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Review

Toxicity Reduction of Industrial and Municipal Wastewater by Advanced Oxidation Processes (Photo-Fenton, UVC/H_2O_2, Electro-Fenton and Galvanic Fenton): A Review

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Abstract: The application of Fenton-based advanced oxidation processes (AOPs), such as photo-Fenton or electro-Fenton for wastewater treatment have been extensively studied in recent decades due to its high efficiency for the decomposition of persistent organic pollutants. Usually Fenton-based AOPs are used for the degradation of targeted pollutant or group of pollutants, which often leads to the formation of toxic by-products possessing a potential environmental risk. In this work, we have collected and reviewed recent findings regarding the feasibility of Fenton-based AOPs (photo-Fenton, UVC/H_2O_2, electro-Fenton and galvanic Fenton) for the detoxification of real municipal and industrial wastewaters. More specifically, operational conditions, relevance and suitability of different bioassays for the toxicity assessment of various wastewater types, cost estimation, all of which compose current challenges for the application of these AOPs for real wastewater detoxification are discussed.

Keywords: wastewater; advanced oxidation processes (AOPs); photo-Fenton; toxicity; bioassays; costs

1. Introduction

Industrial and urban wastewater effluents are considered to be among the most important sources of aquatic pollutants [1]. Due to advances in analytical chemistry, increasingly more pollutants can be identified and quantified at very low concentrations [2]. Negative impacts, such as neuroendocrine, mutagenic and health effects on the aquatic environment, have been reported recently for contaminants even at low concentrations [3–5].

Wastewater treatment plants (WWTP) play the role of a barrier preventing the release of contaminants into the aquatic environment. Most wastewater treatment plants carry out conventional treatment which includes, in the best case, a tertiary step. In practice, the main objectives of tertiary step are removal of nutrients, turbidity and pathogens. As a result, such

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processes as coagulation, sand and membrane filtration, chlorination and UVC disinfection are applied. However, these processes are not effective enough for resistant and recalcitrant pollutant elimination. In accordance with recent studies, traditional urban and industrial WWTPs are not always efficient for the removal of various organic pollutants such as contaminants of emerging concern (CECs) [6], which cause its release into the aquatic environment and damage the stability of ecosystems. In addition, the current directive concerning urban wastewater treatment [7] does not include methodology and control for modern contaminants discharge. Therefore, tertiary treatment of wastewater effluents should aim not only at nutrients, particulate matter removal and disinfection, but also emerging pollutants elimination is needed in order to avoid the discharge of these specific pollutants into the aquatic environment [8].

Among the available technologies for organic pollutants removal suitable for the post-treatment of wastewater effluents are advanced oxidation processes (AOPs) which have received significant attention in recent decades. Generally, AOPs are recommended when the level of chemical oxygen demand (COD) is low which makes AOPs suitable for tertiary treatment for the majority of wastewater effluents [9].

The efficiency of AOPs is usually evaluated based on the chemical analysis of treated water, including the concentration of pollutants (such as emerging compounds), total organic carbon (TOC), COD, etc. However, decomposition of pollutants occurring during AOPs leads to the formation of by-products. These by-products are not always known and not easy to identify due to required sophisticated analytical equipment, for instance, liquid chromatography coupled with time of flight mass spectrometry (LC-TOF MS) [10]. Thus, the chemical analysis might not be the best and not the only way to assess the effectiveness of AOPs. It should also be noted that by-products generated during the AOPs can be more toxic than parental compounds [11–15]. Therefore, chemical analysis alone for the evaluation of the efficiency of AOPs may produce inconclusive results and should be accompanied by toxicity assessment when possible.

In the majority of the studies devoted to wastewater treatment by AOPs, the toxicity assessment is conducted when the optimal conditions of the applied process are already selected (based on maximum COD removal, for example). This is done in order to confirm that no toxic effect is generated for a particular species at chosen optimal conditions. However, some studies do not include toxicity assessment after COD reduction which does not mean that the water could be safe for discharge (as some toxic by-products can possibly be generated). Therefore, toxicity bioassays could also be used for the selection of the optimal condition of the process, especially when the objective is to produce non-toxic wastewater effluent for species indigenous in the receiving aquatic environment.

Among various AOPs used for the detoxification and purification of wastewater, Fenton-based processes such as photo-Fenton is emerging as most studied and one of significant promise. Thus, photo-Fenton is listed among the best available techniques for wastewater treatment in the textile industry [16]. Moreover, the Technology Readiness Level (TRL) of photo-Fenton process for water treatment was reported to be 8 (system complete and qualified) [17], which is only one level below the maximum (TRL 9 "System proven in operational environment"). Judging from the results obtained from Scopus database (Figure 1), the interest in the evaluation of the toxicity of water treated by Fenton-based AOPs is increasing and continues to grow nowadays. However, only about 7% of studies concerned with the toxicity assessment of real (based on real wastewater matrix) wastewater treated by Fenton-based AOPs (Figure 1). Early findings in this area of research were reported in excellent review [18].

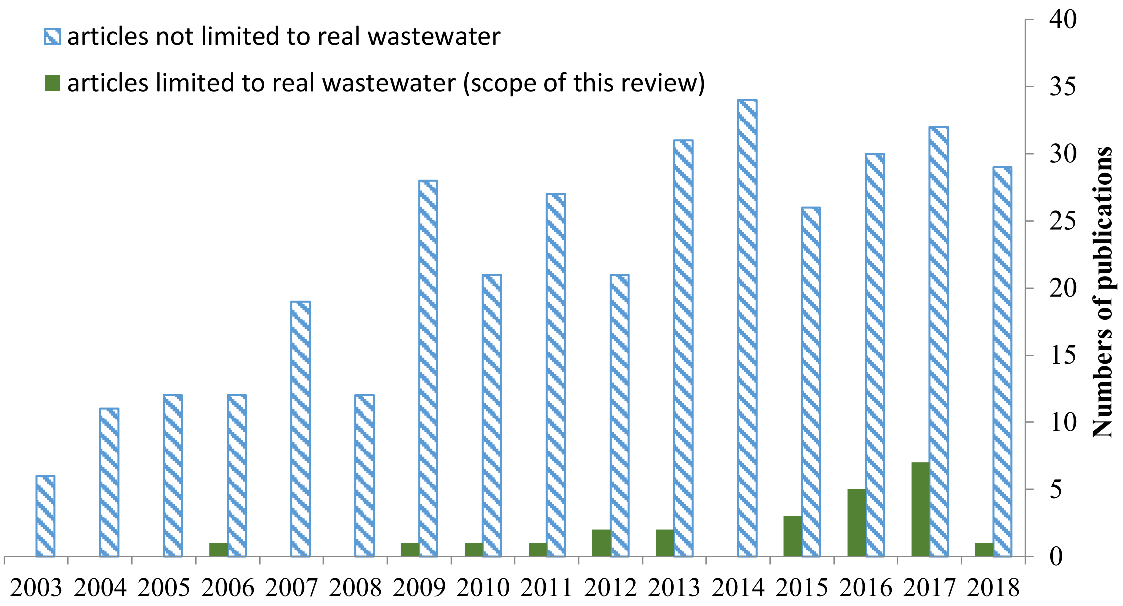

Figure 1. Number of scientific publications per year containing keywords (Scopus): "Fenton", "wastewater" and "toxicity" in the title and/or keywords of article (blue). Number of articles in which real wastewater matrix was used (green).

The main goal of this work is to summarize and critically discuss the recent findings regarding the feasibility of photo-Fenton, UVC/H_2O_2 (in presence of iron), electro-Fenton and galvanic Fenton AOPs for the detoxification of real industrial or urban wastewater (or wastewater matrix). It is important to emphasize that in this review, studies, in which the toxicity assessment was applied for model wastewater were not discussed. Relevant scientific articles for this review were selected using Science Direct, Scopus, Google Scholar and NCBI databases. Obtained literature list was checked manually with the purpose to leave studies, in which (i) only real or synthetic wastewater (municipal and/or industrial wastewater matrix) was used; (ii) toxicity assessment was performed before and after (or during) Fenton-based AOPs. It should be noticed that list of articles used for this review was limited to those published in peer-reviewed journals in English language.

2. Photo-Fenton Process for Wastewater Detoxification

2.1. Main Principles of Photo-Fenton

The Fenton process was called after Henry J.H. Fenton [19], who discovered it during the degradation of tartaric acid in the presence of H_2O_2 and Fe^{2+} as a catalyst. Nowadays there are two generally accepted mechanisms of Fenton reactions [20]. The first mechanism, known as "free radical" or "classical" mechanism was suggested in 1934 by Haber and Weiss [21] and further investigated by Barb et al. [22–24]. In this mechanism, formation of hydroxyl radicals ($HO^{\cdot}$) is considered as a crucial step leading to series of reactions [25], main of which are presented below (reactions 1–4). Generation of hydroxyl radicals occurs during reaction of iron(2+) with hydrogen peroxide (reaction 1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^- \quad (1)$$

Reduction of iron(3+) to iron(2+) takes place in accordance with reaction 2. This reaction can be rate-limiting as it is significantly slower than reaction 1 [25].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (2)$$

Scavenging of hydroxyl radicals by iron(2+) and H_2O_2 (reactions 3 and 4) takes place as shown below.

$$H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad (3)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^{-} \quad (4)$$

According to the "non-classical" Fenton mechanism, ferryl moiety (Fe = O) is generated during reaction between iron(2+) and hydrogen peroxide. Ferryl moiety can be formed when some chelated forms of iron (polycarboxylate and/or macrocyclic ligand) reacts with H_2O_2 [25]. It should be mentioned that some organic pollutants possess capability of chelating iron [25], which possibly may lead to formation of ferryl moietes. The ferryl ions were first suggested as an active oxidant by Bray and Gorin [26]. Reactions representing non-classical Fenton pathway are shown below (reactions 5 and 6).

$$Fe^{2+} + H_2O_2 \rightarrow FeO^{2+} + H_2O \quad (5)$$

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{2+} + H_2O + O_2 \quad (6)$$

Fenton processes applied in water treatment usually require hydrogen peroxide/iron molar ration between 100 and 1000 [25]. Commonly reported optimum pH of Fenton reaction is around 3, which can be explained by speciation of iron [25]. When the pH of the water decreases (2.5–3), the performance of the Fenton process increases due to the higher solubility of iron(3+) in water. At a pH lower than 2.5, the formation of iron complexes such as $[Fe(H_2O)_6]^{2+}$ may occur, as a result, the reaction with H_2O_2 becomes slower and consequently less oxidizing species are generated. At basic pH, iron reacts with hydroxide ions (HO^{-}) leading to precipitation in the form of iron hydroxide $Fe(OH)_2$ or $Fe(OH)_3$. Precipitated iron does not react with H_2O_2 [27]. More detailed consideration of Fenton process mechanism can be found in distinguished papers [25,27,28].

