Evaluation of advanced oxidation processes for water and wastewater treatment — A critical review

David B. Miklos a, Christian Remy b, Martin Jekel c, Karl G. Linden d, Jörg E. Drewes a, Uwe Hübner a, *

a Chair of Urban Water Systems Engineering, Technical University of Munich, Am Coulombwall 3, D-85748 Garching, Germany
b Kompetenzzentrum Wasser Berlin gGmbH, Cicerostrasse 24, D-10709 Berlin, Germany
c Technische Universität Berlin, Chair of Water Quality Control, KF4, Str. des 17. Juni 135, D-10623, Berlin, Germany
d Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, UCB 607, Boulder, CO 80303, USA

Abstract

This study provides an overview of established processes as well as recent progress in emerging technologies for advanced oxidation processes (AOPs). In addition to a discussion of major reaction mechanisms and formation of by-products, data on energy efficiency were collected in an extensive analysis of studies reported in the peer-reviewed literature enabling a critical comparison of various established and emerging AOPs based on electrical energy per order (EEO) values. Despite strong variations within reviewed EEO values, significant differences could be observed between three groups of AOPs: (1) O3 (often considered as AOP-like process), O3/H2O2, O3/UV, UV/H2O2, UV/persulfate, UV/chlorine, and electron beam represent median EEO values of <1 kWh/m3, while median energy consumption by (2) photo-Fenton, plasma, and electrolytic AOPs were significantly higher (EEO values in the range of 1–100 kWh/m3). (3) UV-based photocatalysis, ultrasound, and microwave-based AOPs are characterized by median values of >100 kWh/m3 and were therefore considered as not (yet) energy efficient AOPs. Specific evaluation of 147 data points for the UV/H2O2 process revealed strong effects of operational conditions on reported EEO values. Besides water type and quality, a major influence was observed for process capacity (lab-vs. pilot-vs. full-scale applications) and, in case of UV-based processes, of the lamp type. However, due to the contribution of other factors, correlation of EEO values with specific water quality parameters such as UV absorbance and dissolved organic carbon were not substantial. Also, correlations between EEO and compound reactivity with OH-radicals were not significant (photolytically active compounds were not considered). Based on these findings, recommendations regarding the use of the EEO concept, including the upscaling of laboratory results, were derived.

© 2018 Elsevier Ltd. All rights reserved.
1. Introduction

In recent years, trace organic chemicals (TOC) such as pharmaceuticals, consumer products, and industrial chemicals have been detected in the aquatic environment (Huerta-Fontela et al., 2010). Besides urban and agricultural run-offs, wastewater treatment plant effluents are considered to be the most significant TOC emitters (Lim, 2008; Gros et al., 2010; Luo et al., 2014). TOCs remain in wastewater treatment plant effluents being discharged into surface waters, since conventional physical and biological wastewater treatment can only partially remove these substances (Lim, 2008; Zhang et al., 2008; Luo et al., 2014).

The application of advanced oxidation processes (AOPs) provides a viable and effective attenuation option due to the oxidation of a wide range of TOCs (Comninellis et al., 2008; Klavarioti et al., 2009; Yang et al., 2014; Giannakis et al., 2015; Stefan, 2018). According to the definition of Bolton et al. (1996) and Bolton et al. (2001), AOPs are based on the in situ generation of strong oxidants for the oxidation of organic compounds. This includes processes based on OH-radicals (HO•), which constitute the majority of available AOPs, but also processes based on other oxidizing species favoring sulfate or chlorine radicals. There are various different process technologies which have been investigated for use as AOPs. Several AOPs, especially those involving ozonation and UV irradiation are already well established and operated at full-scale in drinking water treatment and water reuse facilities. However, new studies of numerous emerging AOPs for water treatment (i.e., electrochemical AOP; plasma, electron beam, ultrasound or microwave based AOPs) are constantly being reported by various researchers (Stefan, 2018). The huge amount of different studies and an increasing number of proposed technologies and process combinations pose an enormous challenge for a critical assessment of AOPs concerning their operational costs (i.e., energy consumption, chemical input), sustainability (i.e., resource use, carbon footprint), and general feasibility (e.g., physical footprint and oxidation by-product formation) to enable comparison of their efficiency with other AOPs and alternative treatment processes.

To address this issue, Bolton and coworkers developed figures of merit for the comparison of advanced oxidation processes (Bolton et al., 2001). These are based on electrical energy consumption which often represents a major fraction of the AOP operating costs. For low contaminant concentrations (typically < 100 mg/L), the

**Abbreviations**

<table>
<thead>
<tr>
<th>AOP</th>
<th>Advanced oxidation processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOX</td>
<td>Adsorbable organic halides</td>
</tr>
<tr>
<td>BDD</td>
<td>Boron-doped diamond</td>
</tr>
<tr>
<td>cAOP</td>
<td>Catalytic advanced oxidation processes</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved organic matter</td>
</tr>
<tr>
<td>eAOP</td>
<td>Electrochemical advanced oxidation processes</td>
</tr>
<tr>
<td>E&lt;sub&gt;EO&lt;/sub&gt;</td>
<td>Electrical energy per order</td>
</tr>
<tr>
<td>HAA</td>
<td>Haloacetic acids</td>
</tr>
<tr>
<td>HAN</td>
<td>Haloacetonitriles</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LP</td>
<td>Low-pressure</td>
</tr>
<tr>
<td>MP</td>
<td>Medium-pressure</td>
</tr>
<tr>
<td>NDMA</td>
<td>N-Nitosodimethylamine</td>
</tr>
<tr>
<td>NTU</td>
<td>Nephelometric turbidity unit</td>
</tr>
<tr>
<td>OBPs</td>
<td>Oxidation by-products</td>
</tr>
<tr>
<td>pAOP</td>
<td>Physical advanced oxidation processes</td>
</tr>
<tr>
<td>PDS</td>
<td>Peroxydisulfate</td>
</tr>
<tr>
<td>PMS</td>
<td>Peroxymonosulfate</td>
</tr>
<tr>
<td>THM</td>
<td>Trihalomethanes</td>
</tr>
<tr>
<td>TOCs</td>
<td>Trace organic chemicals</td>
</tr>
<tr>
<td>TOX</td>
<td>Total organic halides</td>
</tr>
<tr>
<td>US</td>
<td>Ultrasound</td>
</tr>
<tr>
<td>UVA</td>
<td>UV absorbance</td>
</tr>
</tbody>
</table>

---
kinetics of destruction of organic contaminants by AOPs can often be described phenomenologically by simple pseudo first-order rate expressions. Thus, the oxidant or energy dosage scales with the volume and treatment goals (i.e. orders of magnitude of reduction per unit volume). Consequently, the figure of merit for electrical-driven AOPs is defined as EEO (electrical energy per order):

"Electrical energy per order is the electrical energy in kWh required to degrade a contaminant C by one order of magnitude in 1 m³ of contaminated water" (Bolton et al., 1996).

