Advanced Technologies in Water Treatment

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Synonyms

Advanced oxidation processes; Ozonation; Fenton reaction; Photocatalysis

Definitions

Advanced oxidation processes (AOPs) are chemical treatment techniques used in water and wastewater treatment. To enhance the water treatment efficiency, *ultraviolet (UV), visible (Vis*) or *solar light irradiation* and *ultrasound technology (US*) are frequently used. *UV* and *Vis* irradiation include bands from 100 to 400 nm and from 400 to 800 nm, respectively. *Solar light* at the Earth surface has a wavelength between 300 nm to 1 mm, including *UV, Vis* and *Infrared (IR) light* regions. *US* is a high-frequency sound, which can decompose many organic pollutants. To accelerate the AOPs, *catalysts* are widely used. These compounds increase the rate of the reaction without being used up.

Introduction: Water Treatment

Conventional water treatment and sustainability

UN Sustainable development goal 6: Clean water and sanitation requires greatly improved treatment for the estimated 80% of wastewater that is released untreated, where this climbs to 95% in some developing countries (WWAP 2017). Such wastewater varies in both its source, such as from industry, urban and agriculture, and components, which may vary over time and location. There are also various emerging pollutants in water, such as antibiotics, pesticides and microplastics (Zhang et al. 2020). A key aspect to meet the sustainable development goal is for wastewater to be viewed more as a resource than as a burden to facilitate its role within a circular economy. Such an approach may become more economically sustainable if resources can also be recovered from wastewater, for instance, the recovery of valuable nutrients (Collinson and García 2013). Wastewater treatment will also become more sustainable through the use of less environmentally harmful chemicals or processes, for instance applying catalysts to reduce the use of chemicals and energy, while also finding synergies with other technologies such as renewable energy (Anastas and Zimmerman 2018; Prasannamedha and Kumar 2020).

Current challenges

Chlorine is widely used for the disinfection of drinking water and the residual chlorine in water is important to avoid recontamination during transport and storage. The continued development of water treatment is important to avoid the possible disinfection by-products arising from disinfection using chlorine (Miklos et al. 2018). Furthermore, the efficient removal of heavy metals, persistent organic pollutants (POPs) and emerging pollutants from water provides a range of current challenges in water treatment. For instance, POPs include antibiotics, dyes and polyaromatic hydrocarbons (PAHs) which arise from a variety of sources and may not be effectively removed from water using chlorine so either an advanced oxidation process (AOP) is required or adsorption as will be discussed below. Similarly, the development of more sustainable flocculants for water treatment is also an active area of research, which aims to avoid the use of aluminium, iron or synthetic polymers as flocculants (Othmani et al. 2020). Considering the overall sustainability of water treatment is also important (Prasannamedha and Kumar 2020), so for instance magnetically recoverable ferrates(VI) compounds were reviewed as sustainable compounds for groundwater remediation, such as removing anions or oxidising pollutants, and this was especially true when they were synthesised using green chemistry processes (Rai et al. 2018).

Advanced Oxidation Processes

Advanced Oxidation Processes (AOPs) are the large group of chemical oxidation reactions, occurring with the generation of $^{\bullet}OH$ or $SO_4^{-\bullet}$ to degrade pollutants present within water. Techniques used for the generation of oxidative radicals are widely different and AOPs can be classified into O_3-based, UV-based, Fenton-based, photocatalytic, physical and electrochemical (Table 1) (Divyapriya et al. 2016; Miklos et al. 2018). It is notable that each process employs various types of technologies and so the given classification should not be considered as strict.

Table 1. The classification of the frequently used AOPs

Advanced oxidation processes					
O_3-based	Fenton-based	UV-based	Photocatalytic	Physical	Electrochemical
O_3 O_3/H_2O_2 O_3/Catalyst O_3/UV	Fe^{2+}/H_2O_2 Fe^{3+}/H_2O_2/UV $Fe^{2+}/S_2O_8^{2-}$/UV Fe^{2+}/H_2O_2/US	UV/H_2O_2 UV/$S_2O_8^{2-}$ UV/Cl_2	UV/Catalyst UV/Catalyst/H_2O_2 UV/Catalyst/ $S_2O_8^{2-}$	Electron beam US Plasma Microwave	Anodic oxidation Fe^{3+}/H_2O_2(e-) UV/Catalyst/(e-) UV/Fe^{3+}/H_2O_2(e-) US/Fe^{3+}/H_2O_2(e-)

Generally, AOPs consist of two stages, formation of oxidative radicals followed by the oxidation of the targeted pollutants. Various process parameters influence the radical formation mechanism and it can be affected by the presence of radical scavenging species in water, such as carbonate and bicarbonate ions (Zhou and Smith 2001). The current applications, proposed mechanisms and principles of O_3-based, Fenton-based and photocatalytic processes are briefly discussed in the following sections.

