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REVIEW

Photocatalytic ozonation of wastewater: a review

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Abstract
Industrialization is inducing water pollution by pharmaceuticals, fertilizers and cosmetics. Many emerging pollutants are non-biodegradable, toxic and recalcitrant to conventional wastewater treatments, thus calling for improved remediation techniques such as advanced oxidation processes which allow complete mineralization of pollutants. Here we review advanced oxidation processes with focus on ozonation and photocatalysis for the degradation of organic and microbial contaminants in wastewaters. Ozonation efficiency is limited by ozone-resistant pollutants, whereas photocatalysis is slow due to charge recombination, yet photocatalytic ozonation overcomes these limitations. Photocatalytic ozonation indeed shows synergy indices of up to 5.8 for treating wastewaters. This resulted in faster reaction kinetics, enhanced pollutant degradation with mineralization achieved in most cases, and reduction of toxicity up to 100%. We also discuss energy requirements.

Keywords Advanced oxidation processes · Degradation · Photocatalytic ozonation · Toxicity · Wastewater

Introduction

The protection of natural water resources and development of new technologies for water and wastewater treatment for reuse are key priorities of the twenty-first century. The environmental degradation caused by emerging biorecalcitrant organic compounds such as pharmaceuticals, cosmetics, fertilizers and resistant microbial pollutants is a global concern resulting in scarcity of fresh water in various parts of the world (Valério et al. 2020). However, the current conventional wastewater treatment technologies are often not effective in meeting the stringent effluent standards targeting the removal of emerging contaminants (Dewil et al. 2017). There is need to develop more effective treatment technologies that satisfy a range of requirements such as complete removal of biorecalcitrant organic pollutants, inactivation of resistant pathogens, less costly, energy efficient and environmentally friendly (Singh 2012; Mecha et al. 2017a, b). In this regard, advanced oxidation processes, especially those driven by solar light, have great potential in wastewater remediation targeting emerging contaminants (Rizzo et al. 2019; Rodríguez et al. 2019).

The advanced oxidation processes are destructive technologies which degrade contaminants. However, despite their overall high degradation efficiency, large-scale practical implementation has not been realized (Matafonova and Batoev 2018). This is partly due to high process costs since they are energy intensive. Also information regarding their performance is not standardized, for instance, a direct comparison of different advanced oxidation processes is difficult. In fact even the use of the electrical energy per order (E_{EO}) concept for comparison is hampered by variation in influencing factors (Miklos et al. 2018). The advanced oxidation processes break down complex organics into simpler, less harmful ones such as carbon dioxide and water, a process known as mineralization (Bethi et al. 2016). However, in cases where mineralization is not achieved, the intermediate products produced may be toxic, thus re-contaminating the treated water and thereby endangering humans, ecological systems and the environment (Wang et al. 2018). This makes it necessary therefore to study the toxicity of treated water before discharge or reuse.

Among the advanced oxidation processes, ozonation and photocatalysis have received wide attention and recently photocatalytic ozonation has come to the limelight. Thus, here in, we review the principles of operation of advanced oxidation processes; performance of ozonation and its limitations;

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performance of heterogeneous photocatalysis and its limitations; combination of photocatalysis and ozonation to overcome the challenges of the individual processes; application of photocatalytic ozonation in wastewater treatment. We also address pertinent aspects required for real application of photocatalytic ozonation such as synergy of the combined processes, toxicity of treated water, energy requirements and photocatalyst recovery and reuse. Figure 1 shows a laboratory scale photocatalytic ozonation system.

Advanced oxidation processes

Principles of advanced oxidation processes

The advanced oxidation processes are near-ambient temperature and pressure processes that involve the generation of highly reactive radicals (Glaze et al. 1987; Miklos et al. 2018). Although advanced oxidation processes make use of different reaction systems, they are all characterized by the production of highly reactive hydroxyl ($^{\cdot}$OH) radicals. The standard redox potential of $^{\cdot}$OH radicals (2.8 V) is much higher compared to that of common oxidants such as ozone (2.07 V), hydrogen peroxide (1.77 V) or even chlorine (1.36 V) (Pelaez et al. 2012). The $^{\cdot}$OH radicals are non-selective and therefore can virtually degrade any organic contaminant present in wastewater including those that are biorecalcitrant (Andreozzi et al. 1999; Valério et al. 2020). This is a useful attribute for an oxidant to be used in the treatment of wastewaters which normally contains a variety of pollutants. The $^{\cdot}$OH radicals can react in aqueous solution through three possible mechanisms: (1) hydrogen abstraction (Eq. 1), (2) electron transfer (Eq. 2) and (3) radical addition (Eq. 3):

$$OH^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \quad (1)$$

$$OH^{\cdot} + RH \rightarrow RX^{+\cdot} + OH^{-} \quad (2)$$

$$OH^{\cdot} + PhX \rightarrow HOPhX^{\cdot} \quad (3)$$

The advanced oxidation processes when properly developed can provide a complete solution to the problem of pollutant abatement (through mineralization) in contrast to the phase separation processes (such as membrane separation and adsorption), which produce sludge that requires final disposal and introduces secondary pollution.

Classification of advanced oxidation processes

Advanced oxidation processes fall under two general categories. The first utilizes light energy such as ultraviolet (UV) light in conjunction with other chemical additives. Under this category are processes such as UV/H_2O_2, UV/ozone (O_3), UV/titanium dioxide (TiO_2) and UV/Fenton. When no light source is used, the technology can be termed as a dark oxidative process. Processes in this category include ozonation, Fenton's reagent, ultrasound and microwaves among others (Gilmour 2012). Thus, advanced oxidation processes include chemical oxidants (H_2O_2, ozone, etc.), Fenton and photo-Fenton processes (Fe^{2+}/H_2O_2/UV), photocatalytic processes (semiconductor with UV/visible light), supercritical water oxidation, electron beams and ultrasounds (Rizzo 2011; Khataee and Fathinia 2013). These processes are based on the in situ generation of highly reactive transitory species (H_2O_2, $^{\cdot}$OH, O_2^{-}, O_3) for mineralization of refractory organic compounds and inactivation of waterborne pathogens (Hoigne 1998; Esplugas et al. 2002; Tsydenova et al. 2015) simultaneously. Due to rapid oxidation reactions, advanced oxidation processes are characterized by high reaction rates and short treatment times, which make them promising in wastewater treatment (Hoigne 1998; Esplugas et al. 2002). A general classification of advanced oxidation processes is given in Table 1.

