A critical review on application of photocatalysis for toxicity reduction of real wastewaters

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Abstract

Advanced oxidation processes (AOPs) such as photocatalysis are widely studied for degradation of organic pollutants of contaminants of emerging concern (CECs). However, degradation of organic pollutants leads to formation of by-products, which may be more toxic than parental contaminants. The toxicity of wastewater treated by photocatalysis is topical issue. In this review paper recent studies concerned with photocatalytic detoxification of real industrial and municipal wastewater were assembled and critically discussed. Such issues as challenges for application of photocatalytic wastewater detoxification, feasibility of various toxicity tests, reuse of photocatalysts, cost estimation, etc. were considered. Based on reviewed literature it can be suggested that photocatalysis might not always be a promising treatment method for degradation of organic pollutants in real wastewaters and/or wastewater detoxification from the application point of view.

Keywords: real wastewater, photocatalysis, advanced oxidation processes (AOP), toxicity, bioassays

1. Introduction

Pharmaceuticals, personal care products, endocrine disrupting compounds, pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs and other contaminants of emerging concern are present in trace concentrations in industrial and municipal wastewater effluents (Lara-Martín et al., 2014, Pintado-Herrera et al., 2014). Wastewater treatment plants do not provide complete elimination of contaminants of emerging concern, which leads to its discharge to receiving environment (Gracia-Lor et al., 2012). Even trace concentrations of these contaminants in aquatic bodies negatively affect aquatic organisms (François et al., 2015, Quinn et al., 2009, Quinn et al., 2011).

Advanced Oxidation Processes (AOPs) are known as promising methods for removal of contaminants of emerging concern from wastewater effluents. Among AOPs, photocatalysis is widely studied for wastewater treatment. Thus, during the last ten years, more than 16,000 scientific articles containing "photocatalysis" or "photocatalyst" were published (Scopus) and each year the number of publications is increasing. These data are not surprising because the photocatalytic properties of semiconductors are studied for wastewater treatment, surfaces with self-cleaning and antifogging properties (Li and He, 2013), purification of outdoor air, indoor air deodorization, cancer therapy, etc. (Rao et al., 2003). Number of scientific publications devoted to photocatalytic wastewater purification and detoxification is shown in Fig.1. It is well known that during photocatalytic decomposition of target pollutants in water, generation of more toxic by-products can occur. Thus, it is of high importance to evaluate toxicity of treated wastewater effluent. Among these, there are also a number of studies investigating the photocatalytic degradation of model pollutants and the toxicity of their TPs (transformation products). Nevertheless, these studies do not represent the real scenario of industrial or urban wastewaters as they use higher pollutants' concentrations

than found in real cases. In this review, only those studies on detoxification of real wastewater (urban or industrial) are considered. By contrast, all studies focused on reduction of toxicity by photocatalysis in model solutions were excluded from this review. The aim of this work is to systemize and analyse research results on detoxification of real industrial and municipal wastewater (IWW and MWW) by photocatalysis, with implications in the toxicity effects.

2. Method

The methods applied in this literature review included identification of the relevant studies and preparing set of questions to be addressed to selected literature relevant to the scope of this review. Identification of relevant literature was performed by searching in Science Direct, Scopus and Google Scholar and NCBI databases using following keywords: "photocatalysis", "toxicity", "bioassays", "wastewater". After that the generated literature list was checked manually (reading materials and methods and results) in order to exclude studies, in which *(i)* real or synthetic wastewater was not used; *(ii)* toxicity assessment of wastewater before and after photocatalytic treatment was not conducted. Moreover, literature reviews were not considered. It should be noticed that only relevant articles published during the period 2009 – 2019 were included to this review. Moreover, relevant studies found during screening other studies were included to the list during literature identifying step. The literature search was limited to articles published in peer-reviewed journals in English language. Reports published in other languages as well as books were excluded from the literature search.

Prepared list of scientific articles was critically analysed through extracting relevant information using the list of questions shown below:

- Which type of photocatalytic nanoparticles was used?

- Was the release of ions from photocatalyst studied?
- Was the issue of separation of photocatalytic nanoparticles (in case these were used) from treated wastewater addressed?
- Which type of photocatalytic thin films was used?
- Was the detachment of nanoparticles from thin films studied?
- Which type of wastewater was used?
- Which irradiation source was applied for photocatalytic wastewater treatment?
- Was the pre-treatment of wastewater, for instance pH modification, performed prior photocatalytic treatment?
- Which type of toxicity tests were applied?
- Was the toxicity assessment conducted during photocatalytic treatment of wastewater?
- What was the scale of performed experiments?
- Was the intensity of irradiation source available?
- Was the treatment time realistic, applicable in real world cases?
- Was the sensitivity of toxicity tests compared?
- Was the issue of photocatalyst reuse addressed?

3. Photocatalysis

Usually photocatalysis is defined as the chemical reaction induced by the absorption of photons by solid material (photocatalyst) (Ohtani, B., 2011). However, there is still some debate regarding the definition of the photocatalytic process (Mills and Le Hunte, 1997). It should be mentioned that the photocatalyst does not undergo any chemical changes during and after the reaction. In the literature, the term "photocatalyst" is often used interchangeably with term "catalyst". It can be probably explained by the fact that

some photocatalytic materials are sometimes used in catalytic reactions as catalysts. However, in terms of thermodynamics, the concept of catalysis and photocatalysis is different. Thus, energy-storing reactions can be driven by photocatalysis ($\Delta G>0$) while catalysis is limited to thermodynamically possible reactions ($\Delta G<0$) (Ohtani, B., 2010). The reaction rate (absolute or relative) of the photocatalytic process is usually referred as photocatalytic activity (Ohtani, B., 2011). Usually five steps are distinguished during photocatalysis (Herrmann, 1999):

- transfer of pollutants to the photocatalyst's surface;
- adsorption of pollutants on the surface;
- photonic activation and decomposition of adsorbed molecules;
- reaction product's desorption;
- removal of reaction products from the photocatalyst's surface.

The main principle of photocatalysis can be explained according to the widely accepted theory. The electron-hole pairs are generated when photocatalytic material is exposed to the light with equal or larger energy than that of photocatalyst's band gap. Formed electron-hole pairs dissociates into electrons (e^-) in conduction band and holes (h+) in valence band. The e^- and h+ lead to the reduction and oxidation of molecules adsorbed on the surface of photocatalytic material. Nevertheless, the electron-hole recombination often takes place, which may lead to the non-occurrence of oxidation and reduction reactions on the surface of photocatalytic material. The increase or decrease of the reaction rate is often associated with an enhanced or suppressed electron-hole recombination, respectively (Ohtani, 2013). According to a recent review in the field (Ohtani, 2013), no direct evidence of electron-hole recombination during photocatalytic process was presented so far.