O_3-based AOPs

O_3 is a highly reactive gas with a low solubility in water. Generally, high-voltage corona discharge is used to generate O_3 from air or purified oxygen. The decomposition of O_3 in water is a radical chain process, where depletion of molecular O_3 is catalyzed by the decomposition intermediates. O_3 molecules are very selective and can oxidize organic compounds with high electronic density sites, while $^{\bullet}OH$ can react with huge number of organic compounds through the electron transfer, H-atom transfer, or insertion mechanisms. O_3 decomposition contains initiation, propagation, and termination steps. The decomposition can be initiated by the presence of OH^-, H_2O_2, UV, some metal ions (for example iron or manganese), natural organic matter and heterogeneous photocatalysts, while the presence of carbonate and bicarbonate ions can inhibit the process (Zhou and Smith 2001).

Ozonation has a wide application in water and wastewater treatment. According to the report of Global Market Insights Inc., the global ozone market is valued at USD 350 million in 2019 and is anticipated to exceed USD 450 million by 2026 with a compound annual growth rate (CAGR) of 3.6%. The industrialization and urbanization coupled with strengthened water purification regulations in the developing countries are driving the market of O_3 generating installments. Ozonation is successfully utilized for the removal of suspended solids, flotations, total organic carbon (TOC) and chemical oxygen demand (COD) as well as for the oxidation of pollutants. However, by-products formation might cause problems during water treatment (Miklos et al. 2018). Another application of ozonation is as an alternative disinfection method, removing pathogenic microorganisms (Wang and Chen 2020). A short review on applications of the ozonation process is shown in Table 2.

Table 2. Sample applications of ozonation in water and wastewater treatment.

Processes	Application	Resulting effects	References
O_3	Sustainable water treatment to reduce the use of antibiotics in animal husbandry	Lower microbial level in the water with a reduced pharmaceutical cost.	(Remondino and Valdenassi 2018)
O_3-H_2O_2	Taste and odor control	Effective reduction in taste and odor	(Beniwal et al. 2018)
O_3-UV	Disinfection	Combination of O_3–UV enhanced inactivation efficiency of the *Bacillus subtilis* spores	(Jung et al. 2008)
O_3-Activated carbon catalyst	COD and TOC removal from textile wastewater	The COD and TOC decreased from 2120 mg/L and 1052 mg/L to 1283 and 695 mg/L, respectively.	(Bilińska et al. 2020)

To improve the efficiency and reduce disinfection by-products from applying O_3 in water treatment various modifications of the process have been developed (Miklos et al. 2018). According to the Sustainable Development Goal 6, by 2030 United Nations aims to achieve equitable access to clean drinking water for everyone (UNICEF and WHO 2019). Unfortunately, water pollution is a global problem and Kazakhstan is not an exception. Most of agriculture and heavy industry discharge untreated wastewater every day. Only 7% of wastewater is fully treated before being returned into aquatic environment. Unsurprisingly, 50-70% of surface water of Kazakhstan rated "polluted" or "highly polluted". Moreover, it is estimated that 1.5% of total mortality in Kazakhstan is caused by poor water quality, which is higher than in the developed countries (for example, UK 0.1%, U.S. 0.4%) (Karatayev et al. 2017). The high death rates are also linked with the inappropriate sanitary facilities and spread of infections like helminths and pathogenic intestinal protozoa (Bekturganov et al. 2016). In this regard, Kazakh government is taking actions towards the sustainable development and accepted the "Ak Bulak" program to increase efficiency of wastewater treatment plants and to provide a clean drinking water to population. Kazakhstan has 87 cities, 30 villages and 6724 rural settlements (Andraka et al. 2015). As the rural areas do not have proper water supply, the use of decentralized water treatment (DWT) systems can resolve the issue. Usually, DWT systems are membrane-based, but recent advancements in ozonation technologies can make the use of the decentralized solar-driven ozonation systems economically attractive for water treatment (Dorevitch et al. 2020).