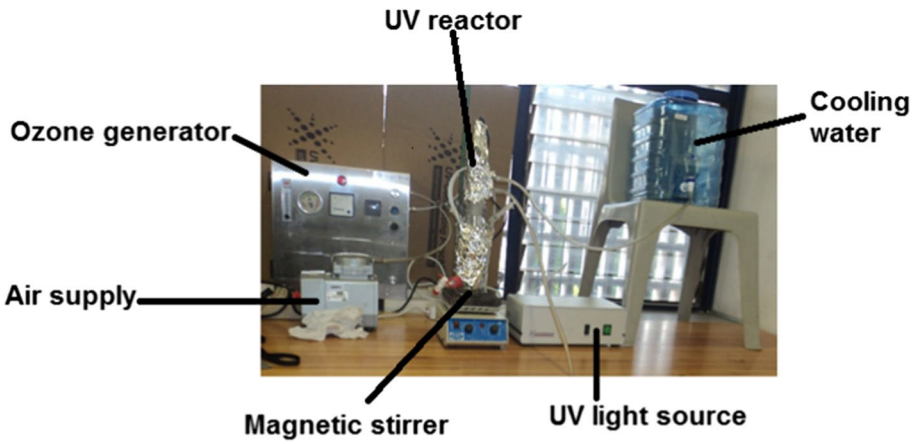

Fig. 1 Laboratory scale photocatalytic ozonation system showing an immersed lamp ultraviolet (UV) reactor with a cooling water circulation system, magnetic stirrer, air supply and ozone generator

Table 1 Advanced oxidation processes showing the different processes, reagents and conditions

Process	Reagents/conditions used	References
Chemical oxidation	Ozone (O_3), hydrogen peroxide (H_2O_2)	Postigo and Richardson (2014), Devatkal et al. (2016) and Mecha et al. (2016c)
Fenton processes	Fe^{2+} and H_2O_2; Fe^{2+} and H_2O_2 with UV light	Rodríguez-Chueca et al. (2015), Ahmed et al. (2017) and Jain et al. (2018)
UV-based processes	UV and O_3; UV and H_2O_2 UV and O_3 and H_2O_2	Ferro et al. (2016) and Mecha et al. (2016a)
Photocatalytic redox processes	Semiconductor (TiO_2, ZnO) and UV light	Kanakaraju et al. (2014) and Mecha et al. (2016b)
Supercritical water oxidation	High temperature and pressure	Busca et al. (2008), Malik et al. (2014) and Tembhekar et al. (2015)
Sonolysis	Ultrasound	Nam et al. (2015) and Rayaroth et al. (2016)

Advantages of advanced oxidation processes

The advanced oxidation processes have unique advantages over conventional treatment processes such as (1) operation under ambient conditions of temperature and pressure, (2) effectiveness in destroying biorecalcitrant organic compounds, (3) mineralization of organic contaminants into carbon dioxide if desired, without any waste disposal problem, and (4) production of minimal harmful by-products (Zhou and Smith 2002; Parsons 2004). In most instances, advanced oxidation processes are used to supplement rather than to replace conventional systems and to enhance the treatment of organic micropollutants and pathogens. They are therefore used as pretreatment to convert recalcitrant pollutants into biodegradable compounds that can then be treated by conventional biological methods. They are also used for the degradation of recalcitrant pollutants as a post-treatment after the biological process to polish the effluent before discharge or reuse (Wang and Xu 2012). The main idea of the combination is the use of a more expensive technology only in the first or final step of the treatment to reduce costs (Černigoj 2007).

Disadvantages of advanced oxidation processes

The major disadvantage of these processes is their high cost resulting from the costly reagents and light energy sources like UV light (Esplugas et al. 2002). However, this can be addressed for instance by the development of visible light active catalysts (hence enable the use of natural sunlight) and improved reactor design to ensure optimal utilization of the oxidants. Recent research efforts have focused more on those photocatalytic processes, which can be driven by solar irradiation to reduce dependency on electrical energy and hence reduce costs (Mecha et al. 2016a, b). The use of renewable and free solar energy in such processes could substantially decrease treatment costs and be more environmental friendly for wastewater decontamination. Among the many advanced oxidation processes that have been studied, ozonation and photocatalysis are prominent for wastewater treatment (Esplugas et al. 2002) and are explored further in this review.

Ozonation

Introduction to ozone

Ozone is a gas with a pungent smell that is generated on-site from dry air or pure oxygen. The formation of ozone is endothermic, and ozone is thermodynamically unstable and thus readily reverts to oxygen ($3O_2 \leftrightarrow 2O_3$) (Zhou and Smith 2002; Gardoni et al. 2012). Ozone is a strong oxidizing agent and is used as a chemical reagent in synthesis, water and wastewater treatment and bleaching agent. Its use in water and wastewater treatment is based on its effectiveness in (2) disinfection, (2) oxidation of biorecalcitrant pollutants, (3) removal of taste and odour and colour and (4) reduction of turbidity (Gray 2014; Mecha et al. 2018). Advantages of ozone include: (1) it can be easily produced from air or oxygen by electric discharge; (2) it reacts readily with organic and inorganic compounds; (3) multiple applications such as disinfection, reduction of chemical oxygen demand, colour, odour and turbidity of the water treated; and (4) any excesses of ozone in water decompose readily to oxygen, without leaving any residue.

Mechanism of ozone oxidation

In aqueous solution, ozone reacts with various constituents in two ways: (1) direct oxidation by molecular ozone which involves selective reactions, such as electrophilic, nucleophilic or dipolar addition reactions with low reaction rates (Hoigne 1998), and (2) indirect mechanism through the decomposition of ozone to produce $^{\cdot}OH$ radicals, which are non-selective and highly reactive (Miklos et al. 2018). Ozone and $^{\cdot}OH$ radicals are strong chemical oxidants and are involved in disinfection and oxidation of contaminants

(Gray 2014). The overall reaction for the production of ·OH from ozone is given as:

$$3O_3 + OH^- + H^+ \rightarrow 2OH^{\cdot} + 4O_2 \quad (4)$$

Limitations of ozonation

A major limitation of ozone is that it oxidizes refractory organic compounds, but only minimal mineralization is achieved (Bashiri and Rafiee 2014) due to the formation of ozone recalcitrant intermediate compounds (Chin and Berube 2005; Mecha et al. 2016c). When used for disinfection, regrowth of the microorganisms cannot be prevented because of the difficulty in maintaining residual ozone. This requires the use of a secondary disinfectant such as chlorine to maintain a residual especially if the treated water is intended for consumption (Demir and Atguden 2016). Other disadvantages include: (1) the yield of ozone generator is low (6–12% from oxygen and 4–6% from air); (2) ozone is unstable and has to be generated on-site due to challenges with storage and transportation; and (3) limitations of mass transfer of ozone into water.