Photocatalytic ozonation takes place in the presence of photocatalyst, UV-vis radiation and ozone. Aside from occurring photocatalytic reaction, caused by the photoexcitation of the photocatalyst's surface, molecules of ozone adsorbed on the surface of photocatalyst. This leads to the formation of active oxygen radicals. It was demonstrated that water molecules react with active oxygen radicals to form hydroxyl radicals (Huang and Li, 2011). Moreover, active oxidising species are produced when ozone absorbs a wavelength shorter than 300 nm (Mehrjouei et al., 2015).

$$O_3 + h\nu \rightarrow {}^{\bullet}O + O_2 \quad (1)$$

3.1. Technical challenges and toxicity

A plethora of studies has been conducted on the photocatalytic treatment of wastewater effluents at lab and pilot scale (Berberidou et al., 2017, Karaolia et al., 2018, Levchuk et al., 2015, Spasiano et al., 2015, Talwar et al., 2018). In many cases, the complete mineralisation of pollutants present in wastewater was not achieved and/or was not expected. In such cases, conventional chemical analysis, which allows to detect and quantify target compounds and their by-products, is limited because it is neither able to evaluate the possible toxicity of the formed compounds nor their potential synergetic effect. Therefore, a toxicity assessment is of crucial importance when wastewater is treated by photocatalysis, especially if the complete mineralisation of contaminants is not an objective.

3.1.1. Photocatalytic materials and their possible contribution to toxicity

3.1.1.1. In the form of powder

In the majority (>60%) of studies devoted to the photocatalytic detoxification of real wastewater, TiO_2 in the form of nanoparticles was used as an aqueous suspension in the contaminated water, also called 'slurry'. This can be explained by the fact that TiO_2 possess almost all the characteristics of ideal photocatalytic material (Carp et al., 2004)

and it is one of the most studied materials for photocatalytic applications. The nanoparticles of ZnO were applied for photocatalytic wastewater treatment in less than 25% of the studies reviewed in this article. ZnO was widely studied for photocatalytic applications, it benefits from relatively high photocatalytic activity, easy production process, low cost, environmentally friendliness, etc. (Qi et al., 2017). However, the possible photocorrosion of ZnO should be mentioned as an important drawback (Kudo and Miseki, 2009). Interestingly, the photodissolution of Zn was reported during the photocatalytic treatment of sewage wastewater effluent with ZnO and it was also suggested to be one of the factors leading to the increase of toxicity (*Vibrio fischeri* bioassay) (Vela et al., 2018a). Thus, the elevated toxicity was observed when the highest concentrations of Zn^{2+} (186 ± 8 μg L^{-1}) were detected in treated water (Vela et al., 2018a). In comparison with ZnO, the dissolution of Ti^{4+} in similar wastewater was reported to be significantly lower (6.1 ± 1.3 μg L^{-1}). These results are in agreement with other studies, which have demonstrated that dissolution of metal from metal-containing nanoparticles can play key role in enhancement of their toxicity (Boyle and Goss, 2018, Brunner et al., 2006, Franklin et al., 2007, Käkinen et al., 2016, Wang, H. et al., 2009). It should be noted that the dissolution and/or photodissolution of photocatalysts is not often monitored during treatment; while it is an important parameter which can significantly affect the toxicity of the water especially if toxic metals such as cadmium are used for the synthesis of photocatalysts. It is noteworthy that TiO_2 was demonstrated to be more efficient for the reduction of toxicity (based on *Artemia salina* bioassay) of textile wastewater effluent than ZnO (Souza et al., 2016). Moreover, TiO_2 P25 was reported to be more efficient for the elimination of toxicity (*Vibrio fischeri* bioassay) of sewage wastewater effluent than other commercially available TiO_2 (Vela et al., 2018b). It can be expected that more studies will focus on comparison of various photocatalysts

for toxicity elimination in the future. Besides TiO_2 and ZnO, rather few photocatalysts were tested in the last ten years for the reduction of wastewater toxicity such as TiO_2 modified with hydrotalcite and iron oxide (Arcanjo et al., 2018), polypyrrole (Lima et al., 2015), Nb_2O_5 (Souza et al., 2016), Fe_2O_3 (Nogueira et al., 2017), graphitic carbon nitride (Moreira et al., 2019).

Despite the relevantly high efficiency of photocatalysts used in the form of dispersed powder for the degradation of emerging organic pollutants and reduction of toxicity, the practical application of this process is hardly feasible due to the technical challenges arising when photocatalyst should be separated from water for further reuse. The separation step is currently among the major limitations for the application of photocatalysis in practice (Chong et al., 2010, Fernández-Ibáñez et al., 2003, Iglesias et al., 2016). Relatively few studies have been reported on the separation of photocatalysts from treated water such as accelerated sedimentation (Fernández-Ibáñez et al., 2003), coagulation with chemical - (Kagaya et al., 1999) and plant-based coagulants (Patchaiyappan et al., 2016), and different filtration methods (Doll and Frimmel, 2005, Ganiyu et al., 2015, Zhao et al., 2002). Among the works considered in the scope of this review, a particle agglomeration process of materials after treatment (Souza et al., 2016) as well as the magnetic separation of TiO_2 modified with hydrotalcite and iron (Arcanjo et al., 2018) was conducted. Another point of concern is the photocatalyst's efficiency loss during its reuse (deactivation) reported by various researchers (Li et al., 2009, Ollis, 2000, Sun et al., 2003). The deactivation of a photocatalyst can be reversible and irreversible (Sauer and Ollis, 1996). As suggested by Ollis (2000), the probable reasons for deactivation are: (1) accumulation of resistance to photocatalysis by-products on the surface of photocatalyst and (2) generation of surface species possessing higher adsorption capacity than reactants. The deactivation of photocatalyst is usually not

observed when experiments are conducted with model pollutants in water (Ahmed and Ollis, 1984, Al-Sayyed et al., 1991, Hidaka et al., 1986, Levchuk et al., 2016). For instance, the deactivation of TiO_2 was not observed after 14 cycles of the photocatalytic degradation of 2,4,5-trichlorophenoxyacetic acid (Barbeni et al., 1987). However, in more complex water matrix and/or in the presence of salts (for instance, coagulants), the deactivation of photocatalyst occurs (Fernández-Ibáñez et al., 2003). Only in 17% of articles on photocatalytic detoxification and purification of wastewater, photocatalytic activity during the reuse of materials was studied. For instance, Arcanjo and co-authors have reused HT/Fe/TiO_2 five times for textile wastewater effluent treatment and observed approx. 17% of its efficiency loss (based on color removal) (Arcanjo et al., 2018). The photocatalytic activity of Fe-TiO_2 composited beds was reported to be very similar even after 70 cycles (based on COD removal) of the hybrid photocatalysis process (Bansal et al., 2018). Lima and co-authors (Lima et al., 2015) reported the deactivation of polypyrrole of approx. 67% after six cycles of textile wastewater decontamination. Interestingly, when a polymer was washed with HCl solution after reaction, the efficiency loss was significantly lower (approx. 16% after six cycles) (Lima et al., 2015). It should be noted that there are only few studies concerned with such an important topic as the regeneration of photocatalytic materials. The following strategies were tested for the regeneration of photocatalysts used for water/wastewater treatment:

- alkaline treatment (NaOH and NH_4OH) (Miranda-García et al., 2014);
- thermal regeneration (Carp et al., 2004);
- exposure to UV in aqueous media or air (Wang, Y. et al., 2015);
- oxidation of by-products bounded to the surface by H_2O_2/UV (Miranda-García et al., 2014);

- washing with deionised water (Kabra et al., 2004);
- refluxing in water at 100ºC with oxygen bubbling (Pan et al., 2013).