Ozonation at the elevated pH

Ozonation of contaminants can be conducted by direct reaction of O_3 molecule or indirect oxidation with $^{\bullet}OH$, which is a product of O_3 decomposition (Wang and Chen 2020). For water treatment purposes, using ozonation is more effective at the elevated pH. Due to the selective nature of direct ozonation, the generation of $^{\bullet}OH$ is influenced by the presence of OH^- ions (Miklos et al. 2018). The mechanism of $^{\bullet}OH$ radical generation in the presence of OH^- and O_3 is shown in Equations 1-4 (Wang and Chen 2020).

$$O_3 + OH^- \rightarrow HO_4^- \quad (1)$$

$$HO_4^- \leftrightarrow HO_2^{\bullet} + O_2^{-\bullet} \quad (2)$$

$$O_3 + O_2^{-\bullet} \rightarrow O_3^{-\bullet} + O_2 \quad (3)$$

$$O_3^{-\bullet} + H_2O \rightarrow {}^{\bullet}OH + OH^- \quad (4)$$

Ozonation of water with a pH > 8 might be an efficient process if the carbonate and bicarbonate ions are not present (Miklos et al. 2018).

Peroxone process
Initially in the peroxone process, the peroxide anion is formed by the dissociation of hydrogen peroxide in water (Equation 5). The peroxide anion is a very efficient initiator of O_3 decomposition which then leads to the formation of $^{\bullet}OH$ (Equation 6) (Zhou and Smith 2001).

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \quad (5)$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^- + O_2 \quad (6)$$

The rate constant between OH^- and O_3 is 7.0×10^1 $M^{-1} \cdot s^{-1}$ versus 5.5×10^6 $M^{-1} \cdot s^{-1}$ between the peroxide ion and O_3. It means that peroxide ions will be very effective O_3 decomposition initiators even at low concentrations. Also, H_2O_2 dissociation is accelerated by the elevated pH. Consequently, the O_3 decomposition rate increases with an increase in pH (Zhou and Smith 2001).

Catalytic ozonation
Catalytic ozonation is divided into homogeneous and heterogeneous catalytic ozonation, based on the solubility of the catalyst (von Sonntag and von Gunten 2015). Generally heterogeneous catalysts offer a more sustainable option due to their potential recyclability often coupled with both reduced energy and chemical usage.
Transition metal ions like Fe^{3+}, Co^{2+}, Cu^{2+}, Mn^{2+} and Zn^{2+} are the most common homogenous catalysts for catalytic ozonation. The mechanism of homogeneous catalytic ozonation is described by two pathways. In the first pathway, O_3 decomposition is accelerated by the presence of metal ions, enhancing $^{\bullet}OH$ generation. In the second pathway, molecular O_3 oxidizes the products of complexation reaction between metals and organic species (Wang and Chen 2020).
A wide range of heterogeneous catalysts for catalytic ozonation has been developed so far. They include metal oxides (such as manganese, iron, and aluminum oxides), carbon-based materials (activated carbon, carbon nanotube, graphene and other), and immobilized catalysts (metals and metal oxides on supports). As heterogeneous catalysis of ozonation takes place in three phases, it is difficult to study the detailed mechanism of the reactions involved. But the following situations are possible in the catalytic system: O_3 is adsorbed onto the catalyst and decomposes, then, generated $^{\bullet}OH$ oxidize the contaminants; molecular O_3 attacks the organics adsorbed on the catalyst; or both O_3 and the organic compounds are adsorbed onto the catalyst and react (Wang and Chen 2020).
Application of catalytic ozonation can increase the removal rate of pollutants and decrease the O_3 usage in water treatment. The efficiency of the process can be enhanced by controlling the pH, dosage of O_3 and catalyst. In addition, the nature and stability, recyclability of the catalyst, the presence of scavenging inorganic ions and the influence of natural organic matter on the ozonation should also be accounted for (Nawrocki and Kasprzyk-Hordern 2010). Furthermore, the heterogeneous catalyst can enable the adsorption of both the O_3 and pollutant on the catalyst surface to facilitate their surface reaction (Bilińska et al. 2020). It is essential with catalysts to investigate any potential leaching of metal ions which will influence the efficiency, mechanism and recyclability as well as potentially creating polluting ions (De Luca et al. 2014).

