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TiO_2 photocatalysts for degradation of micropollutants in water

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Definitions

Micropollutants are water pollutants with the maximum concentrations as high as few micrograms/litre and the minimum concentrations as low as few nanograms/litre of water. Micropollutants typically enter water streams as a result of human activity.

Advanced oxidation processes are water purification technologies which involve generation of strong oxidising species that destroy pollutants.

Photocatalysis is light-activated acceleration of chemical reactions in the presence of a light-absorbing photocatalyst material.

Heterogeneous photocatalysis uses a light-absorbing solid photocatalyst to produce oxidising and reducing species in the presence of light. Heterogeneous photocatalysis is one of the advanced oxidation technologies for water treatment, which uses strong oxidising species to degrade organic pollutants.

Introduction

The demand for clean water is rapidly increasing worldwide, as the global population is growing. The United Nations (UN) recognised access to clean water as a human right and named clean water and sanitation as one of the Sustainable Development Goals (SDG). However, according to the UN report, 2.2 billion people lack access to safely managed drinking water and 844 million people lack even a basic water service (UN, 2018). SDG 6 aims to ensure availability and sustainable management of water and sanitation for all by 2030 (UN, 2018; UN-Water, 2021a). To achieve this goal, the SDG 6 report has identified a number of key targets, such as achieving access to safe and affordable drinking water; improving water quality, wastewater treatment and safe reuse; increasing water-use efficiency; implementing integrated water resources management; and protecting and restoring water-related ecosystems (UN, 2018) (UN-Water, 2021a) (UN-Water, 2021b) (UN-Water, 2021c) (UN-Water, 2021d) (UN-Water, 2021e).

Water is a finite resource, and most of the available natural water resources cannot be safely used for drinking purposes because of the health and safety hazards of the natural and synthetic/anthropogenic pollutants present. Water supply is severely impacted by droughts: an estimated 55 million people globally are affected by droughts every year (WWF, 2019) and the risk of droughts is expected to increase as a result of high temperatures caused by climate change (Huber, 2018). At the same time, pollution of available freshwater resources is worsening as a result

of wastewater generated by agriculture, industrial and domestic usage (UN, 2018). Treating wastewater for reuse is an effective way to reduce or eliminate pollution and to provide clean water (MED-EUWI, 2007; Ritchie, 2018), and therefore to help achieve the SDG 6 target of improving water quality, wastewater treatment and safe reuse (UN-Water, 2021c). Eliminating pollutants from natural waters (rivers, lakes, reservoirs) and from wastewater is a key step towards providing safe drinking water (UN-Water, 2021b). Moreover, treating wastewater before it is discharged into rivers and water streams is essential for achieving the target of protecting water-related natural ecosystems (UN-Water, 2021e). The UN monitors water quality as one of the global indicators of the progress worldwide towards achieving the agenda of SDG6 by 2030 (UN-Water, 2021d).

To achieve this ambitious goal of providing clean water for all, research is needed to monitor the quantity of pollutants present in waters and to develop efficient water treatment technologies to convert wastewater into clean water that is safe to drink. This review will give a brief overview of micropollutants and their occurrence in natural water bodies and in drinking water, and then will describe the working principles of photocatalytic water treatment – one of the advanced technologies for water treatment and removal of pollutants.

Micropollutants

Micropollutants with concentrations ranging from a few micrograms/litres (ppm) to a few nanograms/litres (ppb) of water are found to be present in surface waters, sediments and even in drinking water. The micropollutants originate from three key sources, as shown in Figure 1: agriculture (e.g. herbicides), industrial wastewater (e.g. intermediates of pharmaceutical manufacturing) and domestic wastewater (e.g. pharmaceuticals, hormones and personal care products from households or hospitals) (Schröder et al., 2016). Wastewater from these sources is either sent to wastewater treatment plants (WWTP), or directly discharged into water bodies, such as rivers or lakes. Thus, one of the routes for micropollutants to enter water bodies is by direct discharge of untreated wastewater; for example, agricultural micropollutants such as herbicides leach from soil into groundwater and via run-off to surface water.