Miranda-García and co-authors compared the thermal, alkaline and H_2O_2/UV approaches for the regeneration of immobilized TiO_2 (based on photocatalytic degradation of emerging pollutants) (Miranda-García et al., 2014). Thermal and H_2O_2/UV treatment were reported to be more efficient. Interestingly, after NaOH regeneration, TiO_2 was partially removed leading to the decrease of photocatalyst's efficiency (Miranda-García et al., 2014). It can be expected that more research devoted to separation/recovery and reuse of photocatalytic materials will be conducted in the future, taking into account its significant importance for the practical application. Beyond the technical challenges of the separation and reuse of photocatalysts, the possible risks to aquatic organisms due to the release of some nanoparticles to water should be mentioned as well as the generation of sludge, containing nanoparticles of photocatalysts. When nanoparticles are introduced to aquatic environment their fate (aggregation and its reversibility) is strongly dependant on pH, quality and quantity of natural organic matter, type of released nanoparticles and their surface properties, dissolved and particulate inorganic compounds etc. (Bundschuh et al., 2018). Studies on fate of nanoparticles in the environment are emerging (Boxall et al., 2007, Klitzke et al., 2015, Metreveli et al., 2015, Tso et al., 2010), and behaviour of nanoparticles in complex environmental conditions is not fully understood (Bundschuh et al., 2018). Studies devoted to the risk assessment of nanomaterials used for photocatalytic water treatment to aquatic organisms are available (Lee et al., 2009, Nogueira et al., 2015, Vevers and Jha, 2008). Thus, adverse effects on invertebrates and fish by TiO_2 nanoparticles were reported (Blaise et al., 2008). Lethal toxicity was reported for *Chironomus riparius* (widely used organism for the assessment of sediment toxicity)

exposed for 10 days to artificial sediments mixed with residual (after photocatalytic treatment) nanoparticles of TiO_2 and Fe_2O_3 used for the treatment of olive oil mill wastewater and Fe_2O_3 used for the treatment of kraft pulp mill effluent (Nogueira et al., 2015). Interestingly, toxicity depended not only on the type on nanoparticles, but also on the type of contaminants adsorbed on the NPs surface. For instance, TiO_2 and Fe_2O_3 NPs after the treatment of mine drainage did not promote any negative effects on *Chironomus riparius* (Nogueira et al., 2015). It is not surprising that many studies focus on toxicity assessment of nanoparticles in presence of different contaminants (organic and inorganic) (Ahamed et al., 2019, Canesi et al., 2015, De La Torre Roche et al., 2018, Hartmann et al., 2012, Martín-de-Lucía et al., 2019) as nanoparticles may possibly play role of carrier (Hartmann and Baun, 2010) of organic and/or inorganic pollutants into cells and/or organisms (Kahru and Dubourguier, 2010). For instance, it was reported that metal uptake in various freshwater organisms increases in presence of TiO_2 nanoparticles (Canesi et al., 2015, Fan et al., 2017, Hartmann et al., 2012). More detailed information devoted to toxicity of nanoparticles can be find in excellent reviews (Du et al., 2018, Menard et al., 2011, Turan et al., 2019).

3.1.1.2. Thin films

Photocatalytic slurry systems have been widely studied for treatment of urban and industrial wastewaters (Belgiorno et al., 2007, Biancullo et al., 2019, Fenoll et al., 2019, Moreira et al., 2018, Talwar et al., 2018, Threrujirapapong et al., 2017). Despite high efficiency and relatively low price of slurry photocatalytic systems, it did not lead to many practical applications in wastewater treatment. This can be mainly explained by costly separation of photocatalyst from water after treatment (Bideau et al., 1995, Shan et al., 2010). Therefore, immobilization of photocatalyst on inert supports/substrates in a form of thin films could significantly simplify the separation procedure and enhance

applicability of photocatalytic process. Immobilisation of photocatalysts allows to avoid the possible release of NPs to water, sludge generation and also significantly decrease the cost of the treatment by eliminating the photocatalyst recovery step. However, relatively high preparation costs together with generally reported lower efficiency of immobilized photocatalyst (Levchuk et al., 2016) are the main barriers for practical application of photocatalytic thin films. Interestingly, it was reported that immobilised photocatalyst can achieve a similar level of photocatalytic activity as commercial TiO_2 (P25) for industrial wastewater (IWW) treatment (Barndõk et al., 2016). Sordo et al. (Sordo et al., 2010) demonstrated that the efficiency of fixed-bed reactor filled with TiO_2 immobilized on glass beds is similar to that of slurry photocatalytic system. Several studies were conducted with immobilised photocatalytic materials for wastewater treatment (Barndõk et al., 2016, Gholami et al., 2018, Vaiano and Iervolino, 2018). However, to our knowledge, only a few studies were reported for real wastewater detoxification with immobilised thin films in the last ten years (Barndõk et al., 2016, He et al., 2016, Tichonovas et al., 2017). The TiO_2 (He et al., 2016, Tichonovas et al., 2017) and Fe-TiO_2 (Barndõk et al., 2016) were used as a phototcatalysts. As far as the authors are aware, in the last ten years there were no works investigating such phenomena as the detachment of photocatalytic films from substrate or the possible photodissolution of immobilised photocatalysts used for real wastewater treatment and its possible effect on water toxicity.

3.1.2. Radiation sources and type of wastewater

3.1.2.1. Radiation sources

The photocatalytic wastewater treatment process occurs mostly under UV radiation. The UV generation by conventional UV lamps is relatively expensive and causes the generation of highly toxic waste (during utilisation). From the economic and

environmental point of view, solar energy can be considered as the best radiation source for photocatalysis. However, in countries with a moderate or low availability of natural solar energy, alternative radiation sources can be used. Taking into consideration the Minamata Convention on Mercury (United Nations, 2018) signed by 128 countries, the use of light emitting diodes (LEDs) is becoming more attractive. The number of studies on photocatalytic water treatment in which alternative UV sources, such as solar energy and light emitting diodes (LEDs) are used is increasing (Blanco-Galvez et al., 2006, Levchuk et al., 2015, Spasiano et al., 2015, Vilhunen et al., 2011). Thus, many photocatalysts active in solar and/or visible light have been developed recently (Booshehri et al., 2017, Bouhadoun et al., 2015, Iwase et al., 2013, Morawski et al., 2017, Ratova et al., 2019, Rosman et al., 2018, Sano et al., 2008). It is worth making a point that majority of these photocatalytic materials possess relatively low photocatalytic activity and quantum efficiency. Hence, photo-Fenton is often applied as alternative, despite its pH aggressiveness and requirements for consumables.

Pilot scale reactors for photocatalytic water treatment with LEDs as a radiation source are appearing in the market (Apria Systems S.L., 2018). Taking into account, the fast development of LEDs, it can be expected that LEDs can reach the level of industrial implementation in the near future. In approx. 35% of the articles, the experiments were conducted under solar radiation. For the simulation of solar radiation, xenon arc lamps are often used (approx. 12% of the articles) (He et al., 2016). To the best of our knowledge only one article reported the detoxification and purification of real wastewater using UVA-LEDs as a radiation source in the last ten years (Jallouli et al., 2018). Considering the fast development of LED technology and advances achieved in this field in recent years it may be expected that more research will be conducted on the

photocatalytic detoxification and purification of real wastewater using LEDs as a radiation source.