Ozonation with UV irradiation
UV irradiation (λ<300 nm) is a key initiator of O_3 decomposition. UV decomposes O_3 into oxygen gas and atomic oxygen (Equation 7). Then, the high-energy O rapidly reacts with water resulting in thermally excited hydrogen peroxide (Equation 8), which then decomposes into $^{\bullet}OH$ (Equation 9) (Von Sonntag 2008).

$$O_3 + hv \rightarrow O + O_2 \quad (7)$$

$$O + H_2O \rightarrow H_2O_2 \quad (8)$$

$$H_2O_2 \rightarrow 2{}^{\bullet}OH \quad (9)$$

The O_3/ UV process is attractive because the absorption of O_3 is a lot stronger than H_2O_2 absorption. However, the small amount of H_2O_2 is converted into $^{\bullet}OH$ resulted in the low $^{\bullet}OH$ quantum yield of 0.1 (Von Sonntag 2008). Presently, the UV lamps and O_3 generators, used in the O_3/ UV process, have high energy consumption, which makes industrial application of this process impractical (Miklos et al. 2018). The application of solar UV with O_3 for water treatment to improve the sustainability of the process has been discussed (Beltrán and Rey 2017).

Fenton-based AOPs

Fenton-based processes, such as Fenton and photo-Fenton, are characterized by in situ formation of the reactive species, which then oxidize the organic contaminants in water, resulting in their complete mineralization to produce CO_2 and H_2O. Commonly used homogeneous Fenton reaction involves generation of highly reactive $^{\bullet}OH$ radicals by the decomposition of H_2O_2 in the presence of a soluble catalyst (Fe^{2+}) at acidic pH near 3 (Equation 10) (Brillas and Garcia-Segura 2020).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (10)$$

Representative applications of the Fenton-based processes are shown in Table 3. The mechanisms of some of these processes will be discussed in the next sections.

Table 3. Representative applications of the Fenton-based processes in water and wastewater treatment.

Processes	Application	Resulting effects	References
Homogeneous Fenton (Fe^{2+}/H_2O_2)	Phenol removal	Phenol removal rate of 96% was achieved after 30 min.	(Zhou et al. 2012)
Heterogeneous Fenton (Fe-S/H_2O_2)	Pharmaceutical removal	84.62% of paracetamol was degraded after 40 min of oxidation.	(Van et al. 2020)
Homogeneous Fenton-like (Fe^{3+}/H_2O_2)	Treatment of olive-oil mill wastewater	92.6% of COD and 99.8% of total phenols were removed after 3 h.	(Nieto et al. 2011)
Heterogeneous Fenton-like (polymer-supported, nanosized, and hydrated Fe(III) oxide/H_2O_2)	Degradation of Cu(II) complexes for metal removal from Cu(II)-citrate wastewater	After 6 h of treatment, Cu and TOC removal efficiencies were 81.6% and 75.6%, respectively.	(Liu et al. 2020)
Homogeneous photo-Fenton Fe^{2+}/H_2O_2/UV	Dye removal	100% of color and 99% of COD removal were achieved.	(GilPalvas et al. 2015)
Heterogeneous photo-Fenton 4%Fe-TiO_2/H_2O_2/UV	4-tert-butylphenol removal	93% and 86% removal of 4-tert-butylphenol and TOC after 60 min of treatment.	(Makhatova et al. 2019)
Homogeneous photo-Fenton-like (Fe^{3+}/EDTA/H_2O_2/UV)	Antibiotic removal	77.3% of sulfamethoxazole degradation was achieved after 75 min of treatment.	(De Luca et al. 2014)
Heterogeneous photo-Fenton-like (TiO_2-Fe_3O_4 /H_2O_2/UV)	Antibiotic removal.	85.2% removal of amoxicillin trihydrate was	(Li et al. 2019)

		achieved after four reaction cycles.	

Table 3 illustrates that Fenton-based processes are mainly utilized in the treatment of toxic compounds such as pharmaceuticals, pesticides, phenols, dyes, and metals, which can be present in the aquatic environment.