This figure of merit has been accepted by the International Union of Pure and Applied Chemistry (IUPAC) in 2001 (Bolton et al., 2001) and numerous EEO values have been reported since then in literature for various oxidation processes and applications. Giving a direct link to the electrical efficiency of the AOP, this approach allows not only for a simple comparison of different AOP technologies, but also provides the requisite data for scale-up and economic as well as sustainability analyses for comparison with conventional treatment technologies (e.g., activated carbon adsorption, air stripping).

In aqueous systems, oxidation of a specific compound C follows a second-order reaction, where the relative residual concentration is a function of compound specific rate constant $k_{OH}$ and the $\cdot OH$ exposure. Accordingly, $\cdot OH$ exposure can be determined from experimental data using equation (1).

$$\int (\cdot OH)dt = \frac{\ln(C/C_0)}{-k_{OH}.S}$$  \hspace{1cm} (1)

The $\cdot OH$ exposure is controlled by the radical formation efficiency of the respective process as well as competing reactions with other constituents in the water called radical scavenging. Major radical scavengers are carbonate, bicarbonate, nitrite, and organic matter indicating a strong dependency of compound removal and thus EEO values on the water matrix. Besides radical scavenging, the water matrix might also directly affect the in situ generation of radicals in several processes, e.g. by reducing UV-transmittance or reactions with ozone in ozone-based AOPs. For these reasons, the application of EEO values for a comparison of experimental results from different water matrices is not recommended and comparative studies to evaluate efficiency of different AOPs in a defined water matrix are needed (Bolton et al., 2001). To date, only few studies directly comparing different AOPs are available (Bolton et al., 1998; Müller et al., 2001; Alaton et al., 2002; Katsoyiannis et al., 2011; Ureña de Vivanco et al., 2013; Lutterbeck et al., 2015; Fast et al., 2017) and they are mostly limited to a few established processes. To the best of our knowledge, such a comprehensive comparison across different AOPs has not yet been conducted.

This article provides a critical review of different established and emerging AOPs based on data compiled during an extensive literature study. An initial comparative assessment is conducted based on EEO-values reported in the peer-reviewed literature for different AOPs. Influencing aspects, such as reaction rate constants of target substances, water matrix, process capacity or system parameters are considered and critically evaluated. As a result, recommendations for the use of the EEO-concept in future studies are presented. In addition, this article also provides an assessment on by-product formation in different AOPs based on reaction mechanisms of different oxidants.

2. Background regarding advanced oxidation processes for contaminant removal in water

Technologies for AOPs involve widely different methods of activation as well as oxidant generation and can potentially utilize a
number of different mechanisms for organic destruction. An overview of different established and emerging AOPs is given in Fig. 1, categorized into ozone-based, UV-based, electrochemical (eAOP), catalytic (cAOP), and physical (pAOP) AOPs. However, it is noteworthy that this classification scheme should not be viewed as strict since several processes involve different technologies and thus could be assigned to various categories. The different processes summarized in Fig. 1 represent processes of very different degrees of implementation from well-established AOPs to processes only tested at laboratory scale yet.

All AOPs comprise of two steps, the in situ formation of reactive oxidative species and the reaction of oxidants with target contaminants. Mechanisms of radical formation depend on process specific parameters and can be affected by system design and water quality. Besides radical scavenging also other parameters (e.g., radical mass transfer in surface based AOPs, hydrodynamics) play an important role for efficiency of contaminant destruction. In the following sections, the current status of implementation is reviewed, major mechanisms and principles of radical generation are illustrated, and constraints of different AOPs are briefly discussed. More comprehensive overview on system design, reaction principles and kinetics can be found in various book publications on AOPs (Parsons, 2004; Collins and Bolton, 2016; Stefan, 2018).

Mechanisms for the formation of oxidation by-products (OBPs) in different AOPs are discussed separately in section 3.

2.1. Ozone based AOPs

Ozone has long been used as an oxidant and disinfectant in water treatment. As an oxidant, ozone is very selective and attacks primarily electron-rich functional groups like double bonds, amines, and activated aromatic rings (e.g. phenol). Since its reactions in real aqueous solutions often involve the formation of ·OH, ozonation itself is often considered an AOP or AOP-like process. ·OH can be formed from the reaction of ozone with hydroxide ions (Merényi et al., 2010a, 2010b). The initiation of this reaction, however, is quite slow with a second-order rate constant of 70 M$^{-1}$s$^{-1}$.

In addition, radicals are formed as a side product from the reaction of ozone with organic matter (mainly phenol and amine functional groups) (Buffie and von Gunten, 2006). Especially during ozonation of secondary effluents these reactions are the major contributors to radical formation. Methods to actively initiate formation of radicals include the ozonation at elevated pH and the combinations O$_3$/H$_2$O$_2$ (also called peroxone-process), O$_3$/UV, and O$_3$/catalysts. The combination of ozonation and UV-irradiation will be discussed as a UV-based AOP in section 2.2.

2.1.1. Ozonation at elevated pH

Ozonation at elevated pH is considered as an AOP if ·OH generation is intentionally favored (Elowitz and von Gunten, 1999; Buffie et al., 2006). The pH of treated water influences direct ozonation efficiency since dissociated target organic compounds might have significantly different k$_{OH}$ values (Calderara et al., 2002). Furthermore, the abundance of hydroxide ions directly influences the ·OH generation and therefore indirect ozonation. Especially if the water to be treated has a pH > 8, ozonation applied as an AOP might be a promising process, if the precipitation of calcium carbonate is not of concern.

2.1.2. Peroxone-process (O$_3$/H$_2$O$_2$)

In the peroxone process, ozone reacts with the peroxide anion (HO$_2$) to form ·OH precursors, which are subsequently reacting to ·OH. For a detailed mechanistic description of the peroxone process see Merényi et al. (2010a). Residual H$_2$O$_2$ might have to be destroyed before discharging the treated water to the receiving aqueous environment. The optimum molar ratio for the peroxone process is H$_2$O$_2$/O$_3$ = 0.5 mol/mol (Katsoyiannis et al., 2011; Pisarenko et al., 2012). Typical ozone doses in the peroxone process are 1–20 mg/L. Peroxide can also be formed from reactions of ozone with the water matrix but its contribution to overall ·OH formation during wastewater ozonation is not significant (Nöthe et al., 2009). O$_3$/H$_2$O$_2$ is a well-established process in drinking water treatment and water reuse applications (e.g. Windhoek, Namibia). However, recent studies have shown that benefits for its application in wastewater are limited due to high competition reactions and already efficient radical formation with ozone alone (Hübner et al., 2015). However, it might still be a valuable treatment option to minimize bromate formation during ozonation as discussed in section 3.

