PCDD/Fs because of the large concentration of organic compounds contained in the seepage water.

Other studies related to the photolytic treatment of PCP in water have been reported. On this way, Hong et al. (2000) observed the presence of 1,2,3,4,6,7,8-HpCDD and OCDD as minor transformation compounds of PCP photolysis. They were supposed to be formed through the self-condensation of PCP through the nonachlorohydroxydiphenylether, which is a precursor of OCDD. The rest of 2,3,7,8-chlorinated congeners could be formed by successive dechlorination of OCDD. In addition, Fukushima et al. (2000) reported the formation of OCDD as a photodegradation product of PCP in aqueous solutions containing Fe3+ at both pH 3 and pH 5. The photodegradation of Fe3+-hydroxy complexes gives OH- radicals which degrade the PCP. Intermediates resulting from PCP degradation dimerize via radical coupling reactions leading to OCDD formation. More recently, Holt et al. (2012) found that the concentration of 93 PCDD/F congeners in two chlorinated pesticides increased by 5600% and 3000% after their exposure to natural light during 833 h and 1.6 h, respectively.

3.2. Fenton oxidation

The research developed by Sedlak and Andren (1991) was one of the early works dealing with the potential formation of toxic intermediate products during the Fenton oxidation of CBz. They highlighted the importance of evaluating hydroxylated aromatic and dimeric intermediates, among others, due to their recalcitrant and/or toxic behavior. Although chlorinated biphenyls as well as hydroxychlorobiphenyls were formed as intermediate products, they were finally oxidized when reaction proceeded by subsequent OH attack. On the other hand, Fukushima and Tatsumi (2001) studied the PCP degradation characteristics and pathways by photo-Fenton system in aqueous solutions containing H2O2/Fe3+ or H2O2/Fe2+/Humic acids (HA). In the H2O2/Fe3+ system, the formation of OCDD was detected at pH 5, where PCP exists as PCP hydroxychlorobiphenyl, which is a precursor of OCDD. The same authors did not find the formation of pentachlorohydroxyphenyl radical (PCP•) by attack of OH-. Nevertheless, at pH 3, OCDD formation was not observed. At this pH, PCP is not dissociated and therefore PCP is not formed by OH•. Therefore they suggested that PCP is an initial intermediate to the OCDD production. The same authors did not observe OCDD formation in the H2O2/Fe3+/HA system, concluding that the presence of HA repressed the formation of OCDD during the degradation of PCP due to its binding with PCP intermediates.

Poerschmann et al. (2009), reported the generation of chlorinated benzenediols, hydroxylated chlorobiphenyls, hydroxylated chlorodiphenyl ethers, hydroxylated chlorinated benzofurans and related compounds as a result of oxidative coupling reactions between stabilized radicals, during the Fenton oxidation of 2-chlorophenol under substoichiometric conditions of the Fenton reagent. In a later work, Munoz et al. (2011) studied the Fenton-like oxidation of aqueous solutions containing monochlorophenols within a wide range of H2O2 and Fe3+ concentrations. They identified the formation of PCBs, PCDDs and dichlorodiphenyl ethers in the reaction samples working with substoichiometric H2O2 doses and low Fe3+ quantity. Moreover, during the oxidation of 4-chlorophenol the authors observed the formation of a dark solid residue with empirical formula (C12H4ClO3)Fe, which contained condensed aromatic rings associated to chlorine and iron and was insoluble at pH 3 but soluble under basic conditions. This behavior is a feature of HA that contains a complex mixture of many different acids containing carboxyl and phenolate groups, which are able to form complexes with iron. Similar results were reported by the same authors in a later research (Munoz et al., 2011) regarding the Fenton-like oxidation of diverse CPs. Working at substoichiometric H2O2 doses, a wide variety of chlorinated condensation products including chlorinated diphenyl ethers, biphenyls and dibenzofurans, were detected. Besides, the formation of a similar polymer to that described by Munoz et al. (2011), which contained condensed aromatic rings associated with chlorine and iron, was coating enriched with different concentrations of TCS. These results were also confirmed in aqueous solutions by series of experiments developed under the same conditions. The same authors, Sanchez-Prado et al. (2006), depicted the formation of 2,8-DCDD as a result of the photochemical treatment of TCS, using both UV and simulated sunlight in real wastewaters samples from a sewage treatment plant and in a SPME fiber coating, resulted from the wastewater samples extraction. 2,8-DCDD was confirmed in all experiments at different pH, establishing that its formation was independent of sample pH.

Finally, photocatalysis with UV light and TiO2 as catalyst was used by Sankoda et al. (2011) to degrade TCS in pure water. Under the studied conditions, 90% of the initial concentration of TCS was degraded after 120 min of irradiation. Although 2,8-DCDD was detected as intermediate of TCS degradation, it represented only 0.1% of TCS conversion.
reported. In addition, under the same conditions, the ecotoxicity of the sample after the Fenton oxidation increased with respect to the untreated sample.