One example of inefficient water treatment is the salinization and river pollution problem of the Ili River in Kazakhstan. The Ili River enters the Balkhash Lake, which is a terminal lake with an area of 17000-22000 km^2. Currently, the river is characterized with high concentrations of nitrates, pesticides, heavy metals (Cu, Zn and Cd) and carcinogens, which keep increasing the salinity of the Balkhash Lake. The contaminants in the water originate from anthropogenic factors. The water resources of Ili River are being excessively utilized by Kazakh and Chinese industries and water consumption is highly likely to increase further (Aladin et al. 2013). As most of conventional water treatment plants are based on biological process, they are not designed to remove recalcitrant compounds detected in wastewaters today (Zhou and Smith 2001). The industrial application of Fenton-based processes will increase the quality of such water resources as well as lead developing countries such as Kazakhstan to sustainable management of their water resources.

Fenton and Fenton-like processes

The homogeneous Fenton process involves production of $^{\bullet}OH$ radicals using Fe^{2+} as a catalyst (Equation 11), while Fenton-like processes regenerate the catalytic Fe^{2+} ions through the reaction of Fe^{3+} with H_2O_2 (Equations 12).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (11)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad (12)$$

Fe(II) and Fe(III) compounds are soluble only at acidic pH, which limits the applications of the homogeneous Fenton processes. Consequently, as an increase in pH stops the process with iron precipitation producing sludge (Clarizia et al. 2017), which is problematic as the pH of typical water effluents ranges from 6.5 to 8.5. Consequently, full-scale implementation of Fenton's processes requires the addition of acidification, neutralization, and sludge removal steps to the water treatment process. These steps increase the operational costs and limit the application of homogeneous Fenton-based processes in water and wastewater treatment (Brillas and Garcia-Segura 2020). The use of chelating agents or heterogeneous Fenton process can resolve the issue with pH limitation of Fenton's reaction (De Luca et al. 2014) and avoid the formation of iron containing sludge waste. Fe^{2+} ions and $^{\bullet}OH$ radicals are used in homogeneous Fenton process, while Fenton-like processes may involve using different metal ions (Fe^{3+}, Mn^{2+}, Cu^{2+}, Mo^{4+}, W^{4+}) as a catalyst or co-catalyst and sulfate radicals as an oxidant (Brillas and Garcia-Segura 2020).

In the case of heterogeneous catalysis, reaction occurs on the surface of the solid catalyst at almost neutral pH. The number of solid catalysts including compounds of iron (natural iron deposits, iron oxides like Fe_2O_3 and Fe_3O_4, immobilized iron), iron with other metals (iron compounds deposited or immobilized onto inert support, natural clay and zeolites, iron (nano)composite materials with Al, Cu, Zr, Pd and other metals) and non-ferrous metals (immobilized Cu, Au and Ag) have been studied so far (Nieto et al. 2011; Brillas and Garcia-Segura 2020; Van et al. 2020). Among them iron-based catalysts have proven greater stability and the application of nanostructured materials could enhance the catalytic efficiency by expanding the active surface area. Although there is research conducted on non-ferrous materials in heterogeneous Fenton-like processes, they are limited by the toxicity of Cu^{2+} ions and high cost of precious metals such as Au and Ag (Brillas and Garcia-Segura 2020).

Photo-Fenton and photo-Fenton like processes

Fenton-based processes are very efficient to oxidize recalcitrant compounds and heavily rely on the production of $^{\bullet}OH$ radicals (Equation 10) and the catalyst regeneration (Equations 11 and 12). However, the oxidation products of these compounds may form stable organic complexes with Fe^{3+}

and inhibit the regeneration process of the catalyst (Jain et al. 2018). The application of photo-Fenton processes, where UV irradiation is coupled with Fenton processes, allows the mineralization of iron organic complexes and regeneration of the Fenton catalyst. The use of high-energy UVC light irradiation (λ < 280 nm) enhances the $^{\bullet}OH$ radical production from H_2O_2 (Equation 13), while the Fe^{2+} catalyst can be regenerated by the direct photo-reduction under UVA light (λ = 315–400 nm) (Equation 14) (Brillas and Garcia-Segura 2020).