Municipal and industrial wastewaters are typically treated at wastewater treatment plants before being discharged into water bodies (Mompelat, Le Bot, & Thomas, 2009). However, some of the micropollutants from the untreated (influent) wastewater are still found to be present in the treated water (effluent of WWTP), although with decreased concentration, and can enter water bodies through discharge of water from WWTPs. Water from natural water bodies is further sent to drinking water treatment plants (DWTPs) to purify it and make it safe to drink. Studies found that some micropollutants present in water cannot be removed by DWPT treatment, and can even be present in tap water or drinking water; for example, pharmaceuticals carbamazepine and clofibric acid have been detected in drinking water because of their resistance to degradation (Rodil et al., 2012).

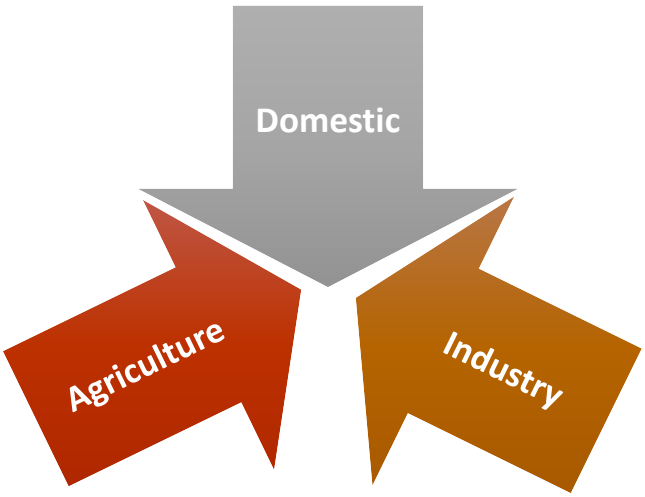


Figure 1 Three key sources of organic water micropollutants

Micropollutants in water are believed to be hazards that may lead to severe long term health problems. Particularly concerning is the presence of antibiotic pollutants in water, which contributes to increasing antimicrobial resistance **(Schaaf N., 2020)**. As an illustration of the ubiquitous presence of a variety of pollutants in water bodies, Figure 2 shows high concentrations of analgesics, antibiotics and other drugs in the surface water and sediments in several regions of Spain (Osorio, Larrañaga, Aceña, Pérez, & Barceló, 2016).

Case studies carried out in various water bodies, such as including lakes and rivers, across the globe confirm that persistent micropollutants are not a regional issue but rather an environmental concern on the global scale, e.g. studies in China (He, Cheng, Kyzas, & Fu, 2016), Spain (Rodil et al., 2012), Mexico (Felix-Cariedo, Duran-Alvarez, & Jimenez-Cisneros, 2013), Brazil (Ide, Osawa, Marcante, Pereira, & de Azevedo, 2017), Malaysia (Al-Odaini, Zakaria, Yaziz, Surif, & Abdulghani, 2013), Switzerland (Buser, Müller, & Theobald, 1998), Sweden (Zorita, Martensson, & Mathiasson, 2009), Finland (Meierjohann, Brozinski, & Kronberg, 2016), South Africa (Archer, Wolfaardt, & Van Wyk, 2017), Turkey (Kucuk et al., 2021), Australia (Scott et al., 2014), Japan and UK (Hanamoto et al., 2018). Some of the key persistent pollutants and their concentrations as reported in studies from various parts of the world are presented in Table 1.

Providing clean drinking water for human use and for the food industry remains a global challenge. Furthermore, water pollution is a global problem because pollutants threaten both human health and wildlife (Schwarzenbach, Egli, Hofstetter, Gunten, & Wehrli, 2010; Tyler, Jobling, & Sumpter, 1998). Research, development and implementation of advanced wastewater treatment technologies is urgently needed to ensure effective removal of pollutants both from drinking water and from water streams.