2.1.3. O$_3$/catalysts

Catalytic ozonation is distinguished between homogeneous and heterogeneous catalytic ozonation, depending on the water solubility of the catalyst. Homogeneous catalytic ozonation can be described as a three-step catalytic cycle as approached by Pines and Reckhow (2002) using Co(II) as a catalyst and oxalic acid: (1) formation of Co(II)-oxalate complex, (2) oxidation by ozone to Co(III)-oxalate complex, and (3) decomposition of Co(III)-oxalate complex forming an oxalate radical and Co(II). Heterogeneous catalytic ozonation mechanisms are mediated by metal oxides (e.g., TiO$_2$, Al$_2$O$_3$, MnO$_2$) and result in more complex reaction paths based on multiple-phase transport mechanisms and respective reactions as described in detail by Beltrán (2004).

Both homogeneous and heterogeneous catalytic ozonation have shown their potential for water treatment at laboratory scale mainly based on lower ozone demand compared to ozonation alone (Bai et al., 2016; Wu et al., 2016a, 2016b; Xing et al., 2016). However, full-scale application is limited due to catalyst recovery and a lack of understanding of the catalytic ozonation mechanisms (Nawrocki and Kasprzyk-Hordern, 2010). Some studies report the use of activated carbon as a catalyst in catalytic ozonation (e.g. Kaptijn, 1997). However, ·OH production in this process is based on the reaction of ozone with pyrrl groups present on the activated carbon surface indicating that it acts rather as a radical promoter than a catalyst, which needs to be continuously renewed to maintain efficient radical generation (Sánchez-Polo et al., 2005).

2.2. UV-based AOPs

UV-based AOPs comprise processes based on UV-irradiation (mostly UV-C) and the combination of UV-light with different radical promoters. UV-fluences applied for advanced oxidation are usually >200 mJ/cm$^2$ and therefore exceed UV-dose requirements for 4-log inactivation of most pathogens including UV-resistant organisms (e.g. adenovirus) (EPA, 2006). UV-irradiation sources usually consist of either low- (LP) or medium-pressure (MP) mercury lamps with mono- or polychromatic emission spectra, respectively. Recently, UV-light emitting diode (LED) light sources with specific wavelength distributions have been investigated and summarized for disinfection purposes (Song et al., 2016). The principal advantages of LEDs compared to conventional medium and low-pressure lamps are the elimination of mercury, unique peak emission wavelengths, compact size and therefore flexible application design as well as a short start-up phase. However, despite the prediction of future UV-LED wall plug efficiencies of about 75% in 2020 (Austin et al., 2013), current diodes emit UV radiation at efficiencies of <10% (Chen et al., 2017). This results in Eeq values for LED systems that are not yet competitive with conventional UV-systems (Wang et al., 2017) and are therefore not
considered in this study.

The most frequently applied UV-based AOP is the combination with H2O2. Other radical promoters such as persulfate (to form sulfate radicals) and chlorine (hydroxyl radicals and radical chlorine species) are also being investigated. Besides established oxidants, Keen et al. (2012) investigated the applicability of nitrate in combination with MP-lamps as an alternative UV-based AOP. However, to the best of our knowledge, no EEO values are available for this process.

2.2.2. UV/O3

The combination of UV-irradiation and H2O2 leads to the photolytic cleavage of H2O2 into two •OH. However, the molar absorption coefficient of H2O2 is relatively low with \( \varepsilon = 18.6 \, \text{M}^{-1} \cdot \text{cm}^{-1} \) at \( \lambda = 254 \, \text{nm} \) resulting in a H2O2 turnover of <10%. If LP UV lamps are used, high concentrations of H2O2 are required to generate sufficient •OH \( (|\text{H}_2\text{O}_2| = 5-20 \, \text{mg/L}) \) leading to the necessity of removing residual H2O2 in a subsequent step. Applied H2O2-doses are mainly set based on economic aspects. However, at higher concentrations also scavenging of •OH with H2O2 \( (\text{kon}_{\text{H}_2\text{O}_2} = 2.7 \cdot 10^7 \, \text{M}^{-1} \cdot \text{s}^{-1}) \) might affect the radical yield (Buxton et al., 1988).

UV/H2O2 for T0Cr removal has been examined widely throughout peer-reviewed journal articles at lab-scale (Wols and Hofman-Caris, 2012; Wols et al., 2013; Keen et al., 2016) for water qualities ranging from ultrapure water to landfill leachate (Xiao et al., 2016; Ghazi et al., 2014). First full-scale applications are already established for potable water reuse (Auedaert et al., 2011) and surface water treatment applications (Kruithof et al., 2007). UV/H2O2 is not established for advanced wastewater treatment mainly because of low UV-transmittance and high scavenging capacity of secondary or tertiary treated wastewater effluents but is used in some potable reuse treatment trains employing integrated membrane systems (ultrafiltration/reverse osmosis) (Drewes and Khan, 2015) based on its negligible OBP formation potential as discussed in section 3.

2.2.2. UV/O3

In the UV/O3 process, UV irradiation \( (\lambda < 300 \, \text{nm}) \) results in a cleavage of dissolved ozone, followed by a fast reaction of atomic oxygen with water to form a thermally excited H2O2. Subsequently, the excited peroxyde decomposes into two •OH (von Sonntag, 2008). Ozone has a molar extinction coefficient of \( \varepsilon = 3300 \, \text{M}^{-1} \cdot \text{cm}^{-1} \) at \( \lambda = 254 \, \text{nm} \), which is significantly higher than that of H2O2 at this particular wavelength. However, due to cage recombinations only a small proportion of generated H2O2 decomposes to •OH resulting in a free •OH quantum yield of only 0.1 (Reisz et al., 2003). Furthermore, both UV lamps and ozone generator need large amounts of electrical energy, resulting in relatively high energy demands for the combination of UV and ozone. Direct oxidation by the combination of ozonation and photolysis covers a wide range of TOCr reactivity and leads to the main advantage of this process. However, low energy efficiency of radical generation might explain that to the best of our knowledge, no published data on full-scale UV/O3 application are available.

2.2.3. UV/SO\(_4\)\(^{-}\)

An interesting alternative to •OH based AOPs is UV/SO\(_4\)\(^{-}\) which generates primarily sulfate radicals (SO\(_4\)\(^{-}\)) for the oxidation of organic contaminants in water (Lutze, 2013; Ao and Liu, 2016; Waciawek et al., 2017; Ike et al., 2018). Sulfate radicals have a strong oxidizing power and are more selective oxidants than •OH (Lutze et al., 2015).