The Fenton process is significantly enhanced when UV radiation is introduced (photo-Fenton) [29]. Under these conditions, additional reactions take place, namely the photo-reduction of iron(3+) to iron(2+) as shown in reaction 7 ($\lambda < 600$ nm) and the photolysis of hydrogen peroxide, (UV/H_2O_2) in reaction 8 ($\lambda < 310$ nm) [30].

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\cdot} \quad (7)$$

$$H_2O_2 + h\nu \rightarrow 2\ HO^{\cdot} \quad (8)$$

The conventional photo-Fenton process usually occurs at a pH of approx. 3.0, molar ratio of H_2O_2/iron between 2 and 150 and molar ratio of H_2O_2/COD between 1 and 3.5 [31–33]. One of the main drawbacks of the conventional photo-Fenton process is the low pH of the water. The pH adjustment (around pH 3) is a relatively easy operation on the laboratory scale, but it is generally regarded as not economically feasible for application on the industrial scale (especially taking into account subsequent neutralization of water and separation of generated sludge). A photo-Fenton reaction can also occur under circumneutral pH (6.5–7.5) in water containing naturally present or added chelating agents, forming dissolved organic complexes of iron [34,35]. It is noteworthy that the concentration of iron in the water can be considerably lower when photo-Fenton is applied compared to the Fenton process (in absence of adequate light) due to the importance of fast iron recycling (reaction 7). Moreover, iron removal may not be required if it is below the established discharge limit.

It should be mentioned that UV/H_2O_2 treatment applied for real wastewater (UV/H_2O_2/RWW) can also include photo-Fenton mechanism. This can be explained by the fact that presence of naturally dissolved iron in urban and industrial wastewaters might favor the mechanism of photo-Fenton process as it was previously reported [36]. According to the literature, photo-Fenton may occur even at very low concentrations (μg L^{-1}) of dissolved iron in water [37]. For instance, it was demonstrated that 0.05–0.09 mg L^{-1} (50–90 μg L^{-1}) of natural iron content was sufficient to drive an efficient photo-Fenton process [37]. In all articles on UV/H_2O_2 included in this review, the concentration of total dissolved iron was in the same rage or above that reported in [36,37]. For instance, total dissolved iron concentration in urban wastewater at one of the largest wastewater treatment plant in Finland (2015–2018) varied from 8.30–9.31 mg L^{-1} (influent) and 0.32–0.47 mg L^{-1} (effluent) [38–41]. Concentration of iron in industrial wastewaters varies significantly depending on the type of industry and other factors. It should be noticed that when UVC lamps are used, the dominant mechanism for radical generation might not be photo-Fenton, while it can be assumed that in presence of naturally available iron (in case of real wastewaters) photo-Fenton reactions may also take place. In order to distinguish these processes, UV/H_2O_2 in presence of iron was called as UV/H_2O_2/RWW in this review.

2.2. Types of Wastewater

The types of wastewater used for detoxification by photo-Fenton and/or UV/H_2O_2/RWW treatment in the last ten years are shown in Figure 2.

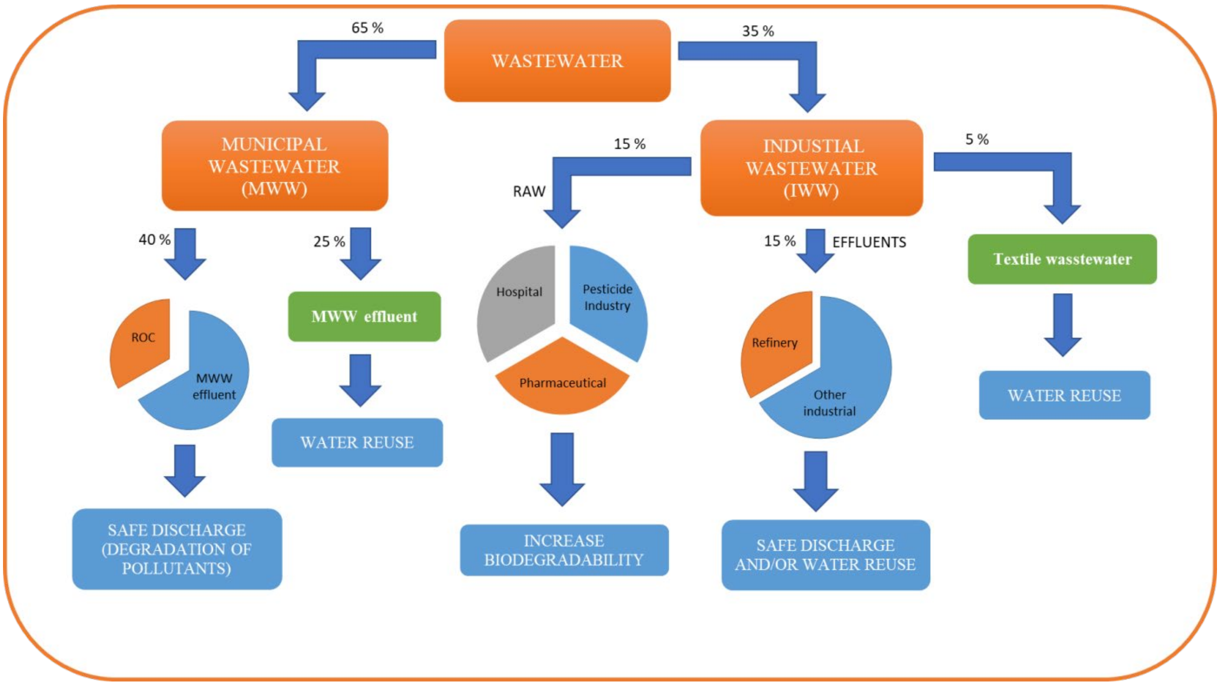

Figure 2. Schematic presentation of types of wastewater used for detoxification by photo-Fenton and/or UV/H_2O_2/real waste water (RWW) in the last ten years.

Approx. 35% of the reviewed articles on photo-Fenton were conducted with industrial wastewater (IWW) from such sectors as refinery, textile, pesticide and pharmaceutical. Influents and effluents of industrial wastewater treatment plants were used. Therefore, the concentration of organic pollutants in IWW varied greatly. The reported results suggest that photo-Fenton treatment can be successfully applied as IWW pre-treatment (before the biological process) causing the increase of its biodegradability [42] as well as post-treatment (after biological process) of IWW effluents leading to the degradation of organic pollutants and the decrease of toxicity [43]. Interestingly, among the reviewed articles, there are studies reporting that the quality of IWW effluent after photo-Fenton was in agreement with the legal requirements (physical, chemical and microbiological parameters) for IWW reuse [43,44]. Moreover, solar photo-Fenton was reported to be efficient not only for the detoxification of textile wastewater but also for its successful reuse in the dyeing and washing stages of the process [15].

As can be seen from Figure 2, the majority of articles (65%) were performed with municipal wastewater treatment plant effluents (MWW) and its concentrates. In general, DOC and COD values for the studied MWW effluents varied in a range of 7–23 mg L^{-1} and 26–83 mg L^{-1}, respectively.

These values were higher for the concentrates obtained from MWW effluents, being 37–53 mg L^{-1} for DOC and 105–200 mg L^{-1} for COD. The highest COD values were observed for raw hospital wastewater (COD, 1350 mg L^{-1}). It was demonstrated that photo-Fenton is efficient as a pre-treatment step (before biological process) of raw hospital wastewater for increasing its biodegradability and detoxification [45] and a post-treatment step (after biological process) of MWW effluents and concentrates for the elimination of pollutants and the detoxification of water [12,46]. The application of the additional post-treatment of MWW effluents, such as the photo-Fenton process in general leads to the decomposition of organic pollutants and detoxification of water. Therefore, such effluents are becoming more attractive for water reuse, especially in areas with water scarcity. Among the reviewed literature there are studies for MWW effluent reuse using UV/H_2O_2/RWW treatment [47–49].