Conventional lamps are still utilised in research with various optical filters in order to study photocatalytic reaction under UVC, UVB and/or UVA radiation. It should be noted that in some articles the radiation intensity of the lamp is not provided and photocatalytic activity is shown as a function of time. Such representation of the experimental results, especially in the absence of lamp intensity, makes it extremely difficult to compare the results with other studies. If the electrical consumption of a lamp is provided, it can be possible to estimate the total energy supplied for the removal of one ppm of TOC or COD, but it is a tedious procedure given the actual conditions of reporting in the scientific literature.

3.1.2.2. Types of wastewater

When working with matrices of real wastewater (urban and/or industrial) a few issues should be taken into consideration. On the one hand high concentration of dissolved organic carbon (DOC) should be considered as it is competing for the oxidizing radicals generated by applied AOP. In order to avoid this problem, biological treatment followed by AOP is often suggested to be applied for wastewater containing CECs, which are not highly toxic for biological process (Oller et al., 2011). In case when pollutants present in wastewater possess high toxicity for biological treatment, it is often proposed to apply first AOP and then continue with a biological treatment when the toxicity level of the wastewater treated by AOP allows it. For wastewaters with extremely low concentrations of CECs nanofiltration (for preconcentration of CECs) can be applied, after which reject water with high concentration of CECs can be treated by AOP (Miralles-Cuevas et al., 2014). On the other hand, there are other issues, such as high levels of carbonates in wastewater, which generally decrease the efficiency of applied

AOP (possible solution – acidification of wastewater), phosphates and sulphates can poison and/or coagulate catalysts, etc.

As shown in Fig. 2, the majority of studies on the detoxification and purification of real wastewaters in the last ten years using photocatalysis and hybrid processes were conducted with industrial wastewaters. In more than 60% of the studies on photocatalytic wastewater detoxification, pre-treatment such as pH adjustment, decreasing concentration of carbonates in water, etc. was applied prior to the photocatalytic process. Both raw and treated industrial wastewater was studied. Therefore, the concentrations of TOC, COD and BOD strongly varied depending on the type of industry, type of the pre-treatment (if applicable), etc. It was reported that photocatalytic treatment can be successfully applied as a pre-treatment method (before biological treatment) for raw industrial wastewater leading to an increase of its biodegradability and decrease of toxicity (Talwar et al., 2018) as well as the post-treatment method (after biological treatment) for industrial wastewater effluents allowing decomposing toxic pollutants (Saverini et al., 2012).

To the best of our knowledge, no studies were reported in the last ten years on the photocatalytic detoxification and purification of industrial wastewater and/or wastewater effluents for water reuse and/or recycling. Approx. 40% of revised articles were devoted to the purification and detoxification of municipal wastewater (MWW) effluents. Among these studies, MWW was mostly used as a matrix for spiking emerging pollutants. Depending on the MWW effluent, the level of COD and dissolved organic carbon (DOC) concentrations were approx. 33-55 mg L^{-1} and 10-13 mg L^{-1}, respectively. However, when the concentration of spiked contaminants was relatively high, DOC was as high as 215 mg L^{-1} (Jallouli et al., 2018). Taking into account relatively low levels of COD, TOC, emerging pollutants (µg L^{-1} or ng L^{-1})

concentrations and disinfection in MWW effluents, it may be considered as a viable source for water reuse, e.g. for recreational and/or agricultural irrigation, although health risk assessment should be conducted due to potential presence of pathogens/CECs in treated water (Malchi et al., 2014). However, no studies on photocatalytic MWW effluent purification and detoxification considered the possible reuse of MWW effluent by now.

3.1.3. Toxicity

Different approaches for acute and chronic toxicity evaluation were applied so far for photocatalytically treated wastewater effluents such as bioassays with bacteria (He et al., 2016, Nogueira et al., 2017, Talwar et al., 2018), seawater invertebrates (Hasegawa et al., 2014, Lima et al., 2015, Souza et al., 2016), freshwater invertebrates (Çifçi and Meriç, 2015), microalgae (He et al., 2016), plants (phytotoxicity) (Tsoumachidou et al., 2017), mammalian cells (genotoxicity) (Saverini et al., 2012), etc. As reported in the majority of the studies, after the photocatalytic treatment, the toxicity of wastewater generally decreases. In approx. 44% of the studies on photocatalytic wastewater treatment, the toxicity was monitored on the course of photocatalytic treatment. Interestingly, in some studies a drastic increase of toxicity was reported during the treatment of MWW effluents (Vela et al., 2018a, Vela et al., 2018b) as well as industrial wastewater (Çifçi and Meriç, 2015, Saverini et al., 2012, Tichonovas et al., 2017). Such behaviour was observed when *Vibrio fischeri* (Vela et al., 2018a, Vela et al., 2018b), *Daphnia magna* (Çifçi and Meriç, 2015) and Ames test (Saverini et al., 2012) bioassays were applied. Generally, this phenomenon can be attributed to possible photodissolution of photocatalyst (Vela et al., 2018a), possible generation of more toxic by-products than parental compounds (Vela et al., 2018b) and/or synergetic toxic effects appearing due to the presence of many individual contaminants in water. An additional toxic effect can

be produced in case of hybrid photocatalysis processes, requiring the addition of chemical agents such as H_2O_2, which is toxic for aquatic organisms. In case residual H_2O_2 concentrations after treatment are relatively high, the elimination of H_2O_2 will be required for the safe discharge or reuse of treated wastewater. For this purpose, filtration through granular activated carbon (GAC) can be successfully applied (Rueda-Márquez et al., 2015). Therefore, it would be interesting to check the toxicity of treated wastewater before and after filtration through GAC without the preliminary removal of H_2O_2 from water samples. Toxicity assessment is an important tool for the optimisation of photocatalytic wastewater treatment when complete mineralisation is not a goal. The results of toxicity assessment during the process can clearly indicate at which moment more toxic by-products are generated and when these are decomposed. Therefore, it can be suggested that the evaluation of toxicity on the course of photocatalytic wastewater treatment is of high significance and should be conducted especially if the practical application of photocatalysis is planned.

Toxicity tests applied for the photocatalytic detoxification of industrial wastewater were: *Daphnia magna*, *Daphnia similis*, *Artemia salina*, *Vibrio fischeri*, Ames test (*S.typhimurium*) and Kirby-Bauer method (zone inhibition using *E.coli*). In general, the toxicity of industrial wastewater is higher than that of MWW effluents. Therefore, all the tested bioassays were reported as an efficient tool for the toxicity assessment of industrial wastewaters.