$$H_2O_2 + hv \rightarrow 2^{\bullet}OH \tag{13}$$

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH^- \tag{14}$$

Much research has focused on the homogeneous photo-Fenton process using Fe^{2+} or homogeneous photo-Fenton like process using Fe^{3+} under UV, visible or solar light (De Luca et al. 2014; GilPalvas et al. 2015; Pliego et al. 2016; Demir-Duz et al. 2019). For instance, De Luca et al. (2014) effectively removed the common antibiotic sulfamethoxazole using photo-Fenton-like process. The pH limitations of the Fenton process were resolved using chelating agents, increasing the solubility of the catalyst at pH 7, while the usage of UV lamps enhanced the $^{\bullet}OH$ generation. Recently, Demir-Duz et al. (2019) demonstrated the possibility of using solar light as the radiation source for the photo-Fenton process and they achieved a removal of 88% of the COD from real petroleum refinery wastewater. Moreover, application of visible LED irradiation (λ = 400-800 nm) in a photo-Fenton process resulted in 95% mineralization of the phenol in wastewater (Pliego et al. 2016). An economic study conducted by Ortega-Méndez et al. (2017) illustrated that the photo-Fenton process was about 50-fold cheaper than photocatalysis with TiO_2. The use of a cheaper irradiation source, such as solar or visible light, might further increase the cost-effectiveness of the homogeneous photo-Fenton process for wastewater treatment. Similarly, the use of LEDs can improve the energy use, lifetime of the irradiation source and consequently the life cycle assessment of such photocatalysis processes in water treatment (Prasannamedha and Kumar 2020).

Heterogeneous photo-Fenton and photo-Fenton like processes occur using different solid catalysts acting in acidic or neutral pH under UV or visible light (An et al. 2013; Makhatova et al. 2019). Similarly, to the heterogeneous Fenton processes, catalysts can be made of only iron on the inert support or iron with other metals. In the recent work of Makhatova et al. (2019), the use of the Fe-doped TiO_2 catalyst prepared by the wet impregnation method resulted in 93% removal of 4-tert-butylphenol from synthetic wastewater. An et al. (2013) used $BiFeO_3$ nanoparticles to treat aqueous solution under visible light irradiation and achieved 91.3% removal of methyl violet dyes after 120 min. The cost of the heterogeneous photo-Fenton and photo-Fenton like processes is determined by the irradiation source and efficiency of the catalyst. The development of highly stable and recyclable (nano)catalysts will increase availability of these processes in water and wastewater treatment. For example, Li et al. (2019) have demonstrated that magnetically recoverable TiO_2-Fe_3O_4 photocatalysts can efficiently degrade the antibiotic amoxicillin. Furthermore, it was demonstrated that the catalyst was easily recovered and reused, achieving an 85.2% removal efficiency after four reaction cycles.

Photocatalytic AOPs

Huge amounts of research have studied wastewater treatment using photocatalysis, where semiconductors are used as the photocatalysts. Semiconductors absorb light energy and convert it into the chemical energy of the electron-hole pairs. The oxidants used for the degradation of organic contaminants are generated by redox reactions catalyzed by the photocatalyst, where the addition of H_2O_2 can intensify such a process. Commonly the most used catalyst is TiO_2, where the P25 nanopowder is available from mass-production (Odling and Robertson 2019). TiO_2-based materials are extensively employed for the degradation of various recalcitrant pollutants under UV irradiation (Li et al. 2019; Makhatova et al. 2019). The application of ZnO-based photocatalysts in water treatment has likewise been widely reported (Divyapriya et al. 2016). TiO_2 and ZnO respectively have a band-gap energy of 3.2 eV and 3.4 eV, consequently they both need high-energy UV irradiation (λ < 380 nm) for excitation. Electron transitions from the valence band to the conduction band occur when the catalyst is exposed to the light (Equation 15). The •OH production is initiated by the reduction of the generated electrons in the conduction band (e_{cb}^{-}) and the oxidation of the formed holes in the valence band (h_{vb}^{+}) in the aquatic media (Equations 16 and 17). Both reactions happen at the surface of the catalyst which helps explains why there is much interest in high surface area nanoscale catalysts. The reaction between e_{cb}^{-} and O_2 results in the formation of the superoxide radical ($O_2^{\bullet-}$), which reduces further generating $HO^{\bullet}$ (Divyapriya et al. 2016).

$$TiO_2 + hv \rightarrow e_{cb}^{-} + h_{vb}^{+} \quad (15)$$

$$h_{vb}^{+} + H_2O \rightarrow HO^{\bullet} + H^{+} \quad (16)$$

$$e_{cb}^{-} + O_2 \rightarrow O_2^{\bullet-} \quad (17)$$

However, only 5 % of the solar light spectrum (λ > 310 nm) falls within the UV region and so it is vital to enhance the performance of the photocatalysts by moving from the UV to visible region. This goal can be achieved by doping TiO_2 with metal ions of Fe, Cu, Co and Ag and non-metal elements such as N, C and S (Divyapriya et al. 2016). This will improve the activity and sustainability of the photocatalytic technologies.