It should be mentioned that in 35% of the reviewed articles devoted to the detoxification of wastewater by photo-Fenton adjustment of pH and/or decreasing concentration of carbonates was performed (for example by the addition of H_2SO_4). Carbonates or hydrogencarbonate present in wastewater can play the role of hydroxyl radical scavengers, as shown in reactions 9 and 10 [9].

$$HO^{\cdot} + HCO_3^- \rightarrow CO_3^{\cdot-} + H_2O \tag{9}$$

$$HO^{\cdot} + CO_3^{2-} \rightarrow CO_3^{\cdot-} + HO^- \tag{10}$$

Therefore, the elimination of carbonates and/or hydrogencarbonates can significantly enhance the performance of photo-Fenton treatment. Taking into consideration that the pH of wastewater treated by photo-Fenton is close to neutral, the acidification of wastewater in order to increase the solubility of iron(3+) and/or eliminate hydrogencarbonates might be associated with relatively high cost on the industrial scale as well as sludge generation. It can be expected that more studies will be conducted in the future on the detoxification of wastewater by the photo-Fenton process at near neutral pH.

2.3. Operational Conditions

2.3.1. Concentration of Iron in Wastewater

Iron concentration in wastewater is of high importance for the performance of Fenton or the photo-Fenton process. As mentioned above, the amount of iron required for photo-Fenton process is significantly lower than that for classical Fenton. In reviewed articles, two main approaches were used: (i) addition of iron to the wastewater and (ii) without iron addition (UV/H_2O_2/RWW process with iron naturally present in the wastewater). Taking into account that iron is often present in many types of wastewaters, in some cases, its concentration might be sufficient for successful photo-Fenton treatment aiming at removal of low concentrations of organic contaminants and disinfection (as it was mentioned above, 50 μg L^{-1} was reported to be sufficient for photo-Fenton process [36]).

The concentration of added iron in industrial and municipal wastewater treated by photo-Fenton varied from 5 to 168 mg L^{-1}, whereas when iron was not added to the wastewater its concentrations were generally at μg L^{-1} level (~60–220 μg L^{-1}). An optimal concentration of iron reported for the photo-Fenton detoxification of municipal wastewater treatment plant effluents, reverse osmosis and nanofiltration concentrates was in the range of 5–60 mg L^{-1}, while the most commonly used concentrations were 5 or 20 mg L^{-1}. For raw hospital wastewater (IWW), a higher iron concentration was applied (135 mg L^{-1}). In general, the iron concentration applied for the detoxification of industrial wastewater by photo-Fenton was higher than that for municipal wastewater, varying in a range of 20–168 mg L^{-1}. When a relatively high concentration of iron is required for the process, iron removal should be conducted after the application of the Fenton or photo-Fenton process in order to achieve discharge limits of iron in wastewater effluents. Maximum permissible concentrations of iron in surface waters (receiving wastewater effluents) are established based on toxicity data and other relevant parameters. To the best of our knowledge, there are only a few studies concerned with the toxicity assessment of iron for aquatic organisms [50–54]. In a recent study, the final chronic value of 251 μg L^{-1} was estimated for iron(3+) at a circumneutral pH based on a toxicity assessment on a taxonomically diverse group of organisms and a mesocosm study [54]. The maximum permissible discharge of iron in wastewater treatment plant effluents is calculated for each case, so the concentration of iron should not exceed the maximum permissible concentration at the control point. In the United States, the recommended iron concentration of 1 mg L^{-1} should be achieved at the end of the initial dilution zone (general and designated use of water) for the protection of aquatic life [55]. According to the general industrial wastewater discharge standards suggested by the Water Environment Partnership in Asia (WEPA), the discharge limit for iron for industrial wastewater is 2 mg L^{-1} [56]. Taking into account the concentrations of added iron in reviewed studies, it is questionable as to whether the residual iron concentration in treated wastewater (after wastewater neutralization when needed) can be in agreement with what is suggested by the WEPA limits.

2.3.2. Concentration of H_2O_2 in Wastewater

Another important parameter for photo-Fenton wastewater treatment is H_2O_2 concentration. The weight ratio of H_2O_2/Fe varied from 2.5 to 25 (80% of reviewed articles) and from 40 to 105 (20% of articles) when iron was added prior to treatment. Generally, there are two different ways of adding H_2O_2 to the reaction: (i) adding the optimal concentration fully before the beginning of treatment [57], and (ii) adding a part of the required amount of H_2O_2 before and during the process (usually when added H_2O_2 is consumed, the next part is added) [12]. An optimal concentration of H_2O_2 reported for the photo-Fenton detoxification of municipal wastewater effluents and its reverse osmosis and nanofiltration concentrates varied from 50 to 102 mg L^{-1}. For the photo-Fenton detoxification of the raw hospital wastewater concentration of H_2O_2 was four times higher (5400 mg L^{-1}) than the initial COD value (1350 mg L^{-1}). In the reviewed studies, the concentration of H_2O_2 added to industrial wastewater for the photo-Fenton process varied from 136 to 6273 mg L^{-1}. Such a huge variation can be possibly explained by the significant difference in the initial TOC and COD levels of industrial wastewaters.

In the majority of reviewed articles devoted to the detoxification of wastewater using the photo-Fenton process (>70%) concentration of residual H_2O_2 (not consumed during photo-Fenton treatment) after treatment was monitored. In some cases, residual H_2O_2 can be as high as 1000 mg L^{-1} [42]. It is noteworthy that the presence of residual H_2O_2 in wastewater effluent can be a problem for water reuse or safe discharge due to the high toxicity of this compound even at low concentrations [58]. Therefore, residual H_2O_2 should be eliminated from treated wastewater before discharge or reuse. In the reviewed works, two main approaches were implemented in order to avoid the presence of residual H_2O_2 in treated water, namely the addition of relatively small concentrations of H_2O_2 (which can be fully consumed during the process) and filtration through activated carbon. It was reported that the decomposition of H_2O_2 is catalyzed by activated carbon [59–62]. Therefore, this process can be defined as catalytic wet peroxide oxidation (CWPO), which is one of AOPs. The CWPO can be considered to be beneficial post-treatment step after the photo-Fenton process leading to the removal of residual H_2O_2 as well as residual hydrophobic organic contaminants.

2.3.3. Irradiation Sources

Irradiation sources are introduced to the Fenton reaction in order to increase the reaction rate, which occurs mainly due to photo-reduction of iron(3+) to iron(2+) (reaction 7; $\lambda < 600$ nm) and the photolysis of hydrogen peroxide ($\lambda = 254$ nm).

The most common UV sources applied for photo-Fenton and/or UV/H_2O_2/RWW water purification in industrial or semi industrial scale are UVC mercury based lamps. Depending on the pressure of mercury vapor, low pressure (LP, 0.01 mbar or 1 Pa) and medium pressure (MP, 1 bar or 100 kPa) lamps can be differentiated. Two main types of LP lamps can be distinguished: pure mercury lamps (standard) and mercury amalgam (usually mercury/indium) [63]. The introduction of LP amalgam lamps to the market was extremely beneficial due to higher specific UVC flux per unit arc length (up to 1000 mW cm^{-1}) in comparison with standard LP lamps (<200 mW cm^{-1}) [63,64]. The main characteristics of MP and LP amalgam lamps are presented in Table 1.

Table 1. Main parameters of low pressure (LP) (amalgam) and medium pressure (MP) lamps [63].

Parameters	LP Amalgam Lamp	MP
UV spectrum	monochromatic (254 nm)	polychromatic (200–600 nm)
Operating temperature (°C)	90–120	500–950
Electrical power (W)	40–500	400–60000
Operation costs	relatively low	high
Amount of liquid mercury (mg):	0	up to 300
Specific UVC flux (W/cm)	<1	<35
UVC efficiency (%)	35–40	5–15
Life-time (h)	<16000	<5000

As can be seen in Table 1, LP lamps emit a wavelength of 254 nm which is suitable for H_2O_2 breaking into oxidizing species. In case of an MP lamp, the emission is polychromatic but most of the spectrum (>280 nm) is not relevant for H_2O_2 decomposition. The main advantage of an MP lamp is the specific UVC flux per unit arc length, which can reach 35 W cm^{-1}. However, the UVC efficiency of an MP lamp is about three times lower than that of an LP amalgam lamp. Moreover, the lifetime of LP amalgam lamps is about three times higher than an MP lamp, which obviously affect the cost. However, if the space is limited, an MP lamp can be used due to high UVC output and a compact reactor design. In our earlier work, we observed that the electricity consumption of MP lamp was about six times higher than that of an LP lamp, while the degradation performance of organic pollutants was similar [43]. Moreover, in case of refinery wastewater treatment by UV/H_2O_2/RWW, the formation of toxic phenolic by-product was detected when an MP lamp was applied which was not the case with an LP lamp [43], suggesting that pathways of organic contaminant degradation varies when different types of lamps are utilized. Similar results were reported earlier for drinking water [65]. In summary, the achieved results indicate that LP lamps are more beneficial than MP lamps. It is noteworthy that the intensity of the lamp is not provided in some articles; moreover, the elimination of organic pollutants is represented as a function of time. The contact time is a useful parameter for the selection of the optimal conditions of the process in case an experimental set-up and wastewater matrix are the same. However, the authors of the present paper believe that the contact time might not be an appropriate parameter when the performance of photo-Fenton and/or UV/H_2O_2/RWW treatment, applied to different wastewaters using various experimental set ups, should be compared. The UVC dose, encompassing the contact time and intensity of irradiation, would be more suitable parameter allowing to compare various studies. Among the reviewed studies devoted to the detoxification of wastewater using photo-Fenton and/or UV/H_2O_2/RWW treatment, LP and MP lamps were used as the radiation source in approx. 39% and 28% of the articles, respectively. In one study [42] high pressure mercury vapor lamp was used as a source of UVA. However, it should be noticed that use of these conventional UV lamps leads to generation of highly toxic wastes at the end of their useful life time. Hence, alternative and more environmentally friendly irradiation sources, such as light emitting diodes (LEDs) and natural solar irradiation may be used in the future. Considering that 128 countries signed the Minamata Convention on Mercury [66], the use of light emitting diodes (LEDs) is becoming more attractive. Taking into account rapid development of LED technology and advances achieved in this field in recent years it may be expected that more studies will be conducted in the future using LEDs as irradiation source.