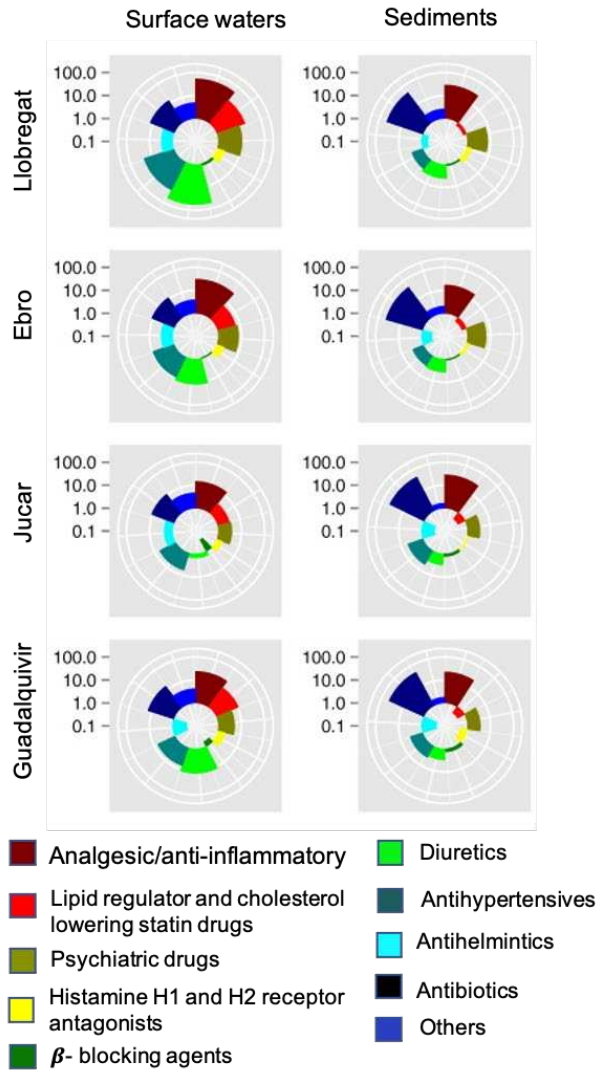
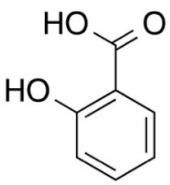
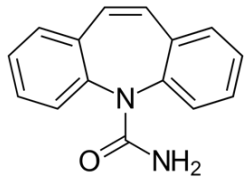
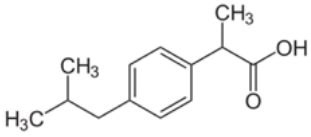
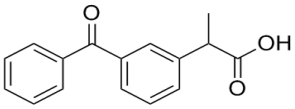
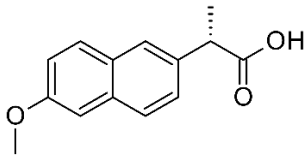
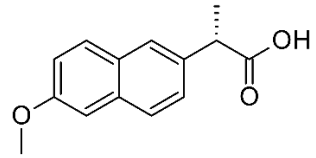
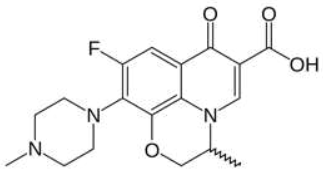
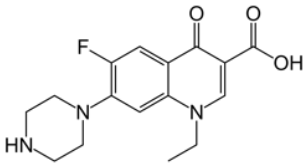
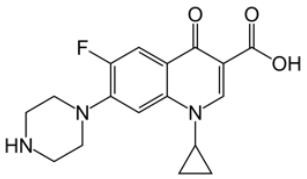


Figure 2 Case study from several regions in Spain showing median concentrations of persistent pollutants in ng/L (Osorio et al., 2016) (reprinted with permission from Elsevier).