In the reviewed articles devoted to photocatalytic wastewater detoxification, the following toxicity tests were applied for the assessment of MWW effluents and synthetic greywater during photocatalytic treatment: *Vibrio fischeri* bioluminescence's assay, *Daphnia magna* immobilisation test, *Pseudokirchneriella subcapitata*, *Anabaena flos-aquae*, *Brachionus calyciflorus*, estrogenic test (HELN ERα cell line), genotoxicity

assessment (LS 174T cell line) and phytotoxicity test. The bioluminescence's assay with *Vibrio fischeri* was among most widely used toxicity tests for MWW effluents. Interestingly, the inhibition of *Vibrio fischeri* growth was reported for MWW effluents spiked with contaminants at environmentally relevant (ng L^{-1} – µg L^{-1}) (Vela et al., 2018a, Vela et al., 2018b) and irrelevant concentrations (mg L^{-1} – g L^{-1}) (Jallouli et al., 2018). However, in some cases, the very low sensitivity of *Vibrio fischeri* was observed even when MWW effluents spiked with the concentration of pollutants at the mg L^{-1} level (Brienza et al., 2016, He et al., 2016). In spite of a large number of pollutants detected in not spiked MWW effluent, the EC_{50} value for *Vibrio fischeri* of 80% was reported (Brienza et al., 2016), which is non-toxic according to (Calleja et al., 1986). Therefore, for the toxicity assessment of real MWW effluents, *Vibrio fischeri* bioluminescence's assay may not be very sensitive. It was shown that a toxicity assay with *P. subcapitata* is not very sensitive for MWW effluent (EC_{50} 98%), while its sensitivity drastically increases when MWW effluents are spiked with pollutants at mg L^{-1} level (Brienza et al., 2016, He et al., 2016). Similar behaviour was reported for *Daphnia magna* and *Brachionus calyciflorus* (Brienza et al., 2016). In spiked MWW effluent, the growth inhibition of *Anabaena flos-aquae* was reported to be approx. 70% and -20% (growth stimulation) before and after treatment, respectively (He et al., 2016). The growth stimulation was attributed to the presence of organic matter, which is the nutrition source for *Anabaena flos-aquae* as well as the decomposition of toxic contaminants (He et al., 2016). Therefore, the toxicity assay with *Anabaena flos-aquae* and other cyanobacteria may not be very representative for MWW due to relatively high organic load serving as a source of nutrition. The very high sensitivity of the estrogenic toxicity test was reported for not spiked MWW effluent, more specifically, estrogenic activity was detected in MWW effluent when it was not possible to detect any known

estrogenic compound using sophisticated chemical analysis (liquid chromatography - mass spectrometry) (Brienza et al., 2016). These results suggest that the estrogenic toxicity test is a very promising tool for MWW effluents. Genotoxicity (LS 174T cell line) of not spiked MWW effluent was not detected neither before no after photocatalytic treatment (Brienza et al., 2016). The phytotoxicity of synthetic greywater before and after hybrid photocatalytic process was tested using the seeds of *Sorghum saccharatum*, *Lepidium sativum*, *Sinapis alba* (Tsoumachidou et al., 2017). The *Sinapis alba* was the most sensitive among the tested plants. A phytotoxicity assay might be a valuable tool if MWW effluent is planned to be reused for the purpose of irrigation.

Photocatalytic ozonation was efficient for the detoxification of IWW as well as MWW effluents. Interestingly, in the majority of reviewed studies devoted to wastewater detoxification by photocatalytic ozonation, bioassays with freshwater invertebrate (*Daphnia*) were implemented. Other bioassays (*Vibrio fischeri*, *Pseudokirchneriella subcapitata*) as well as genotoxicity and cytotoxicity tests were also used. In general, photocatalytic ozonation was efficient for the decrease of wastewater toxicity and all the implemented bioassays were efficient. Tichonovas and co-authors assessed toxicity (*Daphnia magna*) of IWW during photocatalytic ozonation (Tichonovas et al., 2017). They reported a drastic increase of *Daphnia magna* mortality during the process followed by a significant decrease (reaching zero) at the end of the treatment. These results were explained by the higher acute toxicity of degradation by-products than parental pollutants.

Taking into account the possible practical application of photocatalytic wastewater treatment, a preliminary cost evaluation should be performed. For instance, the operational cost of the hybrid photocatalytic process was reported to be \$45.17 m^{-3} (Bansal et al., 2018). Energy consumption can also be very valuable information, based

on which a cost estimation can be conducted. The photocatalytic ozonation is often considered to be expensive for wastewater treatment (Mehrjouei et al., 2015). In the reviewed articles, estimations of energy required for the detoxification of WW were suggested. Thus, photocatalytic ozonation was reported to be the most energy efficient treatment among those studied with the energy requirements 4.49-41.08 MJ/g-TOC (Tichonovas et al., 2017). Another study suggested that the required energy for photocatalytic ozonation varies from 7.3 to 22.0 kWh/m^3 (Mecha et al., 2017).

4. Conclusions

In this work, the feasibility of photocatalysis for toxicity elimination from real wastewaters is critically discussed. Such aspect of photocatalysis detoxification of real wastewater as photocatalytic materials and its reactivation, types of wastewater and bioassays were discussed. Main outcomes of this work are as follows:

- While photocatalytic wastewater detoxification and purification shows potential, most works (>70%) considered in the scope of this review were conducted on the laboratory scale.
- Most studied photocatalytic materials for real wastewater detoxification both in form of powder and thin films are TiO_2 and ZnO.
- Studies devoted to separation and/or recovery and reuse of photocatalytic materials used for real wastewater detoxification are lacking.
- Only few studies were conducted on real wastewater detoxification using photocatalysts in a form of thin film. There is lack of information on behaviour of thin films (detachment of photocatalyst, photodissolution, etc.) during photocatalytic detoxification of real wastewater.
- The evaluation of the photocatalytic treatment costs for real wastewater detoxification by photocatalysis is not always available.

- Based on this revised literature, it can be suggested that standard tests with species such as *Daphnia magna, Vibrio fishceri, Pseudokirchneriella subcapitata* and *Brachionus calyciflorus* might not be sensitive enough when detoxification of municipal wastewater is studied.
- In some cases, toxicity assessment may be even more sensitive than chemical analysis. It is expected that future studies devoted to the detoxification of wastewater by photocatalysis will implement batteries of bioassays (including biosensors) for a more comprehensive evaluation of water toxicity.
- The use of TiO_2 and other photocatalysts for real wastewater treatment has not been investigated as deep as with other AOPs due to the clear reasons, i.e. efficiency of the process strongly decreases in presence of complex mixture of organic pollutants and high levels of DOC, etc. It can be expected that future studies devoted to development of nanomaterials for similar applications might consider issues related to real wastewater matrix.
- The existing gap between materials research and application studies for real wastewater is an actual barrier, which limits further development of application of photocatalysis for real wastewater treatment.