Approx. 33% among the reviewed studies on photo-Fenton wastewater detoxification were conducted using natural solar light as the radiation source. It should be mentioned that the solar photo-Fenton process can be activated by low global irradiance values (200 W m^{-2}) when relatively low concentration of iron and H_2O_2 are present (0.5 mg L^{-1} Fe^{2+}/5 mg L^{-1} H_2O_2) in water [67].

2.4. Toxicity

Both acute and chronic bioassays were applied for the toxicity assessment of wastewater treated by the photo-Fenton process. Bacteria [15,45,68,69], seawater invertebrates [42], freshwater invertebrates [70], microalgae [46], freshwater vertebrates [49], seawater vertebrates [46] and plants (phytotoxicity assay) were used in the last ten years for the toxicity assessment of wastewater treated by photo-Fenton and/or UV/H_2O_2/RWW. In 60% of the reviewed studies, the toxicity of wastewater decreased after the application of the photo-Fenton and/or UV/H_2O_2/RWW process, especially when added H_2O_2 was fully consumed and/or post-treatment step such as CWPO, leading to the elimination of residual H_2O_2 and some trace pollutants, was applied. It is noteworthy that residual H_2O_2 may significantly elevate the toxicity of the water after treatment [43]. Therefore, caution should be applied in the interpretation and comparison of results of various studies on wastewater detoxification by photo-Fenton because in some studies residual H_2O_2 is eliminated before the toxicity assessment [42] while in others it is not [43]. The question regarding H_2O_2 removal prior conducting toxicity bioassays before, during and after the photo-Fenton process may arise. The authors of the present paper tend to believe that in case when the goal is to determine possible toxic effect of treated wastewater to the receiving environment, the water sample should not be modified before toxicity assessment, i.e., the residual H_2O_2 (if any) should not be removed. However, if the goal of the study is to determine the toxic effect of generated during the process by-products the elimination of H_2O_2 before toxicity assessment might be relevant. A toxicity assessment during the photo-Fenton treatment of wastewater was performed in approx. 30% of the reviewed works. In all of these studies, residual H_2O_2 was eliminated prior to the toxicity evaluation. However, a significant increase of toxicity during the photo-Fenton process was observed in MWW effluents with *Vibrio fischeri* [12] and *Lactuca sativa* [13], and in IWW with *Vibrio fischeri* [14] and *Alivibrio fischeri* [15]. These results generally may be ascribed to the formation of more toxic by-products during the photo-Fenton process than parental contaminants and their possible synergetic effect. Another interesting aspect when analyzing the results of toxicity tests is that chelating agents might be added in order to perform photo-Fenton at a near neutral pH [34]. However, as reported in a recent study [70], the addition of certain concentrations of chelating agents such as (S,S)-Ethylenediamine-N,N′-disuccinic acid trisodium salt (EDDS) can be the toxic.

The types of IWW treated by the photo-Fenton process for its detoxification are shown in Figure 2. Bioassays with *Vibrio fischeri*, *Alivibrio fischeri*, *Photobacterium phosphoreum*, *Artemia salina*, *Daphnia magna*, *Paracentrotus lividus* and *Sparus aurata larvae* were used for the assessment of wastewater toxicity before, after and during photo-Fenton treatment. All the above-mentioned toxicity assays were sensitive for IWW. Interestingly, *Daphnia magna* was too sensitive to pharmaceutical wastewater. Thus, after 24 h of exposure all of the organisms were dead not only in the untreated pharmaceutical wastewater, but also in the water samples taken during and after photo-Fenton treatment (hydrogen peroxide was removed from water samples prior toxicity test) [14].

The toxicity tests used for the assessment of hospital and MWW detoxification efficiency by the photo-Fenton process were *Vibrio fischeri*, *Daphnia magna*, *Tetrahymena thermophila*, *Carassius auratus* L., *Sorghum saccharatum*, *Lepidium sativum*, *Sinapis alba*, *Lactuca sativa*, *Spirodela polyrhiza*, *Sparus aurata larvae*, *Paracentrotus lividus* and *Isochrysis galbana*. Among the reviewed articles, the most commonly applied toxicity bioassay for MWW effluents was a standardized *Vibrio fischeri* bioluminescence test with 5, 15 and 30 min incubation time (ISO 11348). Such parameters as short duration required for analysis, well-defined protocols, reproducibility and sensibility, as well as cost efficiency were reported among the main advantages of this test [71–74]. However, it was demonstrated that the standard *Vibrio fischeri* bioluminescence test underestimates or even fails to detect the toxicity of chemical compounds interfering in the biosynthetic process due to insufficient incubation time (acute toxicity assessment) [75,76]. Interestingly, a long-term (chronic toxicity assessment) *Vibrio fischeri* bioassay (7 h and 24 h) was reported to overcome this limitation [76]. This might probably be explained by insignificant acute toxic effect and measurable chronic toxicity of pollutants in MWW on *Vibrio fischeri*. Moreover, the standard *Vibrio fischeri* bioassay cannot always provide relevant biological or ecological information [77]. Thus, *Vibrio fischeri* is marine bacteria, so the results of this test might be irrelevant for the toxicity assessment of wastewater discharged to the freshwater body (not an adequate environment for this species). The *Vibrio fischeri* bioassay was reported to be not sensitive for spiked and naturally present pollutants in MWW effluents before and after photo-Fenton treatment [13,49,69]. These findings are in agreement with another study which demonstrated that effluents from nine different WWTPs were not toxic to *Vibrio fischeri* [78]. It should be noted that some authors reported growth stimulation (hormesis) of *Vibrio fischeri* in MWW effluents [46,68]. However, in some cases, a *Vibrio fischeri* bioassay was reported to be sensitive for MWW effluents, its concentrates and hospital wastewater treated by the photo-Fenton process [45,70,79]. This might be explained by the presence of residual H_2O_2 in water during the toxicity assessment [79] or additional toxicity due to the added chelating agent [70] or significantly higher concentrations of pollutants in WW [45].

Another commonly used toxicity bioassay is the *Daphnia magna* (freshwater invertebrate) immobilization test. High sensitivity, relatively low cost and ease of use were reported among the main advantages of this bioassay [80]. It was only in one study that a *Daphnia magna* bioassay was reported to be not sensitive to MWW effluent before and after photo-Fenton treatment (residual concentration of H_2O_2 was in the range of 15–20 mg L^{-1}) [68], while in other studies this test was sensitive enough [13,70,81]. However, it was suggested by Koivisto in 1995 that this excellent bioassay might not be ecologically relevant since *Daphnia magna* is not a representative zooplankton species [80]. Interestingly, a bioassay with *Tetrahymena thermophyla* was reported to be more sensitive than that with *Daphnia magna* (48 h) for MWW effluents [13].

Toxicity tests with different types of fish are well known and widely used because of high sensitivity. However, fish bioassays are usually time consuming, requiring special equipment and a skilled operator [82]. Shu and co-authors studied the endocrine disruption effect on goldfish (*Carassius auratus* L.) exposed to MWW effluent (untreated, after UV/H_2O_2/RWW and after GAC) [49]. The results of this study revealed acute and sub-chronic endocrine disruptors in the kidney, liver and spleen of goldfish exposed to untreated effluent. Interestingly, the UV/H_2O_2/RWW treatment was not efficient due to the negative acute (7 days) toxicological impact on goldfish (spring, summer and autumn). The efficiency of the UV/H_2O_2/RWW process for the elimination of a sub-chronic (60 days) impact was changing depending on the season. Thus, in spring, no significant difference was observed for the sub-chronic toxic effect between reuse water and water after the UV/H_2O_2/RWW process. However, during the summer season, the potential of UV/H_2O_2/RWW treatment for the remediation of the estrogenic impact in the spleen and kidney of goldfish was observed. These results were attributed to the seasonal variations of estrogenic substances composition in water [49]. Another study by Singh and co-authors reported that 7 days of exposure (acute toxicity) of goldfish to the xenobiotics present in MWW effluent led to the down-regulation of innate immune responses [48]. It was also demonstrated that goldfish have habituated to MWW effluent after 60 days of exposure (sub-chronic). It was suggested that the UV/H_2O_2/RWW treatment applied for filtered MWW effluent may be insufficient for the complete elimination of pollutants (xenobiotics), which may alter the physiology of aquatic organisms in the receiving water body [48]. Moreover, cytokine and cytokine gene expression were suggested to be promising parameters for the safety assessment of MWW effluents subjected to further reuse or safe discharge [48]. Another useful tool for the evaluation of MWW effluent water quality is the goldfish olfaction test reported by Blunt and co-authors [47]. They found that goldfish may "smell" MWW effluents and the exposure of fish to effluents affects the olfactory responses. Interestingly, sub-chronic exposure of goldfish to UV/H_2O_2/RWW treated MWW effluent does not impair olfactory responses, whereas the opposite was true for untreated effluent [47].