Heterogeneous photocatalysis

Overview of heterogeneous photocatalysis

Heterogeneous photocatalysis has become an increasingly viable technology in environmental remediation. A photocatalytic process usually requires the following elements: a semiconductor or photocatalyst, a light source, a reactor system, the pollutant and oxygen (Vamathevan et al. 2001). The oxidizing species either free holes or ·OH radicals are generated under ambient conditions. Heterogeneous photocatalytic technologies have advantages over other advanced oxidation processes such as operation under ambient conditions of temperature and pressure, the use of oxygen from the air as oxidant, the possibility of using solar light to drive the process and the complete destruction of most contaminants without generating secondary waste (mineralization). These attributes are very important from the energy consumption and environmental impact perspectives (van Grieken et al. 2009a; Zangeneh et al. 2015).

Properties of photocatalysts

Photocatalysts are materials that are activated by adsorbing photons and are capable of accelerating reactions without being consumed (Umar and Aziz 2013). Some basic requirements of a good photocatalyst include high photoactivity, biological and chemical inertness, photostability and non-selectivity in most cases (Pirkanniemi and Sillanpää 2002; Kumar and Bansal 2013). To reduce the electrical energy requirements, it is desirable for the photocatalyst to be able to utilize not only UV light, but also visible light from solar energy. The photocatalyst also needs to be inexpensive. Based on these properties, the most popular photocatalyst for use in water treatment is titanium dioxide because it encompasses most of the above-mentioned properties (Andreozzi et al. 1999; Rizzo et al. 2019).

Titanium dioxide as a potential photocatalyst

Titanium dioxide exists in three crystalline forms, namely, brookite, rutile and anatase. Among these, rutile and anatase are the commonly used forms; however, anatase is mostly used in photocatalytic treatment of wastewater. The composition of titanium dioxide is temperature dependent; for instance, rutile is more stable than anatase thermodynamically, but at temperatures below 600 °C the formation of anatase is kinetically favoured (Carp et al. 2004). In most of the photocatalytic studies, anatase has been shown to be more photoactive as compared to rutile. This is attributed to the fact that anatase has a slightly higher Fermi level, higher capacity to adsorb oxygen and a higher degree of hydroxylation of the surface. In terms of light absorption, rutile is able to absorb light with a wavelength of 415 nm, whereas anatase only absorbs at 385 nm (Fujishima et al. 2008). A commercially widely used titanium dioxide, Degussa P25, has been used in many studies due to its high photoactivity under UV light irradiation. It is non-porous, is composed of 70–90% anatase and 10–30% rutile, has a surface area of 55 ± 15 m^2/g and crystallite sizes of 30 nm (Hoffmann et al. 1995; Valério et al. 2020). In most cases, mixed phase titanium dioxide photocatalysts are found to perform better (Carp et al. 2004).

Limitations of titanium dioxide photocatalysis

The efficiency of photocatalytic reactions is dependent on the degree of electron–hole recombination inherent in processes and the light absorption capability of photocatalysts (Vamathevan et al. 2002). Consequently, the conspicuous drawback of titanium dioxide is that after excitation, the photogenerated charge carriers depict a high rate of recombination. The electron–hole recombination declines the overall efficiency of the semiconductor by decreasing the quantum yield of the desired oxidation/reduction processes. This results in slow reaction kinetics resulting from charge recombination. Furthermore, titanium dioxide has a wide band gap (3.2 eV for anatase), which requires UV light to produce ·OH radicals during the photocatalytic process (Nahar et al. 2006; Ambrus et al. 2008). This constitutes a significant energy consumption problem, thereby increasing

the electricity requirements. Moreover, it limits the application of solar radiation, which contains 4–6% UV irradiation. On the other hand, visible light constitutes a large portion of solar light spectrum (approximately 45%) (Castillo et al. 2013), and to apply it in photocatalytic treatment of wastewater, there is need to develop visible light-responsive photocatalysts. This can be achieved by catalyst modification processes to cause a red shift in the semiconductor's light response to the visible spectrum.

The development of a new titanium dioxide photocatalysts with increased activities under visible light can be attained through various modification techniques such as bulk modification, surface modification and sensitization of titanium dioxide (Zaleska 2008; Mital and Manoj 2011; Lazar et al. 2012; Zangeneh et al. 2015). The major practices involve catalyst modification by doping using metal and non-metal ions, metal coating, surface sensitization and increase in surface area by design and development of secondary titania photocatalyst. Among these modifications, metal-ion doping is reported to be effective in improving the visible light activity of titanium dioxide (Silva 2008; Mecha et al. 2016b).

Modification of titanium dioxide using metal-ion doping

Doping titanium dioxide with metal ions is an important approach in band gap engineering to change the optical response of titanium dioxide. The principle entails the introduction of localized bands of orbitals within the titanium dioxide band gap (bathochromic shift). Consequently, this reduces the recombination of photogenerated electrons and holes and extends the light absorption of the photocatalyst into the visible region resulting from charge-transfer transition between the *d* electrons of the metals and the conduction band or valance band of titanium dioxide (Zangeneh et al. 2015).

Transition metal doping species improve the trapping of electrons to inhibit electron–hole recombination during illumination (Mital and Manoj 2011). However, not all transition metals can achieve this; only transition metals such as Fe^{3+} and Cu^{2+} inhibit electron–hole recombination (Vamathevan et al. 2001). They also increase the electron–hole pair separation efficiency, thus inhibiting their recombination and hence improving the photocatalytic activity under visible light irradiation (Pham and Lee 2014). Noble metals such as platinum, gold and silver have high Schottky barriers and thus act as electron traps and facilitate electron–hole separation. There are different mechanisms for noble metal doping on titanium dioxide depending on the photoreaction conditions. They may (1) enhance the electron–hole separation by acting as electron traps, (2) enable visible light absorption and enhance plasmon resonance surface electron excitation under visible light and (3) modify the surface properties of photocatalysts (Sobana et al. 2006).