More recently, Vallejo et al. (2013a) observed an increase in the concentration of PCDD/Fs during the Fenton treatment of different leachate samples from a municipal waste landfill. After 3 h of treatment when almost 90% of COD was degraded, the total concentration of PCDD/Fs in the different leachate samples increased by 30–150% related to the untreated leachate, specially stressed for the major congeners 1,2,3,4,6,7,8-HpCDD, OCDD and OCDF. Since total concentration of 2,3,7,8-PCDD/Fs represented around 80% of the total PCDD/Fs concentration, the TEQ value increased by 12.5–128%.

3.3. Electrochemical oxidation (EOX)

Hong et al. (2003) studied the electrochemical decomposition of 4-chlorophenol with an iridium dioxide anode at 400 A m⁻² of current density. They detected along with the main oxidative-products such as hydroquinone, chlorocatechol and chlorohydroquinone, the formation of hydroxylated dibenzodioxin/furans and hydroxylated chlorobiphenyls as minor products, which were formed during the dimerization of 4-chlorophenol and/or its intermediates.

In a recent work, Valdejo et al. (2013b) carried out the electrochemical degradation of 2-chlorophenol on BDD anodes at current density of 900 A m⁻² and using two different electrolytes, NaCl and Na₂SO₄. After 4 h of treatment and when almost complete mineralization was achieved, the use of NaCl led the concentration of total PCDD/Fs to increase 2.68 · 10⁴ times compared to the untreated sample. At this time, the TEQ was 220 pg-ITEQ L⁻¹, which is several times higher than the maximum level established by U.S. EPA for water ingestion. On the other hand, when Na₂SO₄ was used, the concentration of total PCDD/Fs was 134 times lower than with NaCl and there was no significant formation of toxic congeners, 2,3,7,8-PCDD/Fs, highlighting the relevance of the chloride concentration in the formation of highly substituted chlorinated byproducts.

4. Conclusions

In this manuscript, firstly we offer a critical review of the potential of AOPs for the destruction of PCDD/Fs contained in polluted waters. Among the employed AOPs, photolysis based processes have been reported as effective treatments for destroying PCDD/Fs in water solutions. Although a wide range of operating conditions has been employed, most of the AOPs resulted in a final PCDD/Fs destruction since all of them are based on the generation of extremely reactive OH, responsible of PCDD/Fs degradation. However, more research is required in order to achieve more cost-effective processes and avoid strict reaction conditions and/or external added supplements that are far from simulate mild environmental conditions. In addition, more investigation using real wastewater matrices where PCDD/Fs can coexist with different compounds is necessary.

Secondly, we analyze the potential of PCDD/Fs formation in the application of several AOPs by critically reviewing the works dealing with PCDD/Fs precursors. On this way, data summarized in the second part of this manuscript point out that a broad range of AOPs have the potential to produce PCDD/Fs when they are applied to contaminated water remediation, where PCDD/Fs precursors are present or can be formed as a result of the oxidation treatment. Together with the existence of PCDD/Fs precursors, the presence of chloride in the oxidation medium and low concentrations of the oxidizing agent, such in the case of the Fenton reagent, have been highlighted as variables with high influence on PCDD/Fs formation. Therefore, the present review contributes to emphasize the relevance of the assessment of transformation by-products as well as the correct selection of the operating conditions in extending the understanding of the overall effectiveness of AOPs for pollutant degradation.

Nevertheless, more studies are needed, including their extent to the treatment of real wastewaters, in order to take into account the effect of coexisting organic and/or inorganic species on the generation of transformation products. In this way, the presence of bromine-containing compounds such as polybrominated diphenyl ethers (PBDEs) and brominated flame retardants could lead to the formation of polybrominated dibenzop-dioxins and polybrominated dibenzofurans (PBDD/Fs), whose toxicity, although less studied, is thought to be similar to that of their chlorinated analogs PCDD/Fs. Besides, mixed bromo/chloro polyhalogenated dibenzop-dioxins and dibenzofurans (PXDD/Fs) might be formed. Therefore, the extension of the monitored compounds to other dioxin-like chemicals such as dioxin-like PCBs, some polychlorinated naphthalenes, CDEs, PBDD/Fs and PXDD/Fs, among others, must be taken into account due to their dioxin-like toxicological capacity. Moreover, in addition to target chemical analysis, research works must consider to include toxicity screening in extending the understanding of AOPs effectiveness for pollutants degradation, since toxicity bioassays are able to assess the toxicity of either target and unknown contaminants.

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