The main advantage of TiO_2 photocatalysis is the low cost and commercial availability of the catalyst. Moreover, TiO_2 has high photochemical stability and is non-toxic. However, the full-scale application of TiO_2-based photocatalysis is still problematic due to issues around the separation of the catalyst and mass transfer limitations (Miklos et al. 2018).

There is a wide range of methods used in fabrication of the (nano)photocatalysts and their immobilization on various supports to facilitate their recovery, such as hydrothermal synthesis (Li et al. 2019), wet impregnation (Makhatova et al. 2019), *in situ* polymerization, dip coating, anodization, electropolymerization and electrodeposition (Odling and Robertson 2019) or sol-gel processes (An et al. 2013). For example, Makhatova et al. (2019) prepared Fe-doped TiO_2 photocatalysts using a wet impregnation method, which required mixing in ultrapure water, drying, grinding and calcination steps. Other work by An et al. (2013) prepared $BiFeO_3$ nanoparticles using a sol-gel process, involving formation of the sol by dissolution of the Bi and Fe compounds in 2-methoxyethanol followed by a complete mixing involving addition of citric acid and ethylene glycol. Then, the sol was dried to form a resin at 100 °C, and calcined at 500 °C. The last step was grinding to obtain a powdered catalyst.

The novel materials used for photocatalyst deposition include, but are not limited to, magnetite, zeolite, graphene and graphene oxide, numerous polymers and glass supports. In particular, the use of magnetic materials, such as magnetite and ferrite type materials, simplify the catalyst separation step. It is noteworthy that the photocatalytic activity of these materials is low, and so they mainly act as support material. A large variation of polymers has been studied as inactive supports for photochemical treatment, but such organic compounds are unlikely to have prolonged good stability in the presence of the highly oxidizing species generated (Odling and Robertson 2019). The presence of graphene materials in heterogeneous composite catalysts helps to achieve a narrower band gap energy (Beltrán and Rey 2017).

Different metals (Ag, Au, Cu, Fe, Mn, Mo, Pd, Pt and W) can be used as a catalyst (Fagan et al. 2016; Odling and Robertson 2019; Brillas and Garcia-Segura 2020). Doping with precious metals like Ag, Au, Pt and Pd have been reported to improve the photocatalytic activity of TiO_2 in the visible light spectrum (λ > 450 nm). However, the introduction of these metals may affect the photocatalytic stability by a weakening in the titanium-bridging complex. Therefore, research into non-metal doping (e.g. C, N and S) of TiO_2 has significantly increased especially because they are cheaper and of a lower environmental impact should any leaching occur during their use. Solar and visible light activated TiO_2 photocatalysis was extensively reviewed in its application to treat many emerging pollutants (pharmaceuticals, detergents and disinfectants, pesticides, endocrine disrupting chemicals and additives), bacteria (*Bacillus, Escherichia, Micrococcus, Salmonella* and *Staphylococcus*) and cyanotoxins (Fagan et al. 2016).

In the last decade, a huge amount of research has focused on different semiconductors, but bismuth-based photocatalysts such as Bi_2O_3, $BiPO_4$, $(BiO)_2CO_3$, Sillén-structured BiOX (X = Cl, Br, I), and pentavalent bismuthates (e.g., $NaBiO_3$) are considered as some of the most promising. Bi-based semiconductors have low cost, are non-toxic and have better reduction abilities under visible and solar light than TiO_2. In environmental remediation, they are used for the photocatalytic oxidation of refractory pollutants in water, as well as H_2 generation by water splitting, NO_x oxidation and CO_2 conversion into valuable organic compounds. Bi-based catalysts were linked with various support materials such as carbon quantum dots, graphitic carbon nitrates, graphene, zeolites, and magnetite. Pharmaceuticals such as tetracycline, ciprofloxacin, carbamazepine, ibuprofen, diclofenac and industrial pollutants such as dyes, phenols, bisphenol A, parabens, and methanol have been effectively removed using Bi-based AOPs under visible and solar light irradiation (Siedlecka 2020). However, most research assessed the activity of each photocatalyst by the removal of the target compound and did not detect or identify transformation products. Furthermore, the vast majority studied a single pollutant in a water solution and the impact of other organic and inorganic pollutants have not been investigated. Moreover, Siedlecka (2020) reviewed recent research concerning the elimination mechanism for organic pollutants by bismuth photocatalysts. Namely where a so-called Z-scheme enables an improved charge carrier separation along with a reduced recombination for the bismuth photocatalyst to result in either direct degradation of the pollutants or the generation of oxidising species for this purpose.