Bioassays with plants can be considered as a useful tool for WW effluents quality control, especially in case MWW effluent is used for agricultural irrigation. Among the main advantages of a bioassay with plants, availability of various evaluation endpoints (root growth, shoot growth, germination rate, etc.) and cost-efficiency can be mentioned. However, generally, a long time is needed (4–6 days) to obtain results [82]. Michael and co-authors evaluated the phytotoxic potential of MWW effluent spiked with antibiotics (μg L^{-1}) during solar photo-Fenton treatment using

Sorghum saccharatum (monocotyl Sorgho), *Lepidium sativum* (dicotyl garden cress) and *Sinapis alba* (dicotyl mustard) as indicator species [81]. Root growth was a more sensitive parameter than seed germination. The phytotoxicity of MWW effluent was decreased after the applied photo-Fenton process (residual H_2O_2 was eliminated from water samples before toxicity assessment and pH was neutralized), suggesting the possible reuse of wastewater for agricultural irrigation. The phytotoxicity assessment of MWW effluent before and after solar photo-Fenton treatment using aquatic (*Spirodela polyrhiza*) and terrestrial (*Lactuca sativa*) plants was reported [13]. Interestingly, *Lactuca sativa* was more sensitive than *Spirodela polyrhiza*. The untreated MWW effluent resulted in the stimulation of root elongation attributed to the presence of nutrients in MWW, whereas in case of treated effluent the inhibition of root elongation was observed. The slight inhibition after treatment was ascribed to decrease the organic load and the generation of more toxic by-products [13]. It is noteworthy that growth stimulation often caused by MWW effluent should not be interpreted as an advantageous effect [13].

A battery of bioassays using different species at various trophic levels is known as an efficient tool for the evaluation of WW effluents quality and prediction of the possible effect on the species in the receiving aquatic environment [82]. It is also noteworthy that an adequate toxicity assessment can be achieved when the tested species are widespread, ecologically representative and indigenous to the receiving environment [46]. A battery of bioassays consisting of *Vibrio fischeri*, *Isochrysis galbana*, *Paracentrotus lividus* and *Sparus aurata* was developed for the toxicity assessment of MWW effluent discharged into the marine environment [46]. The *Paracentrotus lividus* was found to be the most sensitive species among those tested. While studying the detoxification of various MWW effluents by the application of UV/H_2O_2/RWW followed by CWPO, Díaz-Garduño and co-authors suggested the decrease of acute toxicity after applied treatment, but not harmless treated effluents for the receiving environment [46]. The efficiency of UV/H_2O_2/RWW followed by CWPO was reported to be higher than that of photobiotreatment (using microalgae) for the detoxification of MWW effluents using a battery of bioassays [8]. García and co-authors investigated the efficiency of raceway pond reactors for MWW effluent disinfection and detoxification by the solar photo-Fenton process and found that there was hardly any decrease of toxicity after treatment for the tested bioassays (*Vibrio fischeri*, *Daphnia magna*, *Tetrahymena thermophila*) [68]. The results of MWW effluent detoxification by photo-Fenton indicate the significance of a toxicity evaluation using a battery of bioassays for understanding the efficiency of the applied post-treatment methods.

Based on the reviewed studies, it can be suggested that standard bioassays and most widely used for municipal wastewater (*Vibrio fischeri*, *Daphnia magna*) are not always sensitive (Figure 3) for the pollutants present in municipal wastewater (not spiked with pollutants or EDDS).

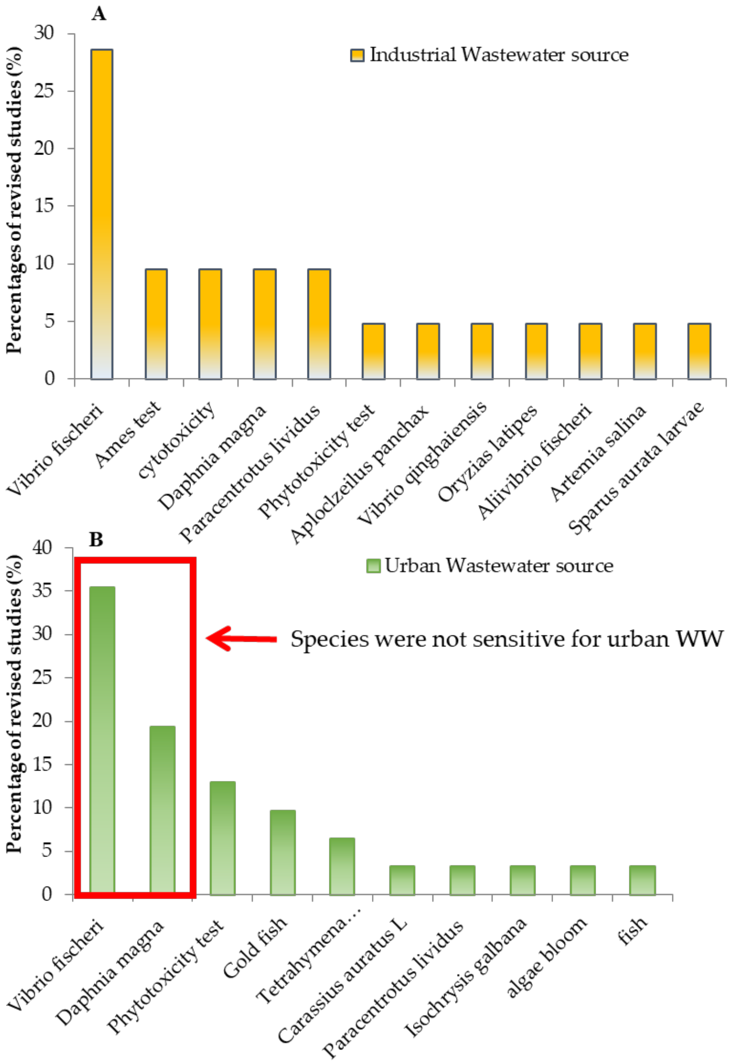

Figure 3. Schematic representation of species used for toxicity assessment in revised studies; A - for industrial wastewater and B - for urban wastewater.

2.5. Cost Estimation of Wastewater Treatment by the Photo-Fenton Process

One of the most promising AOPs for real applications nowadays is photo-Fenton and/or UV/H_2O_2/RWW treatment. The cost of this process was estimated in the majority (approx. 60%) of revised articles devoted to wastewater detoxification. There is much more literature available on cost estimation of photo-Fenton process [83–85], but in this review we have only considered studies, in which WW was used and toxicity assessment was conducted. The electrical consumption of the lamp is among the main contributors to the operational and maintenance (O&M) cost of the treatment. In reviewed articles, the electrical cost (generated by lamp) varied from €1.2 to €1.73 m^{-3} when medium pressure (MP) lamp was used, whereas these values were lower (€0.28 to €1.25 m^{-3}) for treatment with low pressure (LP) lamps. The electrical cost is proportional to the performance of the lamp. Industrial scale MP lamps in general have a relatively low performance of approx. 15% [57], whereas the performance of laboratory scale MP lamps is even lower (approx. 4%). Commonly used LP lamps are more efficient reaching values of performance of approx. 25% and 50% in the laboratory and industrial scale, respectively [44,86]. It was demonstrated that coagulation as a pre-treatment can decrease the electrical cost of the photo-Fenton process (from 350 kWh m^{-3} to 60–100 kWh m^{-3}). Moreover, the combination of coagulation before photo-Fenton and filtration through activated carbon applied after was reported to decrease the energy cost further (45–50 kWh m^{-3}) [79]. In case of solar photo-Fenton, the electrical cost (energy consumption) drastically decreases.

Various reagents are used in the photo-Fenton process, such as H_2O_2, iron salts ($FeSO_4$) and reagents for acidification and neutralization (HCl, H_2SO_4, NaOH, etc.) The cost of H_2O_2 was reported to be €0.7 kg^{-1} [87]. Generally, in reviewed articles, the cost of H_2O_2 required for the photo-Fenton process varied from €0.07 to €0.125 m^{-3} with the exception of €0.93 m^{-3} reported for hospital wastewater treatment. As mentioned before, two different approaches for conducting the photo-Fenton process are used: (i*)* with the addition of iron (Fe^{2+} or Fe^{3+}) or (ii*)* without iron addition (with naturally present iron in wastewater at μg L^{-1} level). The most common reagent used as an iron source is $FeSO_4 \cdot 7H_2O$ and its cost varies from €0.074 to €0.27 kg^{-1} in reviewed works. Depending on the required iron concentration for the photo-Fenton process, the cost of iron addition in reviewed works varied from €0.01 to €0.1 m^{-3}. The acidification of wastewater is required for carrying out conventional photo-Fenton treatment. For this purpose, sulfuric acid is usually used. The price of this reagent is approx. €0.25 kg^{-1} [85]. The cost of H_2SO_4 addition in reviewed studies was estimated to be €0.01–€0.025 m^{-3}. Generally, the cost of water neutralization (conducted by NaOH, €0.55 kg^{-1}) and management of the generated sludge after photo-Fenton is not considered, which is of high importance for real applications. When chelating agents are used for the photo-Fenton process at neutral pH, the reagent cost increases significantly [70].

As shown in Table 2, the total O&M cost of photo-Fenton and/or UV/H_2O_2/RWW treatment (with UV lamps) varies from €0.44 to €2.18 m^{-3}. The results of a recent study revealed that the O&M cost of UV/H_2O_2/RWW treatment of WW was five times higher when an MP lamp was used (€2.18 m^{-3}) compared to LP lamp (€0.44 m^{-3}), whereas the required UV dose and TOC elimination performance were similar [43]. Therefore, it can be suggested that the use of LP lamps, when possible, increases the economic feasibility of the process. Recently, operational costs (OPEX) for a full-scale implementation of UV/H_2O_2/RWW process for municipal wastewater effluent treatment in Sweden was calculated to be 0.064€ m^{-3} (UV-dose 5000 J m^{-2}; H_2O_2 dose 20 mg L^{-1}; dissolved iron 0.12 mg L^{-1}, LP replacement every 1.5 years), from which about 35% was attributed to energy consumption [87]. This estimation is significantly lower than cost estimations performed in revised literature, which can be explained as follows: (i) estimation of operational costs is not very precise when it is based on laboratory scale experiments; (ii) the UV-dose required for removal of residual pharmaceuticals is lower than that needed for decrease of toxicity (safe discharge/water reuse).