Table 1 Some persistent water micropollutants reported in the literature

No.	Pollutant structure	Region	Water matrix	Concentration ng/L	Reference
Personal care					
1	Salicylic acid (used in skincare products) 	Mexico	Groundwater	1-464	(Felix-Cariedo et al., 2013)
		Mexico	Surface water	29-309	(Felix-Cariedo et al., 2013)
		Mexico	Mix water (tanks)	1-106	(Felix-Cariedo et al., 2013)
		Spain	WWTP influent wastewater	2400	(Rodil et al., 2012)

Pharmaceuticals					
2	Carbamazepine (anticonvulsant drug) 	Spain	Surface water	6	(Rodil et al., 2012)
3	Ibuprofen (non-steroidal anti-inflammatory drug) 	Mexico	Surface water	15-45	(Felix-Cariedo et al., 2013)
		Mexico	Mix water (tanks)	1-3	(Felix-Cariedo et al., 2013)
		Spain	WWTP influent wastewater	7500	(Rodil et al., 2012)
		South Africa	Wastewater influent	111.9	(Archer et al., 2017)
4	Ketoprofen (non-steroidal anti-inflammatory drug) 	Mexico	Surface water	21-42	(Felix-Cariedo et al., 2013)
5	Naproxen (non-steroidal anti-inflammatory drug) 	Sweden	Household sewage	20,200	(Zorita et al., 2009)
		Sweden	Effluent water	290	(Zorita et al., 2009)
		Mexico	Surface water	52-186	(Felix-Cariedo et al., 2013)
		Spain	WWTP influent wastewater	750	(Rodil et al., 2012)
		Spain	WWTP effluent water	109	(Rodil et al., 2012)
6	Diclofenac (non-steroidal anti-inflammatory drug)	Mexico	Ground water	1	(Felix-Cariedo et al., 2013)
		Mexico	Surface water	28-32	(Felix-Cariedo et al., 2013)

		Spain	WWTP effluent water	230	(Rodil et al., 2012)
Antibiotics					
7	Ofloxacin 	Sweden	Household sewage	16.7	(Zorita et al., 2009)
		Sweden	WWTP effluent water	10.0	(Zorita et al., 2009)
		China	Pearl river water	7.63	(He et al., 2016)
		China	Pearl river sediment	1.79	(He et al., 2016)
8	Norfloxacin 	Sweden	Household sewage	Below detection limit	(Zorita et al., 2009)
		Sweden	WWTP effluent water	Below detection limit	(Zorita et al., 2009)
		China	Pearl river water	59	(He et al., 2016)
		China	Pearl river sediment	85.25	(He et al., 2016)
9	Ciprofloxacin 	Sweden	Household sewage	3,700	(Zorita et al., 2009)
		Sweden	WWTP effluent water	31.5	(Zorita et al., 2009)

Water treatment technologies

Wastewaters from various sources, such as industrial, municipal, and farm effluents, need customised treatment processes depending on the physicochemical compositions from each individual source (Zaharia, 2017). Conventional water treatment technologies, such as filtration, sedimentation and coagulation/precipitation, are effective for removal of solid particles, microorganisms and chemicals at high concentrations. As the next step, biological treatment techniques are used, where microbes metabolise dissolved complex organic molecules and convert them into smaller molecules – ideally, into the smallest possible end products, such as water, ammonia and carbon dioxide. Additionally, microbes are able to absorb heavy metals. Biological treatments are highly efficient but slow; their disadvantage is the need for disposal of the biological sludge (liquid of semi-solid residue containing high concentrations of waste) after treatment (Gupta, Ali, Saleh, Nayak, & Agarwal, 2012; Rajasulochana & Preethy, 2016; Schröder et al., 2016).

Complete degradation of micropollutants is difficult to achieve by either of these methods; therefore, combinations of several chemical, physical and biological methods are typically used to achieve highly efficient water treatment (Gupta et al., 2012). Moreover, advanced wastewater treatment technologies which combine physical, chemical and biological treatments into one process are being developed. For example, membrane bioreactors, which combine biological degradation of organic matter with membrane filtration, have shown potential for eliminating emerging pollutants. However, high cost and labour intensity of this technology limits its widespread use (Schröder et al., 2016).

To overcome the limitations of the conventional technologies, advanced oxidation processes (AOPs) are being developed (Lee & Park, 2013; Schröder et al., 2016). AOPs involve generation of strong oxidising species (also known as reactive oxygen species), such as $OH^{\bullet}$ radicals, which react with organic molecules and break them down into smaller molecular fragments. Using these methods, non-biodegradable and chemically stable micropollutants can be converted into less complex and less toxic or non-toxic products.