Peroxysulfate \( (\text{PDS, S}_2\text{O}_8\,^2-) \) is homolytically cleaved by UV-C activation. The quantum yield of \( S_2\text{O}_8\,^2- \) is larger than H2O2 (1.4 compared to 1.0) and molar absorption for \( S_2\text{O}_8\,^2- \) is slightly higher as well \( (22 \, \text{M}^{-1} \cdot \text{cm}^{-1} \text{ and } 18.6 \, \text{M}^{-1} \cdot \text{cm}^{-1}, \text{respectively}) \) resulting in a higher generation of radicals using PDS as oxidizing agent (Legrini et al., 1993; Lutze, 2013; Xiao et al., 2016). Peroxymonosulfate \( (\text{PMS, HS}_2\text{O}_5) \) is activated by UV radiation into a SO\(_4\)\(^-\) and a •OH with a quantum yield of 0.52 at pH 7 (Guan et al., 2011). Several studies have investigated the mechanisms and application of UV/PMS (Antoniou et al., 2010; Khan et al., 2014; Mahdi-Ahmed and Chiron, 2014). However, based on its lower quantum yield, high commercial pricing and low availability of EEO values it is not considered in this study (Wacawek et al., 2017).

Recent research has shown the advantages of UV/SO\(_4\)\(^{-}\) compared to UV/H2O2 in lab-scale experiments (Khan et al., 2014; Zhang et al., 2015; Xiao et al., 2016). However, based on more selective reactivity of sulfate radicals, results reveal a higher sensitivity to water matrix changes and DOM composition compared to UV/H2O2 (Ahn et al., 2017). Depending on the respective target compound and water matrix, SO\(_4\)\(^{-}\) based AOPs can be a considerable alternative to •OH-based processes. However, UV/PDS yields in higher formation potential of OBPs in comparison to UV/H2O2 (see section 3).

2.2.4. UV/Cl\(_2\)

UV/Cl\(_2\) is another promising AOP, where UV-activated chlorine forms radical species, i.e. Cl• and Cl\(_2\)• and •OH which then oxidize target compounds (Watts and Linden, 2007). Cl• is a more selective oxidant than •OH, since it reacts favorably with electron-rich contaminants (Fang et al., 2014). The two oxidants mainly used are hypochlorite and chlorine dioxide (Jin et al., 2011; Sichel et al., 2011; Fang et al., 2014; Wang et al., 2016). However, regarding hypochlorite, pH dependency of HOCl/OCl• speciation needs to be considered since it influences the molar absorption coefficient significantly. UV/Cl\(_2\) is especially favorable for waters with lower pH values such as reverse osmosis permeate (Watts et al., 2007). Research has mainly been conducted on lab-scale systems degrading organic indicator compounds (Jin et al., 2011; Sichel et al., 2011; Fang et al., 2014; Wang et al., 2016). A first full-scale application for indirect potable reuse recently started operation at the Los Angeles Terminal Island Water Reclamation Plant (Xylem, 2015). However, Cl• based reactions involve the formation of oxidative chlorine species (e.g., ClO•, OCI•), which might be oxidized by •OH to chlorate, perchlorate and halogenated OBPs (see section 3 for more details).
electrode surface and reactivity range of -OH is limited to about 1 μm (Kapaika et al., 2009), diffusive transport through the boundary layer at the electrode surface is the limiting factor of high oxidation efficiencies. For eAOP processes, hydrodynamic parameters therefore have to be considered, as energy used to pump water, might account for the greatest share of energy consumption in this process. This applies especially if low current densities are used to achieve higher -OH formation efficiency prolonging overall treatment duration and pumping energy requirements.

Apart from the oxidation of ToRsCs in water treatment, BDD-electrodes are investigated for disinfection purposes as well as for the removal of chemical oxygen demand (COD) (Rajab et al., 2013, 2015). Besides the generation of -OH, secondary oxidants, which enhance elimination reactions and disinfection in the bulk solution, can be produced (Rajab et al., 2015). A limiting factor for the applicability of BDD is unintentional formation of halogenated OBPs as discussed in section 3 (von Gunten, 2003b; Bergmann and Rollin, 2007; Bergmann et al., 2011). Nevertheless, several full-scale eAOP systems for COD removal are already applied (Woisetschläger et al., 2015).

2.4. Catalytic AOPs

2.4.1. Fenton process

The combination of ferrous iron (Fe(II)) and H₂O₂ at acidic conditions results in -OH formation (Fenton reaction). Iron acts as a catalyst with maximum catalytic activity at pH = 3, particularly due to the precipitation of ferric oxyhydroxide at higher pH value (Wadley and Waitte, 2004). Excess addition of H₂O₂ leads to the reduction of Fe(III) to Fe(II) (Safarzadeh-Amiri et al., 1996). By substitution of iron oxides by other transition metals, enhanced TOrC removal performance can be achieved (Jiang et al., 2010; Rahim Pouran et al., 2014; Piscitelli et al., 2015). To prevent iron precipitation, the Fenton process is restricted to acidic conditions. Therefore, alternative iron-free Fenton-like processes have recently been investigated as summarized by Bokare and Choi (2014). Main advantages of the Fenton process are operation at low-costs based only on -OH reactions. Unfortunately, the quantum yield of TiO₂ photocatalysis for oxidation and reduction of contaminants is usually very low (Φ = 0.04) due to the fast recombination of electron–hole pairs (Sun and Bolton, 1996). Additionally, an electron donor (e.g. citric acid) may lead to the “filling” of positive holes and increased reduction rates from the negative electrons. For ferrous iron (Fe(II)), this is directly coupled with the Fenton process. Photo-Fenton processes with an organic ligand (e.g. ferrioxalate) have a higher quantum yield and thus a higher efficiency due to the high UV absorption of Fe(III)-polycarboxylates. Additionally, the ferrioxalate complex can absorb radiation up to a wavelength of λ < 550 nm, making it suitable for solar-driven AOPs (Hislop and Bolton, 1999).

A recent review of photo-Fenton applications for wastewater treatment is given by Rahim Pouran et al. (2015).

In TiO₂-based photocatalysis, a semiconductor material is irradiated by UV light (λ < 400 nm). It is usually investigated as suspended colloidal particles or immobilized on different substrates. If photons with sufficient energy hit the photocatalyst surface, an electron is excited to the conduction band, leaving a positively charged hole (h⁺) in the valence band (eq. (3)). These species can cause oxidative or reductive transformations of water constituents, either directly on the semiconductor surface or via radical reactions (eq. (4)). A sufficient amount of dissolved oxygen is necessary for the latter reactions. The combination of oxidation and reduction mechanisms is specific for photocatalysis, whereas other AOPs are based on only -OH reactions. Unfortunately, the quantum yield of TiO₂ photocatalysis for oxidation and reduction of contaminants is usually very low (Φ = 0.04) due to the fast recombination of electron–hole pairs (Sun and Bolton, 1996).