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Table 1 - Toxicity bioassays applied for assessment of wastewater detoxification after photocatalysis, photocatalytic ozonation and photocatalysis-based AOPs

AOP Process and Reference	Experimental conditions	Type of the water	Toxicity assessment	Main outcomes
TiO_2 photocatalysis (Talwar et al., 2018)	Laboratory scale (UVC 20 W/m^2; commercial TiO_2 (Degussa) <u>*Optimal conditions:*</u> TiO_2 0.6 g/L, pH 3.2, time 455 min	Real pharmaceutical industry WW. COD 12425 mg/L; BOD 1727 mg/L; pH 5.8; TDS 1600 mg/L; TSS 3180 mg/L; TS 4780 mg/L; BOD_5/COD 0.178.	*E.Coli* DH-α strain (Kirby-Bauer method	Based on toxicity assessment it was suggested that photocatalytically treated pharmaceutical wastewater was not toxic.
TiO_2 photocatalysis (Degussa P25) (Jallouli et al., 2018)	Laboratory scale (UVA-LEDs 375 W/m^2; TiO_2) <u>*Optimal conditions:*</u> natural pH and TiO_2 loading 2.5 g/L for both municipal and pharmaceutical wastewater	Municipal WW effluent spiked with ibuprofen (6 µg/L, 6 mg/L or 213 mg/L): DOC 215 mg/L; pH 7.3; conductivity 610 µS/cm. Pharmaceutical industry WW was also used: DOC 170 mg/L; pH 7.9; conductivity 3770 µS/cm; concentration of ibuprofen 213 mg/L.	*Vibrio fischeri*	*Vibrio fischeri* bioluminescence inhibition rate of municipal (spiked with 213 mg/L of ibuprofen) and pharmaceutical WW before photocatalysis was 78.3% and 73.9%, respectively. After 240 min of (optimal conditions) toxicity of both types of water significantly decreased leading to inhibition rates of 40.8% and 30.3% for municipal and pharmaceutical WW, correspondently.
TiO_2 photocatalysis (Vela et al., 2018b)	Pilot scale (CPC plant; commercial TiO_2: Degussa P25 and Krono vlp 7000). <u>*Optimal conditions:*</u> TiO_2 200 mg/L and $Na_2S_2O_8$ 250 mg/L.	Sewage WW effluent spiked with malathion, fenotrothion, quinalphos, vinclozoline, dimethoate, fenarimol phtalate (0.3 mg/L of each one). COD 33.1 mg/L; DOC 10.8 mg/L; BOD_5 5 mg/L; SS 3.6 mg/L; turbidity 1.1 UNT; pH 7.2.	*Vibrio fischeri*	Initial value of *Vibrio fischeri* inhibition (60%, untreated wastewater) dropped to 27 ± 6% (after treatment with vlp 7000) and 15 ± 4% (after treatment with P25) after 240 min. For both photocatalysts significant increase of toxicity was observed after about 90 min of treatment, which was associated with generation of some stable intermediates.
TiO_2 photocatalysis (Saverini et al., 2012)	Laboratory scale (MP lamp intensity of irradiation reaching solution (320-390 nm) 10 mW/cm^2; TiO_2:Degussa P25) <u>*Optimal conditions:*</u> TiO_2 0.4 g/L,	Treated WW from citrus fruit transformation factory was used for photocatalytic experiments TOC 21 mg/L.	Ames test (*S.typhimurium* strain TA100), viability of V79 Chinese hamster cells and Comet assay	High level of genotoxicity was observed for both types of WW (before and after treatment with activated sludge). Results of Comet assay demonstrated that 30% of V79 cells (after 1h treatment with 100 µL of wastewater) were damaged. Exposure of *S.typhimurium* to water samples collected within 2h of photocatalytic test indicate relatively high level of genotoxicity,

				which significantly decreased after 2h of photocatalysis.
TiO_2 coated sand (He et al., 2016)	Laboratory scale (Xenon lamp 159 lux) <u>*Optimal conditions:*</u> depth of water column 0.1 m and 96 h of irradiation.	Effluent from urban WWTP spiked with PhACs (propranolol, diclofenac, carbamazepine, ibuprofen with concentration 5 mg/L each). BOD 6 mg/L; COD 35.2 mg/L; DOC 12.2 mg/L; pH 7.3.	*Pseudokirchneriella subcapitata*, *Anabaena flos-aquae* and *Vibrio fischeri*	Spiked PhACs inhibited growth of all tested microorganisms, among which green algae was the most sensitive (almost 100% of inhibition before treatment).After 96 h of treatment, growth inhibition of green algae decreased from almost 100% to 60%. Significant toxicity decline was observed for blue-green algae (from 70% of growth inhibition to -20%). No significant changes of *Vibrio fischeri* growths inhibition were observed during and after treatment.
Photocatalysis with TiO_2 and TiO_2 modified with hydrotalcite and iron oxide ($HT/Fe/TiO_2$) (Arcanjo et al., 2018)	Laboratory scale (mercury vapor lamp; TiO_2 and $HT/Fe/TiO_2$). <u>*Optimal conditions:*</u> TiO_2 (2g/L and pH 4) and $HT/Fe/TiO_2$ (2g/L and pH 10)	Textile mill WW effluent (secondary). COD 78 mg/L; DOC 25.7 mg/L; turbidity 15 TU; pH 9; conductivity 1608 µS/cm.	*Daphnia similis*	Based on results obtained with *D. similis* the toxicity of wastewater effluent was relatively low (EC_{50} 70.7%). After photocatalytic treatment with TiO_2, the toxicity of effluent decreased and EC_{50} was 95%. Interestingly, when $HT/Fe/TiO_2$ was applied, the toxicity of treated effluent was higher (EC_{50} 78.6%) than in case of TiO_2.
ZnO photocatalysis (Vela et al., 2018a)	Pilot scale (CPC plant; UVC, UVB, UVA, VIS+NIR were 0.2 ± 0.1 W/m^2, 2.1 ± 0.6 W/m^2, 29.2 ± 4.1 W/m^2, 1011.6 ± 66.2 W/m^2, respectively).<u>*Optimal conditions:*</u> ZnO 200 mg/L and $Na_2S_2O_8$ 250 mg/L. Concentration of oxygen 8 – 10 mg/L.	Sewage WW effluent spiked with endocrine disruptors. COD 33.1 mg/L; DOC 10.8 mg/L; BOD_5 5 mg/L; SS 3.6 mg/L; turbidity 1.1 UNT; pH 7.2.	*Vibrio fischeri*	The inhibition of *V. fischeri* exposed to WW before treatment was 70%. Slight increase of *V. fischeri* inhibition was detected after 30 min. After solar photocatalysis at optimal conditions (240 min) inhibition of *Vibrio fischeri* significantly decreased (11 ± 5%).
ZnO photocatalysis (Hasegawa et al., 2014)	Laboratory scale (mercury vapor lamp 1850 µW/cm^2; ZnO). <u>*Optimal conditions:*</u> ZnO 1 g/L; pH 8.0 and irradiation time 4h.	Effluent from leather industry (filtered and diluted in distilled water). COD 15 023 ± 60 mg/L; TOC 4685 mg/L; BOD_5 4374 ± 0.1 mg/L; turbidity 331.0 ± 0.02 NTU; pH 3.5 ± 0.7.	*Artemia salina* L.	The LC_{50} of *Artemia salina* L. was 14.9% after 24h of exposure to raw wastewater. After photocatalytic treatment at optimal conditions the LC_{50} was 56.82%. Results indicate that toxicity of wastewater was decreased after photocatalysis with ZnO.