There are several types of AOPs, all of which involve generation of reactive oxygen species: (i) oxidant treatment using ozone of hydrogen peroxide as oxidant species; (ii) Fenton oxidation process – electrochemical oxidation using Fe^{2+} and hydrogen peroxide (Fenton's reagent); (iii) ultrasound or microwave treatment which relies on decomposition of water molecules to form short-lived radicals; and (iv) photochemical methods. Often, a combination of AOPs is used, such as ozone treatment under UV irradiation (UV/O_3) or the photo-Fenton process (Lee & Park, 2013; Malato, Fernández-Ibáñez, Maldonado, Blanco, & Gernjak, 2009).

Photocatalysis is a photochemical AOP, where a photocatalyst material is irradiated by a light source (e.g., sunlight or a UV lamp) to produce free electrons (negative charges) and holes (positive charges). These electrons and holes react with water molecules to produce hydroxyl radicals, which then attack and destroy organic pollutants. The photocatalysis process is highly efficient for removing a wide range of organic pollutants (Kanakaraju, Glass, & Oelgemöller, 2013; Malato et al., 2009). At the same time, the effectiveness of photocatalysis is highly dependent on the nature of the photocatalyst material, and a lot of current research is aimed at optimising photocatalyst materials as well as photocatalytic process conditions.

TiO_2 photocatalyst

Choice of a photocatalyst material

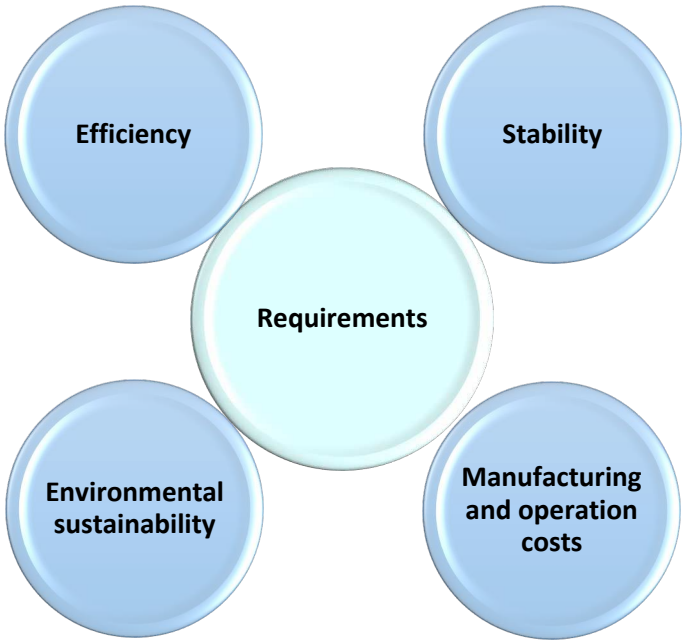


Figure 3 Requirements for a photocatalyst for water treatment.

There are several requirements for an ideal material to be used as a photocatalyst for water treatment (figure 3). First of all, high efficiency of pollutant degradation is required. The efficiency of degradation can be quantified as the difference between the initial and final (at the end of the degradation process) concentration of the pollutant, relative to the initial concentration. The quantum yield of the process can also be measured by determining how much of the pollutant has been destroyed, relative to the intensity of the irradiation (the number of incident photons) (Hoffmann, Martin, Choi, & Bahnemann, 1995; Khataee & Kasiri, 2010; Kudo & Miseki, 2009). Secondly, the photocatalyst should be stable in water; this means that it should not degrade chemically or mechanically in water, and it should retain the efficiency after a large number of reuse cycles. The third important factor is the cost of manufacturing and operation cost of using the photocatalyst for water treatment. Finally, environmental sustainability of the photocatalyst is also an important criterion; it should not increase the toxicity of the treated media nor have hazardous effect on the environment. The four factors are inter-related and help to determine the choice of suitable photocatalysts for water treatment.