Although visible light activity of metal-ion-doped titanium dioxide leads to the reduction of the energy requirements, it still does not solve the challenge of slow reaction kinetics encountered in photocatalysis. Therefore, despite the great potential of heterogeneous photocatalysis for the removal of persistent non-biodegradable organic pollutants from wastewater, it suffers from the significant challenge of low oxidation rate (Augugliaro et al. 2006). This limitation may be addressed through the combination of photocatalysis with other oxidation processes such as ozonation, which is a better electron scavenger than oxygen.

Coupling photocatalysis and ozonation

Motivation for combining photocatalysis and ozonation

Ozone oxidation of organic pollutants is generally a fast process; however, a significant mineralization of the pollutant rarely occurs because of the formation of ozone-resistant and stable degradation by-products such as carboxylic acids (Hsu et al. 2007). These carboxylic acids are formed by opening the aromatic ring and are very resistant to oxidation by ozone, and hence, they limit the mineralization potential (Kasprzyk-Hordern et al. 2003; Zou and Zhu 2008). On the other hand, photocatalysis presents the advantage of achieving complete contaminant mineralization. However, long degradation time is required because of the low oxidation rates (Agustina et al. 2005). To improve the overall performance, heterogeneous photocatalysis has in recent times been combined with other processes, which affect the chemical kinetics and/or the overall efficiency. For instance, the efficiency of titanium dioxide photocatalytic process can be improved by adding oxidant species such as ozone (Rajeswari and Kanmani 2009a). When photocatalysis is coupled with ozonation, the combination influences the photocatalytic mechanisms by increasing the efficiency and decreasing the reaction time in respect of the individual processes (Augugliaro et al. 2006). It reduces the ozone dosage required (Silva et al. 2019), which further leads to low costs of water treatment and reduced formation of ozone disinfection by-products (Meunier et al. 2006). Photocatalytic ozonation has a superior performance than the individual processes (Shinpon et al. 2002; Rajeswari and Kanmani 2009a). For instance, Müller et al. (1998) showed that the advantages of photocatalysis achieving a constant decline in dissolved organic carbon, and of ozonation preventing the accumulation of high intermediate concentrations, were beneficial during photocatalytic ozonation of 2,4-dichlorophenoxyacetic acid. Therefore, integrating ozonation and

photocatalysis enables the exploration of the advantages of both processes and synergies, while also overcoming their individual limitations. Moreover, the similarities between the mechanism of photocatalysis and ozonation and operation under some common process conditions point towards the synergy between these methods leading to better results as compared to individual techniques (Gogate and Pandit 2004). Consequently, there is a growing shift from the use of individual processes to combined oxidation processes, which result in increased overall degradation of several pollutants. This has been attributed to enhanced generation of $^{\cdot}OH$ radicals, eventually increasing the oxidation rates, or improving the contacting of the generated free radicals with the pollutants and effective utilization of oxidants (Wang and Xu 2012).

Factors influencing photocatalysis and ozonation

To explore the combination of photocatalysis and ozone in wastewater treatment, it is necessary to understand the main factors affecting the performance of these processes. In addition, understanding the impact of various process parameters that govern photocatalytic and ozone degradation efficiency is paramount from the design and the operational points of view when choosing a sustainable technique for the treatment of wastewater. Photocatalysis and ozonation reaction rates are affected by operating conditions such as reactor type, oxygen concentration, ozone concentration, solution pH, catalyst loading, substrate concentration and water matrix. The physical and chemical intrinsic properties of the photocatalyst such as the crystal composition, surface area and crystallite size are also important factors. These are described in detail in a previous study (Mecha 2017) and briefly summarized below.

Reactor design/type

Photocatalytic reactors for wastewater treatment can be categorized based on the following aspects: (1) the state of the catalyst in the reactor (slurry or immobilized catalyst photoreactors), (2) the source of irradiation (natural, e.g. sunlight, or artificial, e.g. UV lamp) and (3) the position of the light source (immersed or external) (Silva 2008). In slurry reactors, fine particles of the solid semiconductor material are dispersed in the liquid phase using either mechanical or magnetic stirrers. An air supply is usually provided to scavenge the electrons and prevent electron–hole charge recombination; aeration also helps in catalyst dispersion. Slurry reactors are often used to study degradation kinetics since they are characterized by large catalytic surface area and low mass transfer limitations compared to immobilized catalyst systems (Choi et al. 2009). Regarding the source of light, artificial radiation sources include arc lamps, incandescent lamps, fluorescent lamps and lasers. Instead of artificial light sources, solar radiation can also be used and it is a more convenient and economical source of light, especially in places with high insolation levels. The source of light can be immersed (common in commercial UV reactors) in the reactor or be external (common in solar radiation reactors) to the reactor. Nevertheless, irrespective of the reactor design selected, the primary focus should be that uniform irradiation of the entire catalyst surface is achieved at the incident light intensity. Photocatalytic ozonation reactors are essentially similar to photocatalytic reactors except that instead of oxygen being the electron scavenger, ozone is used.

Irradiation intensity

The extent of light absorption by the photocatalyst and the rate of electron–hole formation depend on the light intensity (Cassano and Alfano 2000). Although the form of the light does not affect the reaction pathway (Gaya and Abdullah 2008), with increase in light intensity, the catalyst absorbs more photons, thus enhancing the production of electron–hole pairs, $^{\cdot}OH$ radicals and contaminant degradation (Zangeneh et al. 2015).

Oxygen and ozone concentration

Oxygen acts as an electron scavenger/acceptor in photocatalytic reactions to produce super oxide radical ions ($O_2^{\cdot-}$), and an optimal oxygen supply should be used (Kabra et al. 2004). It has been reported that oxygen does not affect the adsorption on the titanium dioxide catalyst surface as the reduction reaction takes place at a different location from where oxidation occurs (Gaya and Abdullah 2008). Nevertheless, the dissolved oxygen improves the separation of photogenerated electrons, thus preventing electron–hole recombination (Yamazaki et al. 2001). The absence of oxygen suppresses photocatalytic activity because of the back-electron transfer from charged species present on photocatalyst surface (Chatterjee and Dasgupta 2005). An increase in the ozone concentration increases the pollutants degradation efficiency due to the high oxidant/contaminant ratio (Beltrán et al. 1997). For photocatalytic ozonation, ozone being a better electron scavenger than oxygen makes the oxidation process to take place faster and more effectively. This is because O_3 is more electrophilic than O_2 towards electrons generated on the titanium dioxide surface (Hernández-Alonso et al. 2002).