TiO_2 and ZnO photocatalysis (Çifçi and Meriç, 2015)	Laboratory scale (16 UVA lamps 5.62 mW/cm^2; TiO_2 and ZnO) *Optimal conditions:* TiO_2: pH 5, TiO_2 2 g/L, reaction time 3h; ZnO: pH 9, ZnO 2 g/L, reaction time 3h.	Two WW effluents from dyeing and finishing textile industry (WW1 and WW2). WW1: total COD 370 ± 74 mg/L, soluble COD 230 ± 15 mg/L, TOC 61 mg/L, pH 7.94, conductivity 5.15 µS/cm, alkalinity 436 mg $CaCO_3$/L. WW2: total COD 90 ± 9 mg/L, soluble COD 70 ± 4 mg/L, TOC 60 mg/L, pH 7.65, conductivity 4.50 µS/cm, alkalinity 246 mg $CaCO_3$/L.	*Daphnia magna*	When TiO_2 was applied for treatment of WW1 at optimal conditions, the toxicity of water drastically increased at 120 min of contact time. This was attributed to formation of long chain byproducts after decomposition of aromatic compounds. After 180 min no toxicity was observed. When ZnO was used for treatment of WW2 at optimized conditions, slight increase of toxicity occur at 150 min of reaction (similar reason as in case of TiO_2). No toxicity was detected after 180 min of photocatalytic treatment.
Photocatalysis with TiO_2, ZnO and Nb_2O_5 (Souza et al., 2016)	Laboratory scale (mercury vapor lamp; TiO_2 Kronos, TiO_2 Degussa P25, ZnO Dynamic and Nb_2O_5, BCMM). *Optimal conditions:* pH 3, concentration of photocatalyst 0.25 g/L, 300 min	Textile effluent from jeans industrial laundry. COD 558.50 ± 5.05 mg/L, $BOD_{5,\ 20^o}$ 170 mg/L, turbidity 113.0 ± 2.7 NTU	*Artemia salina*	Values of LC_{50} of *Artemia salina* before and after photocatalytic treatment (300 min, pH 3 and concentration of photocatalyst 0.25 g/L) were as follow: Effluent: 27.59%; TiO_2-P25: 90.86%; TiO_2 Kronos: 61.62%; ZnO: 66.56%; Nb_2O_5: 77.52%. Results indicate that toxicity of textile wastewater effluent significantly decreased after photocatalytic treatment.
Photocatalysis with polypyrrole (Lima et al., 2015)	Laboratory scale (300 W Osram lamp 108 kJ/m^2s; polypyrrole) *Optimal conditions:* polypyrrole 5 mg/mL; 120 min	Textile WW. COD 1111.04 mg/L; TOC 156.75 mg/L.	*Artemia salina*.	Results demonstrated 96.7% of *Artemia* survival after treatment, indicating that treated water is relatively not toxic. Interestingly toxicity tests were not shown for wastewater before treatment.
		Photocatalytic ozonation		
O_3/UV/TiO_2 (Tichonovas et al., 2017)	Laboratory scale (LP lamp; TiO_2 (Aeroxide P25, Evonik) deposited on glass rods; O_3 concentration 1.3 mg/L, air flow rate 11 L/min) *The best conditions among tested AOPs:* the most efficient AOPs were as follows TiO_2/UV/O_3 > UV/O_3 > TiO_2/UV. The	Furniture industry WW after primary treatment. WW diluted 124.4 times: TOC 50 mg/L; COD 130 mg/L; conductivity 186 µS/cm; pH 6.7	*Daphnia magna*	TiO_2/UV/O_3 process (most efficient): mortality (%) of *Daphnia magna* for initial wastewater was 13% after 72h. It drastically increased during treatment, thus, reaching almost 100% (48h and 72h) from 20 to 40 min. During 80-100 min, mortality drastically decreased reaching zero after 60 min (24h of exposure), 100 min

				(48h of exposure) and about 13% of mortality after 100 min for 72h of exposure.
$UV/O_3/ZnO$ (Biglari et al., 2017)	Laboratory scale (UV lamp 254 nm, 1020 $\mu W/cm^2$; ZnO) <u>*Optimal conditions:*</u> ZnO 0.1 g/L, pH 5, O_3 9.2 mg/min, irradiation time 30 min.	WW effluent (pulp and paper industry). COD 4751 mg/L, BOD 386 mg/L, pH 6.2 – 8.7, iron 0.28 mg/L, bicarbonate 280 mg/L, phenol 61 ± 2 mg/L	Daphnia	It was reported that treated wastewater was safe based on conducted toxicity assessment with daphnia.
UV and solar photocatalytic ozonation (Mecha et al., 2017)	Laboratory scale (MP lamp and sun; TiO_2 and modified TiO_2 photocatalysts)	Secondary WW effluent (spiked with 5000 µg/L of phenol). pH 6.8, COD 42 mg/L, DOC 20 mg/L.	MTT assay with Vero cells	Significant toxic effect was observed for untreated WW effluent (cell viability 28.7%). After application of photocatalytic ozonation the toxicity significantly decreased, leading to cell viability of 76% ($UV/O_3/TiO_2$) and 80% ($UV/O_3/TiO_2$-Fe). After solar photocatalytic ozonation the cell viabilities were 58% ($solar/O_3/TiO_2$) and 69% ($solar/O_3/TiO_2$-Fe).
O_3/H_2O_2 O_3/UV $O_3/Xe/Ce\text{-}TiO_2$ $O_2/Xe/Ce\text{-}TiO_2$ (Santiago-Morales et al., 2012)	Laboratory scale (gas flow 0.19 N/m^3h, O_3 concentration 22 g/Nm^3; LP (6.01 ± 10^{-6} E/Ls) and Xe-arc (1.05 ± 10^{-6} E/Ls) lamps) <u>*Optimal conditions:*</u> H_2O_2 (when applied) 30 µL/L, concentration of photocatalytist (when applied) 200 mg/L	Effluent from secondary clarifier from municipal WWTP spiked with 500 ng/L of galoxilide and tonalide was used. pH 7.79, COD 28 mg/L, NPOC 8.1 mg/L, $CaCO_3$ 219 mg/L.	*Pseudokirchneriella subcapitata*, *Vibrio fischeri* and *Daphnia magna*	<u>*P. subcapitata* bioassay</u>: the toxicity increased after 15 min of treatment by photolysis (UV and Xe lamps), O_3/H_2O_2 and $Xe/Ce\text{-}TiO_2$ photocatalysis. After 15 min of O_3, O_3/UV and O_3/ $Ce\text{-}TiO_2$ treatment, toxicity of water decreased. <u>*Daphnia magna:*</u> For all tested processes toxicity decreased. Immobilization observed in raw WW was about 15%, after majority of tested processes this value was about 5%. <u>*Vibrio fischeri:*</u> Toxicity of waster increased after 15 min of photolysis and Xe/ $Ce\text{-}TiO_2$ process. Decrease of toxicity was observed after applied O_3/UV, O_3/Xe and O_3/ $Ce\text{-}TiO_2$.
		Hybrid photocatalysis-based processes		
Combination of photocatalysis, photo-Fenton and	Laboratory (UVA lamps 23 ± 2 W/m^2) and pilot scale experiments (mean intensity of solar UV+Visible light 788W/m^2)	Real effluent from pharmaceutical industry . COD 4800 mg/L; BOD 830	*E.coli* (The Kirby-Bauer method) and zebra fish.	<u>The Kirby-Bauer method:</u> The biggest inhibition zone against *E.coli* was reported for untreated WW. During treatment, the inhibition zone was