Titanium dioxide (TiO_2) is currently the most important and the most widely used photocatalyst material. It came to prominence following the observation of photocatalytic water splitting by Fujishima and Honda (Fujishima & Honda, 1972). Since then, TiO_2 has been extensively researched as a heterogeneous photocatalyst for a wide range of applications such as pollutant degradation, water splitting and hydrogen production, and CO_2 reduction (Fujishima, Zhang, & Tryk, 2008; Kudo & Miseki, 2009). Photocatalytic abilities of TiO_2 lead to promising applications, such as self-sterilising surfaces, self-cleaning and anti-fogging windows (Fujishima et al., 2008). TiO_2 is also commonly used as a white pigment in paints and a UV absorber in sunscreens (Dréno, Alexis, Chuberre, &

Marinovich, 2019), and a photoanode in dye-sensitised solar cells (DSSCs) (Hagfeldt, Boschloo, Sun, Kloo, & Pettersson, 2010).

Figure 4 shows the number of publications referring to "TiO_2 photocatalyst for water treatment" over the past 20 years, based on the results of the ISI Web of Knowledge search. There have been over 2000 publications on the subject, with the numbers rapidly growing each year and exceeding 300 in the year 2020. This large number and rapid growth in publications highlights the increasing interest in TiO_2 as a photocatalyst for water treatment applications.

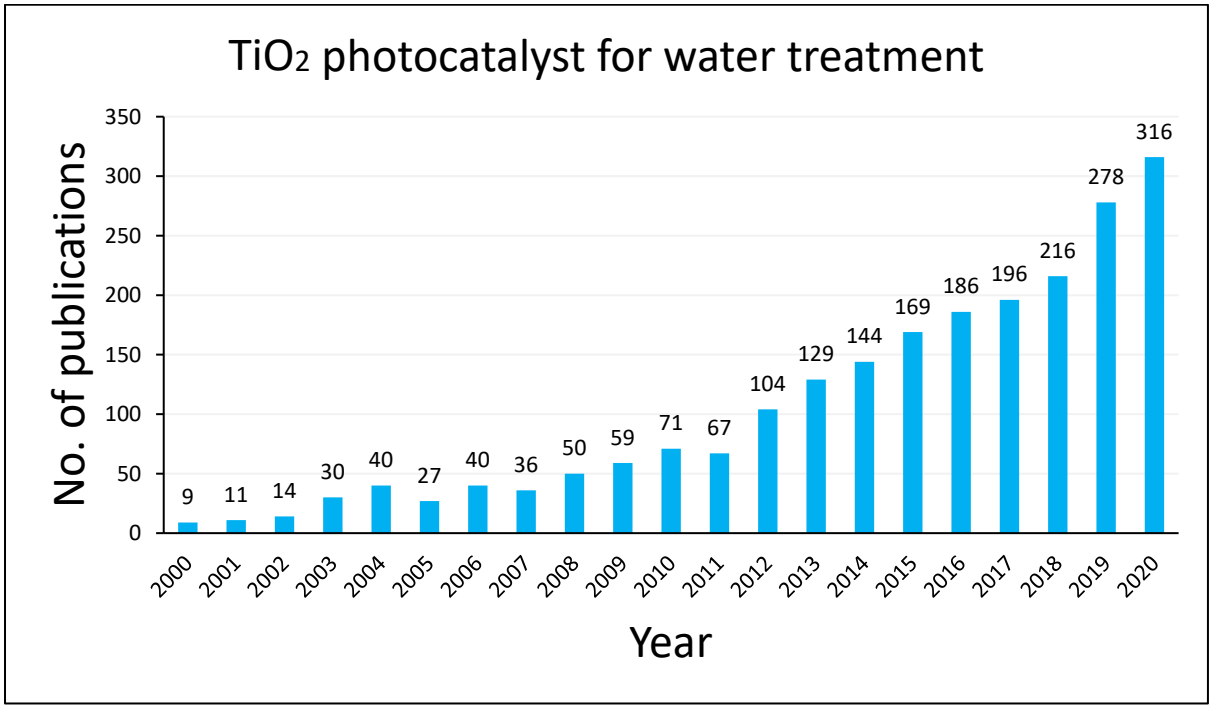
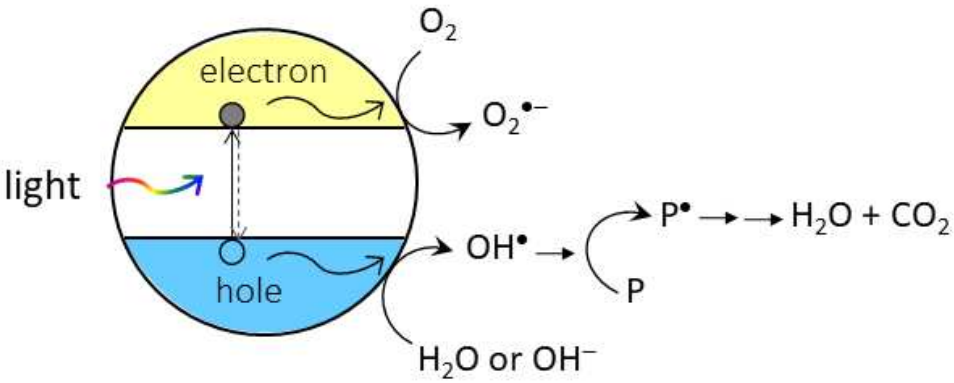