Contaminant concentration

The contaminant degradation rate increases with an increase in its initial concentration to a certain level beyond which leads to a decrease of the degradation rate (Umar and Aziz

2013). This is because of reduction in light penetration into the solution as well as complete catalyst coverage leading to fewer photons reaching the catalyst surface (Nam et al. 2002). Photocatalysis occurs primarily on the surface of the catalyst; thus, the quantity of the contaminant adsorbed on the surface of the photocatalyst should be considered (Guettaï and Ait Amar 2005; Gaya and Abdullah 2008).

Photocatalyst concentration

The concentration of titanium dioxide particles affects the light penetration and the surface area for adsorption. As the catalyst concentration increases, the number of ·OH radicals generated increases (Mozia 2010). Beyond a certain catalyst concentration, solution turbidity impedes the penetration of the irradiation and the reaction rate decreases (Bahnemann et al. 2007).

Initial solution pH

The solution pH determines the surface charge of the photocatalyst and agglomeration of the catalyst particles. It also influences the production of ·OH radicals, since a higher concentration of hydroxyl ions (OH^-) results in a higher production of ·OH radicals. However, pH also affects the electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed (Ahmed et al. 2011). Titanium dioxide is amphoteric in nature, and it responds in different ways under acidic and alkaline conditions. Depending on the point of zero charge of the titanium dioxide, the surface of titanium dioxide will either be positively or negatively charged at different pH values (Bahnemann et al. 2007). The effectiveness of ozone is also pH dependent because pH affects ozone decomposition and chemical speciation. At high pH values, ozone reacts almost indiscriminately with all organic and inorganic compounds present in the reacting medium because of the formation of ·OH radicals, which are non-selective. At low pH values, molecular ozone is the dominant oxidation species (Poznyak et al. 2006); the concentration of dissolved ozone decreases with increase in pH (Sotelo et al. 1989).

Water matrix

The presence of natural organic matter in water and wastewater even at low concentrations is detrimental because it exerts a strong influence on reaction mechanisms and competes with the target micropollutants and microbes for the oxidants. The fast reaction of reactive oxygen species released during ozonation and photocatalysis with unsaturated bonds and aromatic rings present in organic matter molecules is demonstrated by a rapid decline of the UV_{254} during ozonation and photocatalysis (Westerhoff et al. 1999).

Mechanism of photocatalytic ozonation

The mechanism consists of photocatalytic oxidation (Langmuir–Hinshelwood kinetics) and oxidation by ozonation (Beltrán et al. 2009; Mena et al. 2012) and is provided in the literature (Mecha et al. 2016a). The production of ·OH radicals significantly improves the oxidation rate of photocatalytic ozonation compared to photocatalytic oxidation. This is due to the production of more ·OH radicals because O_3 is more electrophilic than O_2 towards photogenerated electrons (Hernández-Alonso et al. 2002); thus resulting in high mineralization and faster reaction kinetics (Li et al. 2003, 2005). Figure 2 illustrates the mechanism of photocatalytic ozonation.

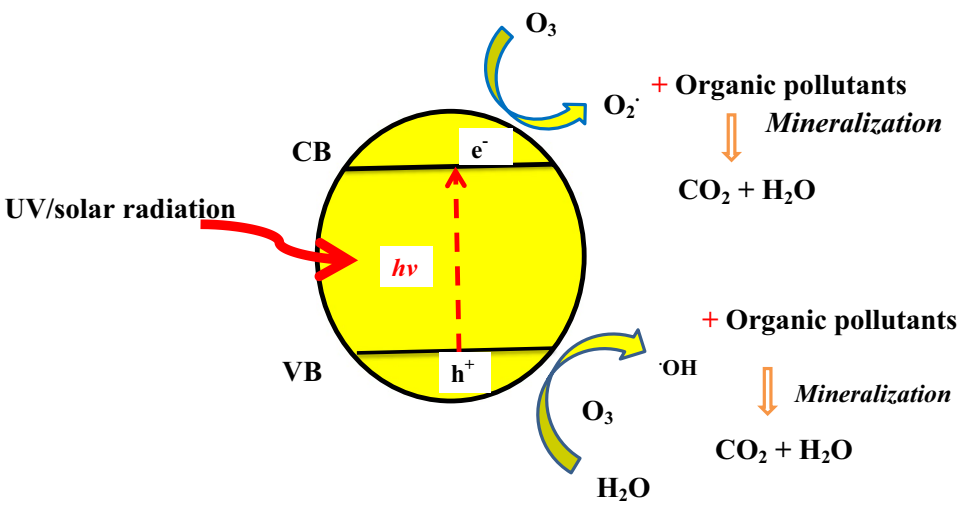

Fig. 2 Mechanism of photocatalytic ozonation. Electron–hole pairs are generated when the photocatalyst is illuminated by UV/solar light. Ozone scavenges the photogenerated charge carriers to form powerful hydroxyl and superoxide radicals on the photocatalyst surface which react with the pollutants and mineralize them to carbon dioxide and water. *CB* conduction band, *VB* valence band, *hv* irradiation energy, h^+ holes, e^- electrons

Application of photocatalytic ozonation in wastewater treatment

Degradation of organic pollutants

Table 2 gives a summary on the use of photolytic and photocatalytic ozonation processes for the degradation of organic contaminants. Most studies have monitored the total organic carbon reduction because the ·OH radicals produced by advanced oxidation processes react non-selectively, thus forming numerous intermediate compounds en route to complete mineralization. Because of this, total organic carbon is a better indicator of the treatment efficiency instead of focusing only on the parent compound (Malato et al. 2016). Mineralization efficiencies of up to 100% have been reported as shown in Table 2. The synergistic effect of photocatalytic ozonation obtained from various studies is also shown for cases where available. The synergy index (SI) was calculated using the equation:

$$\text{Synergy index (SI)} = \frac{R_{\text{Phot+Oz}}}{R_{\text{Phot}} + R_{\text{Oz}}} \quad (5)$$

where R is the percentage contaminant removal and the subscripts represent ozonation (Oz) and photocatalysis (Phot) (Mecha et al. 2016a).