Table 2. Operation and maintenance cost for photo-Fenton process and UV/H_2O_2/RWW.

AOP Process and References	Type of Radiation	Type of Wastewater/Initial TOC or COD	Main Objective	Total Cost
		UV lamps as radiation source		
UV/H_2O_2/RWW + CWPO [57]	MP lamp	Synthetic industrial wastewater; TOC = 40 mg/L; COD = 150 mg/L	Safe discharge or water reuse	The cost of H_2O_2/UV + GAC was estimated to be €1.57 m^{-3} (based on reagent and electrical consumption)
UV/H_2O_2/RWW + CWPO [43]	MP and LP lamps	Refinery effluent; TOC = 35 mg/L; COD = 128 mg/L	Safe discharge or water reuse	The operation and maintenance costs for H_2O_2/UVC + GAC using MP and LP lamps was estimated to be €2.18 m^{-3} and €0.44 m^{-3}, respectively.
UV/H_2O_2/RWW + CWPO [44]	LP lamp	Synthetic industrial wastewater; TOC = 40 mg/L; COD = 146 mg/L	Safe discharge or water reuse	The operation and maintenance cost of H_2O_2/UVC + GAC was estimated to be €0.59 m^{-3}
UV/H_2O_2/RWW + CWPO [8]	LP lamp	Three types of urban wastewater effluents; TOC = 10–13.2 mg/L; COD = 75-85 mg/L	Safe discharge or water reuse	The operation and maintenance cost of H_2O_2/UVC + GAC was estimated to be €0.59 m^{-3}
UV/H_2O_2/RWW [69]	LP lamp	Reverse osmosis concentrate; COD = 65 mg/L	Increase of biodegradability	The electrical energy per order (EE/O) was estimated to be around 50 kWh m^{-3} (in optimal condition, 30 min) followed by biological treatment (consumption considered negligible).

UV/H_2O_2/RWW + BAC [79]	LP lamp	Reverse osmosis concentrate; COD = 105 mg/L	Safe discharge	The electrical energy dose (EED) required for each treatment was calculate. It included the EDD of H_2O_2 production (10 kWh m^{-3}). H_2O_2/UV: ~350 kWh m^{-3} H_2O_2/UV+ BAC: ~60 kWh m^{-3} Coagulation Al + H_2O_2/UV: ~100 kWh m^{-3} Coagulation Fe + H_2O_2/UV: ~60 kWh m^{-3} Coagulation Al + H_2O_2/UV + BAC: ~50 kWh m^{-3} Coagulation Fe + H_2O_2/UV + BAC: ~45 kWh m^{-3}
Photo-Fenton [45]	LP lamp	Hospital wastewater; TOC = 1050 mg/L; COD = 1350 mg/L	Increase of biodegradability	The operating cost concerning only electrical cost is \$0.52 m^{-3}. The reagent cost was estimate to be \$0.01 m^{-3} and \$0.93 m^{-3} for $FeSO_4{\cdot}7H_2O$ and H_2O_2, respectively. Total cost \$1.46 m^{-3}
Solar light as radiation source				
Solar Photo-Fenton [68]	Natural solar light	Secondary urban wastewater effluent; COD = 65.1 ± 1.4 mg/L	Wastewater disinfection	Economical cost calculation was conducted based on simulation of chosen treatment using a secondary effluent flow of 400 m^3 d^{-1}. The total cost was estimated to be €0.15 m^{-3} (including operating and maintenance and reagent cost) for disinfection.
Solar Photo-Fenton [81]	Natural solar light	Municipal wastewater effluent; COD = 26 mg/L	Water reuse	Economical cost calculation was conducted based on simulation of full-scale unit of 150 m^3 d^{-1}. The total cost evaluated was €0.85 m^{-3} (including majority of electrical consumption, reagents, maintenance and investment costs).
Solar-Photo Fenton [70]	Natural solar light	(1) municipal WW effluent (direct treatment (DOC = 23 mg/L); (2) nanofiltration concentrate (DOC = 53 mg/L)	Safe discharge	The total cost (including amortization cost of solar collectors and membrane, operating and maintenance cost and reagents) of four different processes were: pH 3, direct MWW effluent: €0.53 m^{-3} circumneutral pH, direct MWW effluent: €1.17 m^{-3} pH 3, ROC MWW effluent: €0.48 $^{-3}$ circumneutral pH, ROC MWW effluent: €0.76 m^{-3}

For solar photo-Fenton, the total cost varied for conventional photo-Fenton at pH 3 (€0.48 to €0.53 m^{-3}) and circumneutral photo-Fenton (€0.76 to €1.17 m^{-3}). It is noteworthy that solar-photo Fenton was reported to be approx. €0.5 m^{-3} (CPC solar field in case of 14,000 m^2).

3. Electrochemical Technologies Based on Fenton

3.1. Electro-Fenton

During the electro-Fenton process, the continuous in situ electrochemical generation of H_2O_2 occurs in an acidic medium via oxygen reduction at cathode as shown in the reaction below [88].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (11)$$

The generated H_2O_2 decomposition is catalyzed by iron ions according to a classical Fenton reaction. Simultaneously, the regeneration of iron(2+) at cathode occurs (reaction 12) [89].

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (12)$$

Decomposition of organic pollutants occurs via classical Fenton's reaction and anodic oxidation at the anode surface [89]. Parameters such as the type of anode, current intensity, oxygen solubility, generation rate of hydrogen peroxide and pH are critical for the electro-Fenton process.

To the best of our knowledge, only four studies on electro-Fenton process for wastewater treatment published in the last ten years have reported results of toxicity assessment [89–92]. Interestingly, studies on wastewater detoxification applying heterogeneous and homogeneous electro-Fenton were conducted. The latter was performed with the addition of iron as a catalyst. In general, a relatively high concentration of iron was added, such as 0.55 mM [89] and 2 mM (ferrous sulfate) [91]. For the heterogeneous electro-Fenton process, Fe-zeolite Y [92] and waste rice straw-coal fly ash [91] were used as catalysts. Different types of electrodes, such as Ti/RuO_2, graphite and boron-doped diamond, were used as an anode in reviewed works devoted to wastewater detoxification by the electro-Fenton process.

It should be noted that all of the reviewed studies on electro-Fenton were conducted with industrial wastewaters. Generally, the initial COD values of IWW effluents treated by electro-Fenton varied from 160 to 270 mg L^{-1} except textile effluent with COD 1156 mg L^{-1}. Acute and/or chronic bioassays with freshwater bacteria [92], freshwater invertebrate [91] and freshwater fish [89], as well as brackish and freshwater fish [90] were used for the toxicity assessment of wastewater before and after the electro-Fenton process. The acute toxicity of IWW effluents decreased after the application of electro-Fenton when *Aploclzeilus panchax*, *Vibrio qinghaiensis* and *Daphnia magna* bioassays were used. Interestingly, acute and chronic toxicity were reported to be significantly higher after Fenton and electro-Fenton treatment of coking wastewater effluent when an *Oryzias latipes* bioassay was used. These results suggest significant variations in sensitivity of the used species.

Despite the fact that only a few studies have addressed the detoxification of wastewater by the electro-Fenton process, the cost estimation was conducted at half of these. Thus, the total operational cost of the homogeneous electro-Fenton process was estimated to be $9.75 per kg of removed COD [89]. It is important to mention that the average values reported for electrical energy consumption during electrochemical processes was 1.2 to 200 kWh m^{-3}. [93–96]. In terms of the cost per treated water for heterogeneous electro Fenton is around 0.78 CNY per ton of treated water (around €0.1 m^{-3}) [91].

3.2. Galvanic Fenton

Galvanic Fenton was also applied for the detoxification of industrial wastewater [97]. Galvanic Fenton (GF) as Fenton technology can be suitable for wastewater with high turbidity, color, salinity and low biodegradability index [97]. The main principle of the system is based on corrosion of the metal (M) in an acidic environment, which leads to dissolution of the metal and production of hydrogen gas (reaction 13 and 14) [97].

$$M \rightarrow M^{n+} + ne^{-} \quad (13)$$

$$2H^{+} + 2e^{-} \rightarrow H_{2(g)} \quad (14)$$

To the best of our knowledge, only one study in last ten years was published with GF for wastewater treatment and toxicity assessment [97]. In published study iron—copper (Fe/Cu) electrodes were used as an anode and cathode. The ratio H_2O_2/Fe was 19:1 (7840 mg L^{-1} of H_2O_2 and 408 mg L^{-1} of Fe). Toxicity tests with plant (*Lactuca sativa*) [97] were implemented. The treated wastewater was as toxic to *Lactuca sativa* as the untreated one [97]. Interestingly in this case, the concentration of residual H_2O_2 in treated water was relatively high (40 mg L^{-1}). A significant toxic effect (EC50 29.57%) for *Lactuca sativa* was reported to take place with an H_2O_2 concentration of 1570 mg L^{-1} [97].

The results reported in the last ten years on the topic are summarized in Table 3.

Table 3. Toxicity bioassays applied for assessment of wastewater detoxification after photo-Fenton, electro-Fenton and other Fenton-based advanced oxidation processes (AOPs).