Adventages of TiO₂ photocatalysis for ToRc removal include low costs of the catalyst itself and easy commercial availability in various crystalline forms and particle characteristics. Furthermore, the catalyst is non-toxic and photochemically stable. The limitation of heterogeneous photo-catalysis application at full-scale is mainly based on two factors: (1) separation of colloidal catalyst from the water suspension after treatment and (2) mass transfer limitations to the surface of the immobilized catalyst on a substrate (Qu et al., 2013). Despite strong research efforts in the field of photocatalysis, the process is rarely applied in industrial or municipal water treatment facilities because of the low quantum yield for -OH radical production.

2.5. Physical AOPs

2.5.1. Electrohydraulic discharge (Plasma)

Liquid-phase electrical discharge reactors have been investigated as AOPs in water treatment (Locke et al., 2006; Hijosa-Valsero et al., 2014). Strong electric fields applied within the water (electrohydraulic discharge) or between water and gas phase (nonthermal plasma) initiate both chemical and physical processes. Beside the direct oxidation of contaminants in the water, various oxidizing radicals or active species, UV radiation, and shock waves are formed during the discharge, which can promote oxidation (Jiang et al., 2014).

2.5.2. Ultrasound

Sonication of water by ultrasound (US) (20–500 kHz) leads to the formation and collapse of micro-bubbles from acoustical wave-induced compression and rarefaction. These bubbles implode violently after reaching a critical resonance size and generate transient high temperatures (>5000 K), high pressures (>1000 bar) and highly reactive radicals. Destruction of water contaminants occurs by thermal decomposition and various radical reactions (Mason and Pétier, 2004). Cavitation via ultrasound exhibits low interference from water matrix and less heat transfer compared to UV irradiation. A comprehensive review of sonochemical methods is provided by Pang et al. (2011). Sonochemical processes have proven to oxidize various aquatic contaminants in lab-scale
experiments (Mahamuni and Adewuyi, 2010). However, the application of ultrasound is highly energy intensive and results in a very low electrical efficiency of this AOP in comparison to other technologies (Goel et al., 2004; Mahamuni and Adewuyi, 2010). Therefore, the coupling of ultrasound with UV-irradiation (sonophotocatalysis), oxidants (O$_3$, H$_2$O$_2$), or catalysts (TiO$_2$, GAC) to assist in the destruction of organic pollutants (Han et al., 2004; Zhihui et al., 2005; Bo et al., 2006). Microwaves can enhance reaction rates and induce selective heating of the contaminants through internal molecule vibration. Additionally, microwaves can generate UV radiation via an electrodeless discharge lamp for combined MW/UV reactors. Unfortunately, most of the applied microwave energy is converted into heat. Beside the low electrical efficiency (E$_{el}$ not readily available in literature), cooling devices have to be employed to prevent treated water from overheating.

2.5.4. Electron beam

The utilisation of ionizing radiation from an electron beam source (0.01–10 MeV) for water treatment has been tested since the 1980s. The accelerated electrons penetrate the water surface and result in the formation of electronically excited species in the water, including various ionic species and free radicals. The maximum penetration depth of the accelerated electrons is directly proportional to the energy of the incident electrons (e.g. 7 mm, reported by Nickelsen (1994)). Therefore, water is irradiated in a thin film or as a sprayed aerosol. This process exhibits a high oxidizing power and little interference by the water matrix and the electrical efficiency is within the feasibility range (E$_{el}$ < 3 kWh/m$^3$-order for most contaminants (Bolton et al., 1998). Due to the high capital costs for an electron accelerator (usually >1 million US-$), the related risk potential from X-rays and hence the necessary security measures, further development of the electron beam process does not seem profitable.

3. Oxidation by-products

Oxidation by-product generation during the application of AOPs is a critical factor for process viability. The abundance of nitrogen, halogens and dissolved organic matter (DOM) during disinfection of AOPs might lead to formation of organic halogenated by-products such as total organic halides (TOX), trihalomethanes (THM), haloacetic acids (HAA), haloacetonitriles (HAN), and inorganic by-products (e.g., chloride, perchlorate and bromate). All AOPs are based on radical oxidation pathways. However, OBP formation is diverse depending on radical type (e.g., OH-, sulfate- or chlorine-radical), radical exposure, abundance of other influencing water constituents (e.g. radical scavengers), and direct reactions of applied oxidants such as for instance ozone or chlorine. Occurrence and health risks of by-products in drinking water as well as an overview of regulations and guidelines for specific disinfection by-products is comprehensively reviewed (Richardson et al., 2007; Stalter et al., 2016). While assessing the health risks from OBPs is challenging, there is a general desire to minimize their formation. Thus, in the following sections OBP formation is discussed considering main reaction mechanisms divided into reactions with inorganic and organic compounds to identify opportunities to minimize their formation.

3.1. Reactions with inorganic compounds

The oxihalides (chlorite, chlorate, perchlorate and bromate) are potential inorganic by-products of oxidation processes. Bromate (BrO$_3^-$) which is regulated in drinking water worldwide, can generally be formed in a pure -OH reaction if Br$^-$ is abundant in the feed water (von Gunten and Oliveras, 1998). However, this reaction is suppressed by DOM (Lutze et al., 2014) and in processes with excess H$_2$O$_2$ (UV/H$_2$O$_2$, Fenton reaction), where the oxidation of the intermediate HOBr to BrO$_3^-$ is hindered by the fast reductive reaction with H$_2$O$_2$ to Br$^-$ (k = 7.6 · 10$^9$ M$^{-1}$ s$^{-1}$) (von Gunten, 2003b). Therefore, BrO$_3^-$ formation is negligible in most -OH-dominated systems. Chlorate and perchlorate formation during OH-radical processes only occurs under certain conditions. The initial reaction of OH-radicals with Cl$^-$ is slow with a rate constant in the order of 10$^7$ M$^{-1}$ s$^{-1}$ at pH 7 and formation of Cl-radicals can therefore be neglected at neutral conditions (von Gunten, 2003b). If oxidative chlorine species are abundant (e.g., ClO$_2$, OC$^1^-$), however, sequential oxidation by OH-radicals to chlorate and perchlorate is possible. In SO$_4^-$ based processes, BrO$_3^-$ formation may be formed in a direct reaction of Br$^-$ with SO$_4^-$ (k$_{SO_4^-}$ = 3.5 · 10$^9$ M$^{-1}$ s$^{-1}$ (Redpath and Willson, 1975)) in the absence of DOM (Lutze et al., 2014). In addition, BrO$_3^-$ formation may occur from SO$_4^-$ reaction with Cl$^-$ to form -OH and Cl$^-$ turning SO$_4^-$ based process into a Cl$^-$ and -OH dominated process.

In some cases, -OH are directly formed on active surfaces (e.g. the anode surface in eAOPs or the catalyst surface in heterogeneous cAOPs) and can only react within the diffusion limited zone of about <1 μm (Kapalka et al., 2009). These conditions might induce high radical densities at the surface allowing kinetically unfavored oxidation of Cl$^-$, Br$^-$ and intermediate species forming bromate, chlorate and perchlorate (e.g. Bergmann and Rollin, 2007). A detailed literature review on OBPs formation in eAOPs has recently been compiled by Chaplin (2014).