Figure 4 Number of publications referring to "TiO_2 photocatalyst for water treatment" between 2000-2020, based on the ISI Web of Knowledge database search on 15-4-2021.

Mechanism of photocatalysis



As the first step in photocatalysis, a photon of light with the energy higher than the bandgap energy of the photocatalyst material is absorbed by the photocatalyst particle. This is the photoexcitation

process depicted in **Figure 5**, which promotes an electron (negative charge) to the conduction band and leaves behind a hole (positive charge) in the valence band, thus creating an electron-hole pair. This electron-hole pair can recombine (and thus return the photocatalyst particle into its original state before photoexcitation without carrying out any chemical processes) or get separated to form a free electron and a free hole. The electron and the hole then then can diffuse to the surface of the photocatalyst particle and interact with adsorbed water species: the hole can oxidise water molecules and hydroxyl ions to generate strong oxidising species such as the hydroxyl radical $HO^{\bullet}$, while the electron can reduce species such as dissolved oxygen molecules to form the superoxide radical $O_2^{\bullet-}$. The superoxide radical, in its turn, can react with water hydrogen to form another powerful oxidising species, the peroxide radical $HOO^{\bullet}$. The key reactions involved in photocatalytic production of reactive oxygen species are:

1. $TiO_2 + h\nu \rightarrow e^- + h^+$
2. $h^+ + OH^- \rightarrow HO^{\bullet}$ (Alkaline medium)
3. $h^+ + H_2O \rightarrow H^+ + HO^{\bullet}$ (Neutral and acidic medium)
4. $e^- + O_2 \rightarrow O_2^{\bullet-}$
5. $O_2^{\bullet-} + H^+ \rightarrow HOO^{\bullet}$

The powerful oxidizing species formed in these steps can react with organic pollutant molecules present in the water solution at or near the photocatalyst particle surface and break down these molecules into smaller fragments, ultimately into water and carbon dioxide (Kanakaraju et al., 2013; Khataee & Kasiri, 2010; Kudo & Miseki, 2009; Lee & Park, 2013). Overall, the efficiency of a photocatalyst to breakdown pollutants is determined by its ability to generate oxidising species. All the processes depicted in **Figure 5** affect the efficiency of a photocatalyst: light absorption, charge recombination, charge separation and charge diffusion, and oxidation and reduction processes on the photocatalyst surface.