Adsorbents to remove pollutants

It is important to consider the wider sustainability of applying wastes as adsorbents for pollutants in water treatment. For instance, considering whether the waste has limited reuse options, such as using waste carpet for the removal of heavy metals or anionic nutrients (Collinson and García 2013); plastic wastes (Zhang et al. 2020); fly ash, Bayer residue, ground granular blast furnace slag, coconut shell, ground concrete, masonry, and wood wastes (Grace et al. 2016). Alternatively, some waste absorbents studied in water treatment could be used in other ways such as utilising crop wastes for animal food, for instance peanut shells or rice husks were studied in water treatment (Grace et al. 2016; Burevska et al. 2018) but may alternatively be added to animal food. Similarly, the seasonality of any waste stream should be considered as water treatment is required all year round, whereas some biomass wastes may be seasonal and prone to biodegradation upon storage. For instance, chitin does not have this problem as it is a natural polymer which is commercially derived from seafood wastes. Consequently, chitin is an abundant material that is stable and is easily modified to chitosan. Chitosan, often after further modification, has been widely studied for applications in water treatment including the flocculation of natural organic matter (Loganathan et al. 2020) and the removal of dyes, heavy metals, several persistent organic pollutants and bacteria (Qu and Luo 2020). Similarly, a range of membranes from natural polymers such as alginic acid, cellulose, chitosan, and starch have been reviewed in the water treatment for wastewater and emulsions containing oils, heavy metals, antibiotics, and viruses (Mansoori et al. 2020). A range of agricultural waste materials have been converted to stable activated carbons for instance via pyrolysis techniques applying both conventional heating and microwaves for applications in wastewater treatment (Ukanwa et al. 2019).
The removal of antibiotics is a growing challenge, such as sulfamethoxazole where conventional chlorine treatment may lead to disinfection by products therefore adsorption coupled with catalytic ozonation has been reviewed (Prasannamedha and Kumar 2020). Furthermore, such adsorption processes using wastes will be more sustainable if the adsorbent can subsequently be regenerated as was shown for sludge derived activated carbon when removing the antibiotic ciprofloxacin, where the activated carbon was regenerated with H_2O_2 oxidation (Gupta and Garg 2019).

Future Directions

Naturally in this review it was not possible to cover the huge range of research reported concerning water treatment, however the aim was to include discussion of several recent examples that highlight sustainable aspects. The processes applied in water treatment are ever evolving as new pollutants emerge with differing challenges and so researchers in this area are encouraged to develop new treatment processes with reference to the wider sustainability of the process. For example, to consider carefully any wastes generated and their possible disposal or regeneration options. As a result, catalytic processes will continue to be actively researched because of their lower demands for chemicals and energy, with heterogeneous catalysts being favored due to their ease of recycling. Cost and toxicity are also key factors and so it is expected that low cost and low toxicity metals will be favored in the future. More studies are expected using wastes as adsorbents especially where the material produced from the process is either biodegradable, shown to have a low environmental impact or can be easily regenerated. With some reported water treatment processes there is also a need to further study the treatment of actual wastewater where the solution may contain several pollutants and display variation in properties such as the pH and ionic strength compared to model studies in a laboratory experiment.

Cross-References

- Cities of the future and water
- Climate Change Impacts on the Water Industry
- Cyanotoxins and microalgae toxins
- Emerging Contaminants for Urbanisation in Waterways
- Eutrofication
- Future Scenarios for Sewage and Drainage Systems
- Local Communities in Water and Sanitation: Practices and Challenges
- Phytoplankton Primary Productivity
- Solar Disinfection
- Water as a requirement for sustainable development and conflict resolution
- Water Availability and Access
- Water quality and Economy

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