In ozone based AOPs at elevated bromide concentrations (>100 μg/L), direct reaction of ozone can lead to 5–50% conversion of bromide to bromate, depending on ozone exposure. The fast decomposition of ozone in AOPs limits this reaction (von Gunten, 2003a), but significant bromate formation was still observed at elevated ozone dosages in the O$_3$/H$_2$O$_2$ process (Hübner et al., 2015). Since chloride is not oxidized by ozone, chlorate formation is only relevant for ozonation, if pre-oxidation by reactive chlorine species is applied (von Gunten, 2003b). As discussed above, formation of chlorate, perchlorate and bromate is not critical in UV based AOPs, but other inorganic by-products can be formed. If DOM-containing water samples (10 mgC/L) are exposed to vacuum UV or LP-UV irradiation, H$_2$O$_2$ formation can reach up to 1.5 and 0.3 mg/L, respectively (Buchanan et al., 2006). Furthermore, photolysis of nitrate may form nitrite during UV irradiation. While the molar absorption coefficient of nitrate at λ = 254 nm is low (ε = 4 M$^{-1}$cm$^{-1}$), it increases dramatically below 240 nm (Sharpless and Linden, 2001) revealing higher nitrite formation potentials for MP and VUV systems.

3.2. Reactions with organic compounds

Reactions of -OH with DOM generally involve hydrogen abstraction, electrophilic addition and radical combination. Despite their electrophilic character, these reactions are quite diverse and formation of significant OBP concentrations was not observed in -OH dominated oxidation processes for general water applications.
UV/H₂O₂, for example, was described as an AOP without significant OBP formation and no or minor increase of genotoxic activity if applied to surface water (Linden et al., 2005). Some studies, however, describe significant organic OBP formation during UV/H₂O₂ at high pH and Cl⁻ concentrations (>1 g/L) evaluated as adsorbable organic halides (AOX) (Baycan et al., 2007). Despite the slow reactivity of “OH with Cl⁻ at high concentrations of Cl⁻ formation of chloride radicals (Cl·, Cl₂·) and active chlorine species (e.g., Cl₂, OCI⁻, HOCl) is sufficient. These species can subsequently react with organic compounds by addition and substitution reactions resulting in halogenated OBPs (Oppenlander, 2003). Main formation paths of halogenated organic OBPs (e.g., THM, HAN and HAA) are based on reactions between oxoacids/hypohalites (HOX/OX⁻) and DOM, where the addition of halogens to DOM increases following the order Cl⁻ < I⁻ < Br⁻ (von Gunten, 2003b). Consequently, UV/chlorine process may involve formation of AOX. In contrast, under mass transfer limited conditions organic OBPs are continuously generated (Bagastyo et al., 2012).

In ozone based AOPs, the main pathway for generation of halogenated organic compounds is still the reaction of HOX/OX⁻ with DOM as described above. Formation of bromo-organic compounds (=10 μg/L depending on bromide concentration) during raw surface water ozonation has been confirmed by Huang et al. (2005). Since the oxidation of OI⁻ and OIO⁻ by ozone is fast (pH < 8), reaction of HOI with DOM can be neglected for ozonation processes (von Gunten, 2003b). Formation of HOCl⁻ is not relevant for ozonation based on the low reactivity of ozone with chloride, as described in section 4.1 resulting in a low relevance of chlorinated organic OBPs. Of higher concern is the formation of N-Nitroso-dimethylamine (NDMA), a highly carcinogenic substance mainly formed by chlorination of nitrogen- and organic carbon-containing waters. Some studies reported its occurrence after ozonation (Andrzejewski et al., 2008). Detailed reaction pathways for NDMA formation during ozonation are proposed by Yang et al. (2009). However, NDMA is not a major by-product of ozonation (von Gunten, 2003b; Andrzejewski et al., 2008). During UV/chlorine NDMA formation could be inhibited in a pilot-scale system by quenching excess chlorine with thiosulfate (Sichel et al., 2011).

In UV-based processes, NDMA is effectively removed by UV-photolysis (Stefan and Bolton, 2002; Mitch et al., 2003; Sharpless and Linden, 2003). Other AOPs are less efficient removing NDMA due to moderate and low second-order rate constants with “OH (kOH = 3.8 × 10⁸ M⁻¹s⁻¹ (Wols and Hofman-Caris, 2012) and ozone (kO₃ = 0.052 M⁻¹s⁻¹ (Lee et al., 2007)). A common strategy to control NDMA concentrations in water is the removal of precursors, such as dimethylamine, which can easily be oxidized by ozonation or AOP (Lee et al., 2007). However, also subsequent biological steps are effective to mitigate NDMA (Drewes et al., 2006).

Recently, researchers have shown the potential of mutagenic organic by-product formation during application of medium-pressure UV irradiation to water containing nitrate (Hofman-Caris et al., 2015; Kolkman et al., 2015). The photolysis products of nitrate (mainly peroxynitrite) react with DOM by hydroxylation, nitration and nitrosation reactions forming organic OBPs (Martijn et al., 2014). While potential reaction mechanisms have been proposed (Reckhow et al., 2010; Shah et al., 2011), a comprehensive understanding has not yet been completed. However, nitrated aromatic compounds are expected to be the most toxic OBPs formed in this process (Martijn et al., 2014).

4. Comparison of advanced oxidation processes

EEO values derived for a specific AOP are depending on the molecular structure, the physico-chemical characteristics, such as specific reaction rate constants, and the concentration range of the respective contaminant (only if > 1 mg/L). Furthermore, water matrix, process capacity and energy independent process parameters (e.g., oxidant or catalyst dose) can have a significant influence on the efficiency of the process. In general, EEO values should only be determined for an AOP which is optimized with respect to oxidant demand, reactor geometry, and other process-specific parameters. All these interdependencies should be kept in mind while comparing different AOP technologies via EEO. Hence, the boundary conditions in which EEO values were determined are very important for the overall comparison of AOPs via EEO.

It should be noted that additional energy demand for chemicals or catalysts is not reflected within this figure of merit. The demand for auxiliary oxidants (e.g., H₂O₂), however, can be reflected within the EEO concept by regarding H₂O₂ as “stored electric energy” (Rosenfeld et al., 2006). For example, Müller et al. (2001) calculated an equivalent of 10 kWh for 1 kg of H₂O₂ (100%) based on the commercial prices in Germany. However, the majority of published EEO values are limited to the electricity which is directly used in the process, e.g. for ozone generation or UV-lamp operation.