AOP Process	Experimental Conditions	Type of the Water	Toxicity Assessment	Main Outcomes
Photo-Fenton and/or UV/H_2O_2/RWW				
Photo-Fenton [45]	Laboratory scale (LP lamp 10 W). Optimal conditions: pH 3; COD:H_2O_2:Fe(II) 1:4:0.1; residual H_2O_2 was 30 mg/L	Hospital wastewater. TOC 1050 mg/L, COD 1350 mg/L, pH 7.3	*Vibrio fischeri*	Drastic decrease of toxicity was observed after 2 h of photo-Fenton treatment at optimal conditions.
Photo-Fenton [42]	Laboratory scale (high pressure lamp; UVA 1100 W/m^2). Optimal conditions: H_2O_2 6273 mg/L; Fe^{2+} 60 mg/L. Residual H_2O_2 1000 mg/L	Industrial WW from pesticide factory diluted 20–5% (*v*/*v*)	*Artemia salina*	On the course of the treatment inhibition of *Artemia salina* decreased. *Artemia salina* inhibition was 13 ± 6% after treatment (60 min of contact time).
UV/H_2O_2/RWW [69]	Laboratory scale (LP lamp, 12.89 mJ/cm^2). Optimal conditions: H_2O_2 3 mM, pH 4	Reverse osmosis concentrate (ROC). DOC 21 mg/L; COD 65 mg/L; pH 8.5	*Vibrio fischeri*	The untreated ROC was non-toxic. After ROC treatment using UVC/H_2O_2/RWW (after 30 and 75 min of contact time) no toxicity was detected.
UV/H_2O_2/RWW [49]	Pilot scale (MP lamp, UV fluence of 1000 mJ/cm^2). Optimal conditions: 20 mg/L of H_2O_2	Municipal WW effluent. TOC 11 ± 2 mg/L; pH 7.4	*Carassius auratus* L. and *Vibrio fischeri*	*V. fischeri* showed no significate differences response to tested water. Applied UV/H_2O_2/RWW treatment was inefficient due to negative acute (7 days) toxicological impact.
UV/H_2O_2/RWW [48]	Pilot scale (MP lamp, UV fluence of 1000 mJ/cm^2) Optimal conditions: 20 mg/L of H_2O_2	Municipal WW effluent after ultrafiltration step (UF)	Gold fish innate immunity	Acute innate immune response deficiencies were reported for goldfish exposed to reuse water during 7 days. After sub-chronic exposure of fish to reuse water evaluated innate immunity parameters in kidney were at the same level as control sample (after GAC filtration).
UV/H_2O_2/RWW [47]	Pilot scale (MP lamp, UV fluence of 1000 mJ/cm^2). Optimal conditions: 20 mg/L of H_2O_2	Municipal WW effluent after ultrafiltration step (UF)	Gold fish	After acute exposure, olfactory impairment was observed after UV/H_2O_2/RWW treatment as well as for untreated reuse water. However, after sub-chronic exposure, olfactory impairment was not observed for UV/H_2O_2/RWW treated water,
Solar Photo-Fenton				

Solar photo-Fenton [70]	Pilot scale (CPC reactors). *Optimal conditions:* Fe(III):EDDS = 1:2; H_2O_2 50 mg/L; Fe(III) 0.1 mM for WWTP effluent and 0.2 mM for NF stream.	Two different types of water: (1) municipal WW effluent (direct treatment, D): DOC 23 mg/L; pH 7.5; (2) nanofiltration concentrate (NF concentrate, C): DOC 53 mg/L; pH 8.0;	*Vibrio fischeri*, *Daphnia magna*	Acute toxicity: Initial undiluted effluents were classified as slightly toxic for *V. fischeri* (Class II) and toxic for *D. magna* (Class III). All treated water samples were toxic for *V. fischeri* (Class III) and slightly toxic for *D. magna* (Class II), except NF concentrate (C + 0.4 mM of EDDS), which was highly toxic to *D. magna* (Class IV). Chronic toxicity: All initial and treated water samples (undiluted) exposed to *D. magna* for 21 day belonged to Class III. It should be noted that adaptation of resistant *D. magna* was observed when sufficient amount of DOC was available. The EDDS at studied concentrations increase the toxicity of water.
Solar photo-Fenton [68]	Pilot scale (CPC and raceway pond reactors (RPR)). *Optimal conditions*: pH set to 7, H_2O_2 50 mg/L and Fe^{2+} 20 mg/L, 120 min.	Secondary effluent from municipal WWTP was used: DOC 18.9 ± 5.1 mg/L, COD 65.1 ± 1.4 mg/L, pH 7.7 ± 0.2	*Vibrio fischeri*, *Daphnia magna* and *Tetrahymena thermophila*.	Chronic toxicity for *T. thermophila* decreased after photo-Fenton treatment leading to slight growth stimulation. No acute toxicity was produced by secondary effluent before and after treatment for *D. magna*. Significant stimulation of *V. fischeri* growth was observed in secondary effluent before treatment, which decreased after treatment.
Solar photo-Fenton [14]	Pilot scale (CPC reactors). Photo-*Optimal conditions:* H_2O_2 66 mM, Fe^{2+} 20 mg/L	Industrial pharmaceutical WW. DOC 775 mg/L, COD 3420 mg/L, pH 3.98	*Vibrio fischeri*, *Daphnia magna*	The toxicity of WW increased during the treatment followed by slight decrease. *D. magna* died in all wastewater samples after 24h of exposure.
Solar photo-Fenton [12]	Pilot plant (CPC reactors). *Optimal conditions*: for SE: Fe^{2+} 5mg/L, H_2O_2 50 mg/L + 50 mg/L and t_{30W} 336 min; for RE: Fe^{2+} 5mg/L, H_2O_2 50 mg/L and t_{30W} 276 min	Simulated WW (SE) and real municipal WW effluent (RE). The TOC of RE was 55 mg/L, pH 8.	*Vibrio fischeri*	SE: During photo-Fenton toxicity increased reaching EC_{50} value (60 min) and disappearing in the end of the experiment (336 min). RE: During photo-Fenton, toxicity was increasing. The EC_{50} value was reached after (25 min) and further increased during the treatment.
Solar photo-Fenton [15]	Semi-pilot scale (CPC plant) *Optimal conditions:* 20 mg/L of Fe^{2+}, H_2O_2 500 mg/L and pH 2.8.	Textile WW. DOC 92.4 ± 46 mg/L, COD 300 ± 99mg/L, pH 6.9 ± 0.2	*Aliivibrio fischeri*	The EC_{50} of initial WW was 30.3% (3 acute toxic units). After treatment (from 180 min) the value of toxic units decreased till 1 (non-toxic). After 90 min, toxicity started to increase (7.5 a, T.U. at 150 min).

Solar photo-Fenton [81]	Pilot scale (CPC plant). *Optimal conditions*: Fe^{2+} 5 mg/L, H_2O_2 concentration 75 mg/L,	Municipal WW effluent. DOC 7.45 mg/L, COD 26 mg/L, pH 6.8, Fe^{2+} 0.29 mg/L	*Daphnia magna* and Phytotoxicity test (*Sorghum saccharatum, Lepidium sativum, sinapis alba).*	Seed germination inhibition was eliminated at the end of the treatment for all plants. Root and shoot inhibition was decreasing during the treatment. No toxic effect was observed for *D. magna* after 24 h of exposure to untreated effluent. During photo-Fenton treatment, the toxicity drastically increased reaching peak at 120 min. After 300 min of contact time, the toxicity effect for *D. magna* was lower than that in untreated wastewater effluent.
Solar photo-Fenton [13]	Pilot scale (RPR). UV 26 W/m^2. *Optimal conditions*: 50 mg/L of H_2O_2; 20 mg/L of iron x 3 times during experiment; pH 6.5	Municipal secondary WW effluent (filtered by 20 µm). DOC 20.6 mg/L, pH 7.6,	*Tetrahymena thermophyla, Daphnia magna, Lactuca sativa* (phytotoxicity); *Spirodela polyrhiza* (phytotoxicity); *Vibrio fischeri*	The *T. thermophyla* was the most sensitive species, followed by *D. magna* and *L. Sativa* for initial wastewater. After 90 min of the treatment, 5% of immobilization *of D. magna* was observed. No toxic effect was observed for *T. thermophyla* during and after photo-Fenton process. For *L. Sativa* statistically significant inhibition of root elongation was observed after 20 min and 90 min of. The *V. fischeri* was not sensitive to initial and treated wastewater effluent.
Solar photo-Fenton [98]	Pilot scale. *Optimal conditions:* Fe^{2+} 5 mg/L, H_2O_2 60 mg/L, pH 2.8, (photo-Fenton). TiO_2 20 mg/L (photocatalysis)	Real municipal WW effluents. DOC 13–23 mg/L; COD 32–63 mg/L	*Vibrio fischeri*	No significant changes in toxicity of wastewater after treatment were detected.
Combination of Photo-Fenton with other treatment processes				
UV/H_2O_2/RWW + CWPO [57]	Laboratory scale (MP, 150W, 5.7 W_{UVC}). *Optimal conditions*: 320 mg/L of H_2O_2, UVC dose 7.51 Ws/cm^2 and 3.5 min of GAC.	Synthetic industrial WW prepared using matrix of urban WW effluent. TOC 40 mg/L; COD 150 mg/L	*Paracentrotus lividus* (embryo-larvae development, fertilization); *Vibrio fischeri*	*P. lividus* embryo-larvae development was the most sensitive test. The H_2O_2/UVC/RWW treatment increased the toxicity of initial water for both species. The toxicity drastically decreased after CWPO.
UV/H_2O_2/RWW + CWPO [44]	Laboratory scale (LP lamp, 2 W_{UVC}). *Optimal conditions:* 200 mg/L of H_2O_2, UVC dose 8.8 Ws/cm^2 and 2.3 min of GAC	Synthetic industrial WW based on matrix of urban WW. TOC 40 mg/L; COD 146 mg/L; pH 7.14	*Sparus aurata larvae* and *Vibrio fischeri*	The most sensitive specie was *Sparus aurata larvae*. The water after H_2O_2/UVC/RWW treatment was more toxic than final effluent (after CWPO step).