iron oxide catalysis using Fe-TiO_2 composite beds (Bansal et al., 2018)	<u>*Optimal conditions:*</u> H_2O_2 dose: 1155 mg/L, pH 3-3.5, process time 6h and dose of Fe-TiO_2 equal to 102% area of reactor bed covered with composite beds (under artificial radiation source).	mg/L; TDS 1320 mg/L; TSS 620 mg/L; turbidity 742 NTU; pH 5.07; chloride 25 mg/L; sulfate 526 mg/L.		decreasing, which corresponds to decrease of toxicity. <u>Zebra fish bioassay:</u> After 96h of bioassay zebra fish survival level was 100. The zebra fish toxicity assay was not conducted for untreated wastewater.
Solar-induced Fenton-assisted TiO_2 photocatalytic hybrid process (Tsoumachidou et al., 2017)	Bench (UVA lamp $1.232 \cdot 10^{-4}$ E/min) and pilot scale (solar radiation) <u>*Optimal conditions:*</u> TiO_2 0.5 g/L, H_2O_2 0.5 g/L, Fe^{3+} 0.0035 g/L	Synthetic effluent simulating the actual grey WW. DOC 93 mg/L; pH 3.36; conductivity 47.6 µS/cm	*Vibrio fischeri*, *Sorghum saccharatum*, *Lepidium sativum*, *Sinapis alba*	*V. fischeri* (5 min): 87% of inhibition (before treatment) and 10% (after 247.34 min); *V. fischeri* (15): 91% of inhibition (before treatment) and 18% (after 247.34 min). The EC_{50} values (15 min) significantly increased during treatment process. *Sinapis alba* was more sensitive to raw wastewater than other tested plants.
TiO_2/UV and Fe_2O_3/UV TiO_2/H_2O_2/UV and Fe_2O_3/ H_2O_2/UV (Nogueira et al., 2017)	Laboratory scale (UV lamp with emission peak at 312 nm; commercial TiO_2 and Fe_2O_3). <u>*Optimal conditions:*</u> for pulp mill effluent: pH 3.0, TiO_2 0.75 g/L; Fe_2O_3 0.75 g/L, concentration of H_2O_2 75 mM). For mining WW: TiO_2 1 g/L; Fe_2O_3 1 g/L.	Bleach kraft pulp mill secondary WW effluent: COD 391 ± 2 mg/L, pH 8.8 ± 0.05. Acid mine drainage: pH 2.58 ± 0.07, S 402.3 ± 1.8 mg/L, Cu 1.0 ± 0.05 mg/L, Zn 48.0 ± 1.6 mg/L, As 1.2 ± 0.15 µg/L, Al 74.0 ± 0.7 mg/L, Pb 13.5 ± 1.05 µg/L, Cd 56.2 ± 1.5 µg/L	*Vibrio fischeri*	*Kraft pulp mill effluent*: toxicity of water after photocatalytic treatment with TiO_2 (0.5g/L and 0.75 g/L) and Fe_2O_3 (0.25 g/L and 1.0 g/L) slightly decreased. But the increase of toxicity was observed when other concentrations of TiO_2 (0.25 g/L and 1.0 g/L) and Fe_2O_3 (0.5 g/L and 0.75 g/L) were applied. Photocatlysis in combination with H_2O_2 was more efficient for removal of toxicity with best results attributed to Fe_2O_3 and 75 mM of H_2O_2. *Mining effluent*: toxicity decreased when photoctalytic treatment was applied using TiO_2 and Fe_2O_3. Addition of H_2O_2 led to decrease of toxicity, except in case of 5 min exposure when toxicity increased.
Solar photocatalysis and photo-Fenton (Brienza et al., 2016)	Pilot scale (average UV intensity 70 W/m^2) <u>*Optimal conditions:*</u> TiO_2 (Evonik P25)0.7 g/L; solar photo-Fenton was conducted with 100µM of iron sulfate, 200 µM of monopersulfate and sulfuric acid (initial pH	Municipal WW effluent after biological treatment. TOC 26.3 ± 0.6 mg/L; conductivity 669 ± 21 µS/cm; pH 7.2 ± 0.2.	*Vibrio fischeri*, *Daphnia magna*, *Pseudokirchneriella subcapitata*, *Brachionus calyciflorus*,	The EC_{50} values obtained for *V. fischeri*, *D. magna*, *P. subcapitata*, and *B. calyciflorus* for initial WW were 80%, 90%, 98% and 90%, respectively (non-toxic). Estrogenic activity was detected in raw WW even when estrogen was

	of water was adjusted to 2.6).		estrogenic tests (HELN ERα cell line); *In vitro* genotoxicity assessment (LS 174T cell line)	not possible to analyze by chemical analysis. Estrogenic activity did not decrease after solar photolysis, while after photocatalysis and photo-Fenton it was reduced. Genotoxicity before and after applied treatments was not detected.
		Catalytic ozonation		
Heterogeneous catalytic ozonation (Zhuang et al., 2014)	Laboratory scale *Optimal conditions*: sewage sludge based AC impregnated with Mn and Fe (1 g/L) and $ZnCl_2$ as activation agent was used. O_3 flow 500 mL/min, O_3 concentration 15 mg/L.	Lurgi coal gasification WW after biological treatment was used. COD 130-180 mg/L, BOD5/COD 0.05-0.07, TOC 45-60 mg/L, bicarbonate 40-60mg/L, pH 6.5-7.5.	*Daphnia magna*	Changes in acute toxicity were monitored on the course of catalytic ozonation. Residual ozone was eliminated before toxicity assessment. Inhibition rate observed for WW prior catalytic ozonation was about 65%. Toxicity was decreasing during treatment reaching highest detoxification (15%) with Mn impregnated catalyst. During zonation slight increase of toxicity was detected in the beginning of the treatment. Catalytic ozonation was more efficient than ozonation for wastewater detoxification.
Heterogeneous catalytic ozonation (Wu et al., 2016)	Catalyst: iron shavings (38CrMoAl steel) 20 g/L; O_3 10.8 mg/L	WW effluent from dyeing and finishing industry. COD 142 ± 6 mg/L, DOC 44 ± 1 mg/L, BOD_5 1.0 ± 0.5 mg/L, pH 7.37 ± 0.14.	*Photobacterium phosphoreum*	The inhibition of bacteria for wastewater effluent before catalytic ozonation was 51%, whereas after treatment it was 33%. Results suggested decrease of wastewater effluent toxicity.
Heterogeneous catalytic ozonation (Ma et al., 2018)	Pilot scale (catalyst: iron shavings). *Optimal conditions:* O_3 dosage 10.2 O_3/min, hydraulic retention time 30 min.	WW effluent from dyeing and finishing industry. COD 165 ± 20 mg/L, DOC 76 ± 6 mg/L.	*Photobacterium phosphoreum*	After treatment of wastewater by catalytic ozonation at optimal conditions, the toxicity slightly decreased. Thus, the inhibitory effect for untreated wastewater was 29.3 ± 3% and for treated affluent 25 ± 2%