Several peer-reviewed journal articles deal with the direct comparison of different AOPs in a defined experimental setup with controlled conditions, i.e. in terms of water quality to be treated, target contaminant and other process conditions, with the aim to reveal the most efficient AOP technology. However, many of these studies are lacking important information, neglecting relevant parameters or testing removal of substances with specific reactivity to oxidants other than “OH, e.g. ozone-reactive or photolytically degradable compounds. Furthermore, comparison is only conducted in few water matrices and generalization of those results and their transfer to application with other water types, contaminants etc. should therefore be made with careful consideration of the respective conditions.

For this reason, we critically reviewed and compared reported EEO values from different AOPs. Results are discussed and put in context to studies showing direct comparison, if available. In addition, we analyzed major influencing factors on EEO determination based on literature data for the UV/H₂O₂ process.

4.1. Comparative screening of EEO values for different AOPs

EEO values for numerous AOPs from literature data are illustrated in Fig. 2 as box plots sorted according to their respective median values. A summary of all data including specific information on water type, system size and measured compounds is given at Mendeley Data (https://doi.org/10.17632/n7h8kb4dhf.2). Only data meeting the following criteria were included in the figure:

- Incorporated data is published in a peer-reviewed process
- Manufacturer data and data from non-peer reviewed sources are included if detailed information about the experimental setup is given
- If kinetic data is available, compounds, which are susceptible to direct oxidation by e.g. ozone or UV-photolysis will not be regarded. Threshold values for rate constants in O₃- and UV-based processes are set at kO₃ < 10 M⁻¹s⁻¹ and kUV < 10⁻³ m²J⁻¹

Data evaluation was conducted in three steps: screening of EEO values, single outlier detection and removal and descriptive statistics. Outlier detection was performed by the Dixon test assuming log-normal distribution for all data sets using an online tool available at http://contchart.com/outliers.aspx. Significance testing was performed using the two-sample t-test provided by another online tool (http://www.evanmiller.org/ab-testing/t-test.html) assuming log-normal distribution for all data-sets.

Reported EEO values for individual AOPs often vary by several
orders of magnitude. In case of ozonation, the strong variability might be explained by the dependence of radical formation from water matrix, since it is only initiated by hydroxide ions at elevated pH or from ozone reactions with organic matter. Little variability of other processes might either indicate lower sensitivity to water quality and system design or limited experimental differences in literature data, e.g. oxidation with microwaves was only tested in ultrapure water.

Despite cases of high variability, significant differences between AOPs can be observed from the literature study. Based on median values, AOPs are classified in three groups: processes with median EEO values < 1 kWh/m³ (O₃, O₃/H₂O₂, O₂/UV, UV/H₂O₂, UV/persulfate, UV/chlorine and electron beam) represent a realistic range for full-scale application (group 1). Photo-Fenton, plasma and eAOP with median EEO values of 2.6, 3.3, and 38.1 kWh/m³ (1–100 kWh/m³), respectively, are likely too energy intensive for most practical applications (group 2). However, they might still provide attractive solutions for specific challenges and full-scale applicability of these processes should be further investigated. EEO values for group 2 processes are significantly higher than values of group 1 (p = 0.045). Processes with EEO values > 100 kWh/m³, i.e. UV-based photocatalysis, ultrasound and microwave-based AOPs representing high median values of 335, 2616 and 543 kWh/m³, respectively, are considered as not (yet) energy efficient AOPs. Significance of difference between group 2 and 3 is calculated as p = 0.002.

There are only few quality studies directly comparing processes from these different groups. A direct comparison of UV/H₂O₂ and BDD treatment for aniline removal from synthetic wastewater solutions confirmed lower EEO values for UV/H₂O₂ by about 30% (Benito et al., 2017). However, extensive concentrations of H₂O₂ were applied in this study (1–5 g/L) that might have influenced calculated EEO values of UV/H₂O₂ by re-scavenging of •OH by H₂O₂.

Observed differences between AOPs in the first group are statistically not significant (p = 0.2 in between all AOPs) and most likely depend on experimental conditions. This is confirmed by several studies comparing O₃/H₂O₂ and UV/H₂O₂. Sutherland and co-workers published a comprehensive evaluation of MTBE oxidation from five contaminated groundwaters with highly variable water quality characteristics (Sutherland et al., 2004). Depending on water type and adjusted pH, either O₃/H₂O₂ or UV/H₂O₂ achieved lower EEO values. In contrast, Lester et al. (2011) reported lowest EEO values for O₃/H₂O₂ followed by O₃, UV/H₂O₂/O₃, UV/O₃ and UV for pharmaceutical degradation in phosphate buffer. Also, Müller et al. (2001) showed advantages of the O₂/H₂O₂ combination in comparison to UV/H₂O₂ and UV/O₃. A recent study compared the efficiency of UV/PDS and UV/H₂O₂ during iodoacids degradation, considering most relevant influencing factors (e.g. photosusceptibility and process capacity) (Xiao et al., 2016). Special emphasis was directed to water matrix and oxidant dose effect.

Fig. 2. Overview of published EEO-values of different AOPs sorted according to median values. For O₃- and UV-based AOP data, only substances resistant to direct ozonation/photolysis are shown (references are shown in Table S1). Median values and number of data points are reported on the second and third y-axis, respectively.

Fig. 3. Overview of published EEO-values of the UV/H₂O₂ process, classified into lab-, pilot- and full-scale data. n refers to the number of data points behind the boxplots. Median values are reported next to the 50th percentile line.
Results revealed higher energy efficiencies for the sulfate radical based AOP by a factor of >3. However, comparison of these processes using single compounds or specific compound groups needs to be evaluated carefully since sulfate radicals react more selectively than \( \cdot \)OH.

4.2. Principal influences on EEO-values shown at the UV/H\textsubscript{2}O\textsubscript{2} process

Most boxplots for individual AOPs in Fig. 2 reveal high variances, being mainly based on data variability considered in this review. Water quality, process capacity and the selection of target chemicals are key parameters, which may lead to large deviations of EEO values within one process. Effects of these factors is exemplarily illustrated in the following section using the dataset of UV/H\textsubscript{2}O\textsubscript{2}, which is one of the most intensively investigated AOPs and therefore supplies high data density of EEO values (n = 149, excluding single outliers and data of photo-susceptible compounds). However, transferability of influencing factors is not ensured for other AOPs since most influences are process specific.

4.2.1. Influence of process capacity

EEO values from UV/H\textsubscript{2}O\textsubscript{2} studies conducted at laboratory, pilot and full scale are illustrated in Fig. 3. Median EEO values decrease with process capacity from 2.2 kWh/m\textsuperscript{3} at lab-scale to 0.68 and 0.5 kWh/m\textsuperscript{3} for pilot- and full-scale applications, respectively. A significant difference could be observed (p < 0.05) between lab- and pilot-scale data. The median values indicate that up-scaling enhances energy efficiency, which confirms the findings from Bolton and Stefan (2002). Results furthermore emphasize that comparison of lab-scale energy consumption not necessarily represents operation at full-scale. If possible, energy demand should rather be estimated based on full-scale system design with relevant operational parameters (i.e., oxidant dosage, UV-fluence) determined in standardized lab- or pilot-scale experiments.