However, very few studies have calculated the synergistic effect of combining two or more advanced oxidation processes. This information could be very useful in the practical implementation of these processes. The few that have calculated the synergy factors have reported values from 1.2 to 5.8 despite treating different contaminants and using different experimental conditions. The mineralization of biorecalcitrant organics also improves the biodegradability of the wastewater as reported (Espejo et al. 2015; Van Aken et al. 2015) and is summarized in Table 3. Biodegradability is evaluated using the ratios biological oxygen demand/chemical oxygen demand, biological oxygen demand/dissolved oxygen demand and biological oxygen demand/total oxygen demand (Alvares et al. 2001). An increase of the ratio indicates that the wastewater sample is becoming

Table 2 Degradation of organic contaminants in various wastewaters using photocatalytic ozonation

Process	Contaminants	Concentration	%Removal	SI	References
UV/TiO_2/O_3	Tetracycline	1–100 mg/L	90% TOC	1.20	Valério et al. (2020)
UVA/TiO_2/O_3	Acetamiprid and atrazine	100 µg/L		1.05–1.27	Silva et al. (2019)
O_3/UVA/magnetite	Pharmaceuticals and personal care products	100 µg/L	81% TOC	NR	Espejo et al. (2015)
O_3/UV/Vis/TiO_2	Amoxicillin and diclofenac	0.1 mM	68% TOC	NR	Moreira et al. (2015)
O_3/UVA/TiO_2	Diclofenac	30–80 mg/L	75% DOC	NR	Aguinaco et al. (2012)
O_3/vis/WO_3	Phenol	200 mg/L	100% TOC	NR	Mano et al. (2011)
TiO_2/UV/O_3	Carbendazim	40 mg/L	80% TOC	1.5–2.2	Rajeswari and Kanmani (2009b)
O_3/UV/TiO_2	2,4-Dichlorophenoxyacetic acid (2,4-D)	0.045 mM	100% TOC	1.2–5.8	Giri et al. (2007)
UV/TiO_2/O_3	Phenol in wastewater	5 mg/L	>99%	4.31	Mecha et al. (2016a)
VUV/O_3	Sodium *n*-butylxanthate	160 mg/L	88% COD	1.53	Fu et al. (2016)
ZnO/O_3	Phenol	100 mg/L	90% phenol	1.24	Dong et al. (2011)
UV/Ag–TiO_2/O_3	Atenolol	20 mg/L	93% TOC	1.36	Ling et al. (2016)
O_3/UV–vis/TiO_2	Oxalic acid	10 mmol/L	100% TOC	NR	Mano et al. (2015)
O_3/TiO_2/UVA	Diuron		80% TOC	1.83	Solís et al. (2016)
UVA/TiO_2/O_3	4-Chloro-2-methylphenoxyacetic acid	5 ppm	60% TOC	NR	Solís et al. (2015)
TiO_2/O_3/UV	Polyvinylpyrrolidone	200 mg/L	90% TOC	1.2	Suave et al. (2014)

NR-value not reported, *SI* synergy index, *TOC* total organic carbon, *DOC* dissolved organic carbon, *COD* chemical oxygen demand

Table 3 Biodegradability of different types/sources of wastewater treated using advanced oxidation processes

Process	Wastewater type	Performance	References
Fenton and O_3	Tannery wastewater	Biodegradability index increased to 0.34	Sivagami et al. (2018)
O_3/UVA/Fe(III)	Synthetic secondary effluent	Biodegradability increased by 75–100%	Espejo et al. (2015)
Ozonation	Primary wastewater	Biodegradability increased by 140%	Mecha et al. (2016c)
Ozonation	2,4-Dichlorophenol-containing wastewater	Biodegradable fraction increased and the refractory COD decreased	Van Aken et al. (2015)

increasingly easier to treat by biological methods and thus the non-biodegradable compounds have been degraded to more biodegradable forms.

Disinfection of wastewater

Table 4 gives a summary on the use of photolytic and photocatalytic ozonation processes for disinfection of water and wastewater targeting a variety of microorganisms. Notably few studies have determined the synergistic effect of combining two or more advanced oxidation processes. However, the reported cases depict considerable synergy.

Evaluation of toxicity of treated wastewater

The degradation of contaminants into less harmful pollutants using highly reactive hydroxyl radicals distinguishes advanced oxidation processes from other wastewater treatment processes such as adsorption and membrane separation which transfer contaminants from the liquid phase (treated water) to the solid phase (sludge) (Sievers 2011). Photocatalytic ozonation is capable of breaking down organic pollutants and transforming them to mineral acids and carbon dioxide. Although destruction of contaminants is generally beneficial, the formation of by-products or transformation products that retain harmful biological activity is a possibility. Therefore, there is need to assess the toxicity evolution during this process to determine the safety of the treated wastewater and also to inform the implementation of suitable technologies (Linden and Mohseni 2014). Evaluation of toxicity is mainly done using biological tests (Žegura et al. 2009). Studies have demonstrated a reduction or even elimination of toxicity from wastewater treated by advanced oxidation processes. For instance, the acute toxicity of phenol and the intermediate compounds was reduced significantly after treatment using catalytic ozonation (Farzadkia et al. 2014); this was because of the degradation of phenol to aliphatic and low chain carboxylic acid products. Also, there were no compounds with oestrogenic effects observed after photocatalytic ozonation of wastewater (Moreira et al. 2016). The reduction of toxicity is attributed to the production of final oxidation products that are more hydrophilic, thus reducing their ability to penetrate cell membranes and cause damage to the cells (Huber et al. 2003; Escher et al. 2009). The attainment of a higher biodegradability and/or lower toxicity of the intermediate and final products compared with the parent compounds, is desirable benefits of applying photocatalytic ozonation for wastewater treatment. Table 5 shows the findings of toxicity assessment of wastewater treated using advanced oxidation processes including ozonation and photocatalysis.