UV/H_2O_2/RWW + CWPO [43]	Laboratory scale (LP lamp, 2 W_{UVC} and MP, 5.7 W_{UVC}). Optimal conditions: LP: 280 mg/L of H_2O_2, UVC dose 5.28 Ws/cm^2 and 6 min of GAC; MP: 175 mg/L of H_2O_2, UVC dose 6.57 Ws/cm^2 and 3.5 min of GAC	Industrial WW effluent from refinery company. TOC 35 mg/L; COD 128 mg/L; pH 7.14	*Paracentrotus lividus* (embryo-larvae development and fertilization) and *Vibrio fischeri*	The ranking of water toxicity from more to less toxic for *V. fischeri* was: effluent of H_2O_2/UVC (IV, TU) > Initial water (II, TU) > total effluent (0, TU). *P. lividus* fertilization test also showed same order of water toxicity. During H_2O_2/UVC/RWW process the toxicity of water increased 400 times in comparison with the initial wastewater. *P. lividus* embryo-larvae development was the most sensitive test. In this case, the toxicity ranking (starting from more toxic) was as follows: initial wastewater > H_2O_2/UVC/RWW effluent > final effluent.
UV/H_2O_2/RWW + CWPO [46]	Laboratory scale (LP lamp, 2 W_{UVC}). Optimal conditions: 50 mg/L of H_2O_2, UVC dose 6.00 Ws/cm^2 and 5 min of GAC	Different urban WW effluents: (D1) urban, (D2) Urban + industrial (D3) Urban + hospital. BOD_5 10–13.2 mg/L; COD 75–83 mg/L; pH 7.42–8	*Paracentrotus lividus* (embryo-larvae development, fertilization), *Vibrio fischeri* and *Isochrysis galbana*. *Sparus aurata larvae*,	The most sensitive endpoints were sea urchin larval development (D1 and D2) and mortality of fish larvae (3) for WWTP effluents. The PT-Value summarize that MBT treatment reduce the toxicity from highly toxic (pT index III and V) to slightly toxic (I and II).
UV/H_2O_2/RWW + CWPO [8]	Laboratory scale (LP lamp, 2 W_{UVC}) Optimal conditions: The TOC/H_2O_2 optimal ratio 5, UVC dose 6.00 Ws/cm^2 and 5 min of GAC.	WW effluents (1) urban (W1), (2) urban + hospital (W2), (3) urban + industrial (W3). COD 75–85 mg/L; pH 7.42–8	Different algae species (primary producer), *Daphnia* (invertebrate) and fish (vertebrate)	Toxicity drastically decrease after MBT treatment, reaching negligible risk (RQ < 0.01). Algae were the most sensitive species among tested. After MBT negligible risk was obtained for all tested effluent.
UV/H_2O_2/RWW + BAC [99]	Laboratory scale (LP lamp, irradiation 12.89mJ/cm^2). Optimal conditions: 4 mM of H_2O_2	Reverse osmosis concentrated (ROC). DOC 44.6 ± 5.8 mg/L; COD 200 ± 27 mg/L; pH 7.8–8.4	*Vibrio fischeri*	It was observed that before and after treatment steps, ROC did not demonstrate toxic effect for *V. fischeri*. It was not specified if residual H_2O_2 was eliminated from water samples prior toxicity assessment.
UV/H_2O_2/RWW + BAC [79]	Laboratory scale (LP lamp, 8.91 mJ/cm^2). Optimal conditions UVC dose 16.10^3 mJ/cm^2, H_2O_2 3mM (H_2O_2/UVC)	Reverse osmosis concentrate (ROC). DOC 37 mg/L; COD 105 mg/L; pH 7.7	*Vibrio fischeri*	*V. fischeri* test showed that initial ROC was not toxic. However, after the UVC/H_2O_2/RWW treatment the toxicity of water increased (EC_{50}: 13%). After final BAC step no toxicity was observed.
Homogeneous and heterogeneous electro-Fenton				
Electro-Fenton process [89]	Optimal conditions: elapsed time 137 min, current 1.10 A, ferrous sulfate 0.55 mM.	Textile WW. pH 3, BOD 196 mg/L, COD 1156 mg/L	*Aploclzeilus panchax*	The mortality reached 100% when organisms were exposed to untreated wastewater during 1 min. After applied treated no mortality was observed after 96 h.

Heterogeneous electro-Fenton process [92]	<u>*Optimal conditions:*</u> graphite anode and Fe-zeoliteY catalyst at neutral pH. Current density was 10 A/m^2 and cathodic potential −0.7 V	Coking wastewater effluent. pH 7.2, COD 225 mg/L, TOC 84 mg/L	*Vibrio qinghaiensis sp. Nov.-Q67*	The toxicity of effluent was decreased by 50–60% after applied treatment as compared to untreated wastewater.
Fenton and electro-Fenton [90]	Effluent was subjected different treatments such as Fenton, electro-Fenton and coagulation.	Effluent of coking WW (after treatment in anaerobic, anoxic and oxic reactors). COD 160 ± 27 mg/L, TOC 50 ± 10 mg/L, pH 6.5–7.5	embryos and larvae of *Oryzias latipes* (Japanese medaka)	The acute and chronic toxicity was significantly increased after Fenton and electro-Fenton treatment. The acute and chronic toxicity of MBR and coagulation effluents were lower. Endocrine disruption effect was not detected for MBR, Fenton and electro-Fenton effluents.
Heterogeneous electro-Fenton [91]	<u>*Optimal conditions:*</u> CPE 2.0 g/L, aeration rate 5 L/min, current density 10 mA/cm^2	WW from typical azo dye WW plant. COD 270 ± 30 mg/L	*Daphnia magna*	Residual H_2O_2 was removed from water samples by heating during 1 h. Acute toxicity significantly reduced during applied treatment.
		Galvanic Fenton		
Galvanic Fenton [97]	<u>*Optimal conditions:*</u> pH 2.8, H_2O_2/Fe^{2+} ratio 19:1 (H_2O_2 7840 mg/L and Fe^{2+} 408 mg/L).	Industrial WW. pH 7.95, total COD 5264 mg/L, TOC 1744 mg/L, iron 1.48 mg/L	*Lactuca sativa*	The EC$_{50}$ value reported for raw WW was 64.05%, whereas this value after galvanic-Fenton was 65.07%. The residual H_2O_2 after galvanic-Fenton was 40 mg/L.

4. Conclusions

In this article, the feasibility of real municipal and industrial wastewater detoxification by Fenton-based advanced oxidation processes was reviewed. Based on the analyzed literature, it can be concluded that in general the application of Fenton-based AOPs for wastewater detoxification is feasible. However, it is of high importance to assess the toxicity of water on the course of AOP treatment because in the majority of cases the generation of more toxic than parental compounds occurs. It is important to mention that maximum process efficiency (in terms of COD and/or TOC removal) does not coincide with maximum detoxification.

Toxicity bioassays were demonstrated to be an efficient tool for the assessment of wastewater detoxification. Based on the reviewed studies, it can be suggested that standard bioassays and most widely used for municipal wastewater (*Vibrio fischeri*, *Daphnia magna*) are not always sensitive for the pollutants present in municipal wastewater (not spiked with pollutants or EDDS). Moreover, the use of single toxicity bioassay might not be sufficient for the evaluation of wastewater toxicity after the application of Fenton-based AOPs due to the large variation of sensitivity of different species. Hence, a battery of bioassays is more suitable for the estimation of treated wastewater toxicity. The use of biologically representative, widespread and indigenous species is among the main requirements for an adequate battery of bioassays leading to a realistic evaluation of the possible environmental risks of treated wastewater effluents. In recent years, the batteries of bioassays for the assessment of urban wastewater effluents discharged to the marine aquatic environment after pot-treatment by Fenton-based AOPs were developed. It is expected that future studies devoted to the detoxification of wastewater by Fenton-based AOPs will implement batteries of bioassays (including biosensors) for a more comprehensive evaluation of water toxicity. Additionally, from the reviewed literature on wastewater detoxification by photo-Fenton, it can be expected that future research will be conducted using a more realistic approach regarding wastewater pre-treatment avoiding when possible, the acidification of wastewater prior treatment, addition of excessive amount of reagents, removing residual H_2O_2, etc. This might enable not only a decrease of the operation and maintenance (O&M) costs but also the possible risks for organisms in the aquatic environment.

From the O&M cost point of view, the lowest O&M cost estimation reported for the detoxification of wastewater effluent in the scope of this review was €0.44 m^{-3} (personnel cost was not included), whereas the average O&M cost of conventional treatment of municipal wastewater in WWTP with a flow of approx. 10,000 m^3 day^{-1} is approx. €0.5—0.6 m^{-3} (including personnel cost; southern Spain). Interestingly, it was reported that the O&M cost of wastewater detoxification by photo-Fenton can be significantly decreased when preliminary microfiltration, coagulation aiming at more economically feasible removal of organic matter (suspended and/or colloidal) and increasing of water transmittance is applied. Moreover, application of additional polishing step such as catalytic wet peroxide oxidation (CWPO) after photo-Fenton can remove residual hydrogen peroxide, reduce the toxicity and the cost of the treatment. The total cost (investment and maintenance costs for the period of 5 years) estimation of a full scale unit (150 m^3 day^{-1}, equivalent to 1000 pe) for treatment of secondary urban wastewater effluent by solar photo-Fenton (removal of antibiotics and toxicity reduction) was reported to be €0.85 m^{-3}.

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