4.2.2. Influence of compound reactivity

Energy efficiency of AOPs is also dependent on compound reactivity. Therefore, gathered EEO values from reviewed UV/H\textsubscript{2}O\textsubscript{2} publications were correlated to second-order rate constants (kOH) of photo-resistant target chemicals. Results indicated a slightly negative correlation (R\textsuperscript{2} = 0.21), confirming, that substances with higher kOH values are more efficiently oxidized with a lower energy effort (Fig. S1). However, due to the low correlation coefficient the influence of other parameters (e.g. process capacity) is assumed to be higher.

4.2.3. Influence of water quality

Water quality mainly affects the UV/H\textsubscript{2}O\textsubscript{2} process by UV-transmittance and radical scavengers. Therefore, EEO values were investigated based on water characteristics reported from the respective article. Since numerous water types were included in all data gathered, ranging from ultrapure lab water to industrial wastewater effluents, EEO values were classified into main water application groups: pure water, drinking water, groundwater and wastewater applications. Pure water applications include lab-scale experiments with deionized and ultrapure water but also pilot-scale applications with reverse osmosis permeate (i.e. in water reuse). Drinking water applications summarize UV/H\textsubscript{2}O\textsubscript{2} processes with surface water after pre-treatment with various process combinations. Groundwater applications include AOPs at contaminated sites as well as drinking water applications from groundwater. Wastewater consists of secondary and tertiary effluent from municipal wastewater treatment plants and industrial applications. Resulting EEO values of pure water, drinking water, groundwater, and wastewater applications are presented in Fig. 4 as box plots. Median EEO values of each application were determined as 2.7, 0.63, 2.7 and 2.2 kWh/m\textsuperscript{3}, respectively. However, no significant difference could be observed between different groups (p > 0.05). The concentration of radical scavengers and UV absorbance (UVA) are the most influential parameters for radical yield and radical oxidation efficiency. Consequently, waters with higher scavenger concentrations (and different scavenger composition) and higher UVA should result in higher EEO values. Surprisingly, ultrapure water applications reveal the highest median EEO value in this comparison. A possible explanation for this finding might be the predominant use of pure water in lab-scale experiments which biases the illustration as already discussed in section 4.2.1. Data comparison from drinking and wastewater applications reveal higher energy needs with increasing scavenger content. Especially, DOC and consequently UVA are expected to be higher in this order.

![Fig. 4. Reviewed EEO values of the UV/H\textsubscript{2}O\textsubscript{2} process: Effect of different water matrix applications; n refers to the number of data points behind the boxplots. Median values are reported next to the 50\textsuperscript{th} percentile line.](image)

![Fig. 5. Overview of published EEO-values of the UV/H\textsubscript{2}O\textsubscript{2} process, classified into data based on medium- and low-pressure lamps. Headline shows the number of data points behind the boxplots. Median values are reported next to the 50\textsuperscript{th} percentile line.](image)
In contrast to drinking water, the median EEO value from ground-water applications is similar to wastewater oxidation. Groundwater may contain strongly variable inorganic concentrations, e.g. alkalinity (HCO$_3^-$/CO$_3^{2-}$), but also reduced species like manganese and iron, which might significantly scavenge OH-radicals.

Overall, the operational classification of AOPs presented in Fig. 4 did not suggest any significant effects of water matrix on EEO values, probably because the selected categories like pure water, drinking water, groundwater and wastewater are not specific enough and can include a wide range of different applications and water qualities. Therefore, a direct correlation of water quality parameters with reported EEO values was also investigated. Considered as most relevant parameters, DOC, UV transmittance and turbidity (reported as NTU) data were provided for 124, 131 and 31 of the reviewed 147 data sets, respectively. A direct relationship within the reviewed data set between EEO values and DOC concentrations, UV transmittance or NTU, however, could not be revealed (Figs. S2 and S3).

4.2.4. Influence of lamp type

The influence of different lamp types on EEO values is illustrated in Fig. 5. MP UV lamps result in significantly higher EEO values compared to LP lamps (p < 0.001). The respective median values can be determined as 1.0 and 0.4 kWh/m$^3$. This is not surprising, since the molar absorption coefficient of H$_2$O$_2$ increases at wavelengths <260 nm and LP lamps depict higher (<35% at 254 nm) energy efficiencies than MP lamps (<10% at 254 nm). Inevitably, LP lamps yield in a higher H$_2$O$_2$ activation and consequently in lower EEO values. This was also confirmed by Rosenfeldt et al. (2005), who directly compared LP and MP UV lamps for the oxidation of 2-methyl-isoborneol (2-MIB) and geosmin. Raw blend surface water and filtered clearwell water were used in lab-scale reactors. EEO values revealed that LP lamps can be more energy efficient than MP lamps for *OH generation.

5. Conclusions

This study provides a critical review of different established and emerging AOPs including a mechanistic discussion of process-specific by-product formation. To facilitate a comparison of energy efficiency, data were collected for various AOPs in an extensive analysis of peer-reviewed journal articles and critically compared based on reported EEO values. Despite high variability of results from individual processes, significant differences between AOPs efficiency were observed. Based on reported EEO values, processes were classified into (1) AOPs with median EEO values of <1 kWh/m$^3$ (O$_3$, O$_3$/H$_2$O$_2$, O$_3$/UV, UV/H$_2$O$_2$, UV/persulfate, UV/chlorine, electron beam), (2) processes with median EEO values in the range of 1–100 kWh/m$^3$ (Photo-Fenton, plasma, and electrolytic AOPs) and (3) UV-based photocatalysis, ultrasound, and microwave-based AOPs (median EEO values of >100 kWh/m$^3$), which are considered as not (yet) energy efficient AOPs. A more detailed evaluation of data for the UV/H$_2$O$_2$ process showed highest impact of UV-lamp type, water matrix, and process capacity (lab-scale vs. pilot- and full-scale) on resulting EEO values. No significant correlation could be observed between EEO values and compound reactivity with OH-radicals. In addition, reviewed literature indicates that by-product formation from hydroxyl radicals is not critical unless formed at high density on surface areas (e.g. in electrolytic AOPs). However, AOPs involving other oxidants such as ozone, sulphate radicals or chloride radicals need to be evaluated in more detail since site- and process-specific by-products might be formed.

This study confirmed the main limitation to use the EEO concept for a general comparison of different AOPs due to the variability of the above-mentioned influencing factors. However, if all factors are considered within a direct comparison, the EEO concept provides a powerful figure of merit to directly compare and evaluate AOPs based on energy efficiency.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2018.03.042.

References


Bolton, J.R., Bircher, K.G., Tumas, W., Tolman, C.A., 2001. Figures-of-merit for the