Energy requirements

The efficiency of advanced oxidation processes mainly depends on factors such as contaminant type and concentration, water matrix and constituents, and reactor configuration and design (Linden and Mohseni 2014). Since these factors may vary widely and are difficult to control, meaningful comparison cannot be done based on them. Therefore, comparisons of advanced oxidation processes can be done based on the energy requirements. The advanced oxidation processes utilize a lot of electrical energy (Esplugas et al. 2002), electricity cost is a major operating cost (Bolton et al. 2001). To enable the estimation of energy consumed by different advanced oxidation processes, the International Union of Pure and Applied Chemistry proposed the use of figures of merit (Bolton et al. 2001; Miklos et al. 2018). Thus, for advanced oxidation processes based on electrical energy consumption, the electrical energy per order (E_{EO}) is used, while for the solar-driven systems, the collector area per order (A_{CO}) is used. The E_{EO} is calculated as follows (Bolton et al. 2001):

$$E_{EO}=\frac{Pt\times 1000}{V\log\left(C_i/C_f\right)} \quad (6)$$

where P is the power input, t is the treatment time, V is the volume of water treated, C_i and C_f are the initial and final concentrations of contaminant, respectively, and the factor 1000 converts g to kg (Cardoso et al. 2016).

Table 4 Disinfection of wastewater using photocatalytic/photolytic ozonation

Process	Contaminants	Concentration	%Removal	SI	References
UV and O_3	Antibiotic-resistant bacteria	10^3 CFU/mL	3–4 log	NR	Sousa et al. (2016)
UV/O_3	Faecal coliforms	10^6 CFU/mL	72%	NR	Bustos et al. (2014)
	Total coliforms	5×10^6 CFU/mL	78%		
UV/O_3	*E. coli* ATCC 25922	7×10^3 CFU/mL	3 log	NR	Magbanua et al. (2006)
UV/TiO_2/O_3	*E. coli, S. enterica*, *V. cholerae*	10^3 CFU/mL	3 log	1.86	Mecha et al. (2017a)
UV/O_3	*P. aeruginosa*	10^5 CFU/mL		3.28	Oh et al. (2007)
UV/O_3	Chlorotetracycline-resistant bacteria	5.7 log	5 log	NR	Lee et al. (2011)
UV/O_3	Aerobic plate count bacteria	5.5 log	99.9%	NR	Diaz et al. (2001)

The initial microbial concentration, disinfection efficiency, synergy index (SI) are shown (NR-value not reported)

Table 5 Toxicity assessments of different types of wastewater treated using various advanced oxidation processes such as ozonation, photolytic and photocatalytic ozonation

Process	Wastewater type	Performance	References
Ozonation	Secondary effluent	Increased breeding rate (up to 74%) of *Daphnia magna*	Petala et al. (2009)
Ozonation/activated carbon	Secondary effluent	Reducing the baseline-toxic equivalent concentrations by 79% and the oestrogenicity below the detection limit	Macova et al. (2010)
Ozonation and activated carbon	Secondary effluent	Biological activity was reduced by 62% (AhR response) and 99% (oestrogenicity)	Reungoat et al. (2010)
Ozonation and activated carbon	Secondary effluent	Reduction of in vitro oestrogenic activity by > 75%.	Stalter et al. (2010)
Ozonation	Secondary effluent	Reduction of genotoxicity and acute invertebrate toxicity	Cao et al. (2009)
UV and UV/H_2O_2	Surface water	No significant genotoxic response was observed after treatment	Martijn and Kruithof (2012)
Ozonation	Secondary effluent	No formation of oestrogenic by-products was observed	Kim et al. (2004)
Ozone/UV	Chlorophenols	Production of non-toxic products for *Daphnia magna* compared to parent compounds	Trapido et al. (1997)
TiO_2/UV-A and TiO_2/UV-A/H_2O_2	Textile effluent	Effective acute toxicity removal was obtained	Arslan-Alaton (2007)
H_2O_2/UV	Surface water	No cytotoxicity of treated water observed after 120 min	Miranda et al. (2016)
TiO_2/UV/O_3	Secondary effluent	Treated wastewater was increasingly becoming less toxic. Cell viability increased from 28.7% (untreated water) to 80% after treatment	Mecha et al. (2017b)
O_3/UVA/Fe(III)	Synthetic secondary effluent	Toxicity decreased by 95% after treatment	Espejo et al. (2015)
O_3/UV/Vis/TiO_2	Urban wastewater	No toxicity in treated water	Moreira et al. (2015)

However, due to the large expenses incurred when using electricity to run advanced oxidation processes, it is imperative to explore the use of less costly options. This has prompted accelerated research efforts on the use of the renewable sources such as natural sunlight. The development of visible light active photocatalysts enables the use of sunlight for photocatalytic processes which are environmental friendly and cost-effective (Tsydenova et al. 2015; Mecha et al. 2017b). Table 6 shows the energy consumption by advanced oxidation processes during wastewater treatment.

Recovery and reuse of photocatalyst

The recovery and reuse of photocatalysts in slurry reactors is a major concern for the large-scale utilization of photocatalytic processes in a sustainable way. This is necessary considering that the treatment of real wastewaters containing different types of contaminants may affect the catalyst activity and hence catalyst life (van Grieken et al. 2009b). Studies conducted in this area have showed that suspended photocatalysts can be recovered using a variety of ways such as filtration or centrifugation and reused multiple times without a significant decrease in performance. For example, Rupa et al. (2007) reported that silver-doped titanium dioxide could be reused at least three times, and Swarnakar et al. (2013) observed insignificant reduction in catalytic performance of titanium dioxide films that were reused five times. This shows that the photocatalysts are robust and stable against a variety of contaminants in wastewater. Hence with proper recovery, regeneration and reuse strategies, they can make photocatalytic ozonation sustainable. A summary of findings from previous studies is provided in Table 7.

Conclusion

The presence of biorecalcitrant organic pollutants in water sources has accelerated exploration of the use of advanced oxidation processes such as ozonation and photocatalysis. In this review, these processes were evaluated and their individual merits and demerits discussed. For instance, photocatalysis is limited by low oxidation rates arising from electron–hole recombination. On the other hand, ozonation suffers low mineralization rates attributed to the production of intermediate compounds that are ozone resistant. Potential ways of overcoming their individual drawbacks were explored. These include development of visible light active titanium dioxide photocatalyst to utilize solar light, thereby reducing energy costs and coupling of ozonation and photocatalysis to enhance the reaction kinetics. There is great potential of the

Table 6 Energy consumption, as electrical energy, by advanced oxidation processes (AOP) for water and wastewater from different sources

Process	Water type	Energy consumption	References
Ozonation	Lake water	For 90% p-chlorobenzoic acid transformation 0.035 kWh/m^3	Katsoyiannis et al. (2011)
UV/H_2O_2	Lake water	For 90% p-chlorobenzoic acid conversion 0.17–0.75 kWh/m^3	
Ozonation	Wastewater	For 90% p-chlorobenzoic acid transformation 0.2 kWh/m^3	Katsoyiannis et al. (2011)
UV/H_2O_2	Surface water	For a 90% degradation of atrazine 1.87 kWh/m^3 for medium-pressure lamps, 0.73 kWh/m^3 for low-pressure lamps, and 2.17 kWh/m^3 for dielectrical barrier discharge lamps	Lekkerkerker-Teunissen et al. (2013)
Ozonation Ozonation/UV	Secondary effluent	For a 90% removal of pharmaceuticals and personal care products 0.09 kWh/m^3 (O_3) and 1.09 kWh/m^3 (O_3/UV)	Kim and Tanaka (2011)
Ozonation, catalytic ozonation, photocatalysis	Municipal wastewater	For 90% pharmaceutical compounds removal to be: ozonation (0.23), O_3/H_2O_2 (0.22), catalytic ozonation (0.22), UV-C TiO_2 photocatalysis (0.87) and solar TiO_2 photocatalysis (0.20) kWh/m^3	Álvarez et al. (2011)
Various AOPs	Distillery effluent	Chemical oxygen demand and colour removal: O_3/UV (1.19); O_3/UV/H_2O_2 (1.04); O_3/UV/Fe^{2+} (0.76); O_3 (0.64); O_3/Fe^{2+} (0.64); UV/H_2O_2 (0.27); UV/H_2O_2/Fe^{2+} (0.097); O_3/UV/Fe^{2+}/H_2O_2 (0.01) kWh/m^3	Asaithambi et al. (2015)
O_3/UV/TiO_2	Phenol solution	28.1 kWh/m^3	Suzuki et al. (2015)
O_3/UV/TiO_2	Secondary effluent	7–22 kWh/m^3	Mecha et al. (2017b)

Table 7 Photocatalysts recovery and multiple reuses after treatment of various wastewaters using photocatalysis and photocatalytic ozonation

Application/water matrix	Photocatalyst	Performance and reuse	References
Solar photocatalytic ozonation	O_3/Light/CF-TiO_2	After several cycles of use, no loss of activity observed	Rodríguez et al. (2019)
Catalytic ozonation of oxalic acid	$SrTiO_3$	Photocatalyst stable and efficient after four cycles of reuse	Wu et al. (2011)
Catalytic ozonation (surface water)	TiO_2	Photocatalyst stable and efficient after four cycles of reuse	Gracia et al. (2000)
Methyl orange solution	Ag/TiO_2 thin films	Photocatalyst stable and efficient after six cycles of reuse	Arabatzis et al. (2003)
Disinfection of *E. coli* suspension	Fe–Cd/TiO_2	Photocatalyst performance (> 99%) after four uses	Feilizadeh et al. (2015)
Disinfection of *E. coli* suspensions	Immobilized TiO_2	Photocatalyst stable and efficient after three cycles of reuse	van Grieken et al. (2009b)
Dyes and inactivation of bacteria	Ag/AgBr/TiO_2	No loss of activity after eight cycles of reuse	Hu et al. (2006)
Reactive Blue 220 (RB-220) dye	Ag–TiO_2 core–shell nanoparticles	Minimal decrease in activity after three cycles of reuse under UV light irradiation and solar light	Khanna and Shetty (2014)
Synthetic municipal wastewater	TiO_2 P-25	Photocatalyst activity after 5 reuse experiments almost constant	Kositzi et al. (2004)
Dyes and inactivation of bacteria	Ag/TiO_2 nanomembrane	No decrease in activity after 5 cycles of reuse	Liu et al. (2012)
Reactive Yellow-17	Ag–TiO_2	No decline in activity after three cycles of reuse	Rupa et al. (2007)
Oxalic acid	Fe-TiO_2	No decrease in activity throughout the 5 repeated runs	Teoh et al. (2007)
Secondary wastewater	TiO_2 doped with Ag, Cu, Fe with ozone	No significant decline in performance after three cycles	Mecha et al. (2017b)

photocatalytic ozonation process. In particular, solar-enhanced photocatalytic ozonation holds promise as an environmentally friendly technique for wastewater remediation. Additional benefits of using photocatalytic ozonation including (1) the use of a single reactor instead of two (reduced reactor costs and hence capital costs), (2) synergy between the two processes when used simultaneous as opposed to when they are employed separately and (3) potential reduction in reactor residence times are attractive benefits. The assessment of the recovery and reuse of photocatalysts, energy requirements and toxicity assessment of the treated wastewater are necessary as demonstrated in this study so as to make the process more sustainable. Based on the findings of the review, the following recommendations are proposed:

a. Further studies on solar-powered photocatalytic processes to reduce dependence on electricity and decrease process costs.
b. Most studies have been performed on laboratory scale. The information obtained in laboratory scale studies is not sufficient for large-scale operation. There is need to perform pilot scale studies on photocatalytic ozonation of wastewater to generate sufficient data especially on mass transfer limitation of reaction kinetics and mixing so as to guide the upscaling to large-scale treatment systems.
c. The possibility of recovery and reuse of photocatalysts is very crucial as a way of reducing costs and also preventing secondary pollution of treated wastewater by photocatalyst particles. There is need to develop appropriate techniques suitable especially in large-scale applications.
d. Studies demonstrated that synergy indeed exists between photocatalysis and ozonation when employed together. Based on the fact that process conditions play a significant role in this synergism, there is need to develop mathematical models that can be employed in the design of systems that maximize on synergy and performance effectiveness to make these processes economically competitive to the existing conventional processes.
e. Given the impressive performance of photocatalytic ozonation in the degradation of recalcitrant organics in wastewater, it is necessary to explore the use of this process in related applications such as pretreatment of substrates for bioenergy production and treatment of biosolids to reduce soil pollution among others.

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