Structure and properties of TiO_2 photocatalyst

TiO_2 is an amphoteric oxide with titanium atoms providing acidic sites and oxygen providing basic sites. It has three polymorphs, rutile, anatase and brookite (Figure 6). The rutile phase is thermodynamically the most stable phase; however, the anatase phase possesses better photocatalytic activity (Luttrell et al., 2014). The brookite phase is the least stable; some reports showed its high activity as a photocatalyst, but it is not generally used as a photocatalyst because of its low stability (Di Paola, Bellardita, & Palmisano, 2013; Kandiel, Robben, Alkaim, & Bahnemann, 2013). Commercial TiO_2 photocatalysts typically consist of a mixture of anatase and rutile phase (Siah, Lintang, Shamsuddin, & Yuliati, 2016). Table 2 compares morphological and electronic properties of some commonly used commercial TiO_2 materials. The most commonly used commercial photocatalyst P25, which contains ~80% anatase and ~20% rutile, typically shows higher photocatalytic efficiencies that either the pure rutile or the pure anatase phase. This high efficiency is attributed to efficient charge separation between the rutile and anatase phases (Hurum, Agrios, Gray, Rajh, & Thurnauer, 2003).

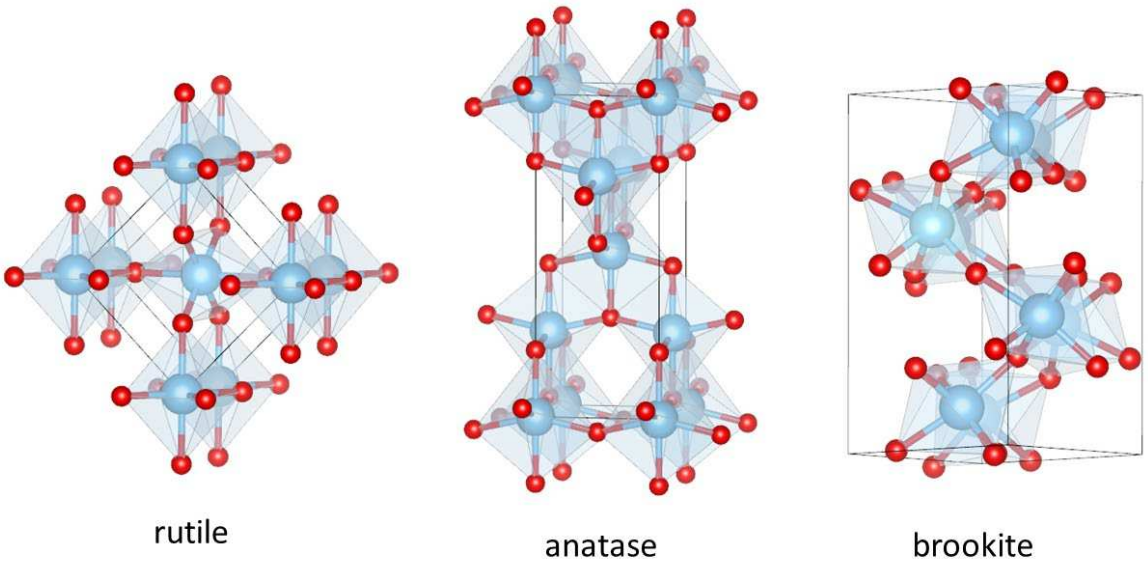


Figure 6 Bulk structure of TiO_2 rutile, anatase and brookite

Table 2 Comparison of properties of commercial TiO_2 mixed phases reported in (Siah et al., 2016)

Photocatalyst	Crystallite size, nm		Anatase : Rutile ratio	Bandgap energy, eV	Specific surface area, m^2/g
	Anatase	Rutile			
P25	17.9	61.8	80:20	3.37	50
P90	10.4	53.4	92:8	3.40	91
UV100	9.2	-	100:1	3.36	290
N100	17.1	-	100:1	3.30	104

TiO_2 can be synthesised in the form of nanoparticles, thin films, nanotubes or nanowires. Techniques for TiO_2 powder nanoparticles synthesis have been extensively explored; some of the most widely used synthesis approaches are sol-gel, hydrothermal and solvothermal methods and chemical vapour deposition (Chen & Mao, 2006). Synthesis methods require high calcination temperatures or energy intensive processing to obtain crystalline TiO_2 suitable for photocatalytic degradation of pollutants. Several research studies explored alternative bio-inspired green synthesis (Anastas & Warner, 1998) routes to synthesize titania at low temperature (Durupthy, Bill, & Aldinger, 2007).

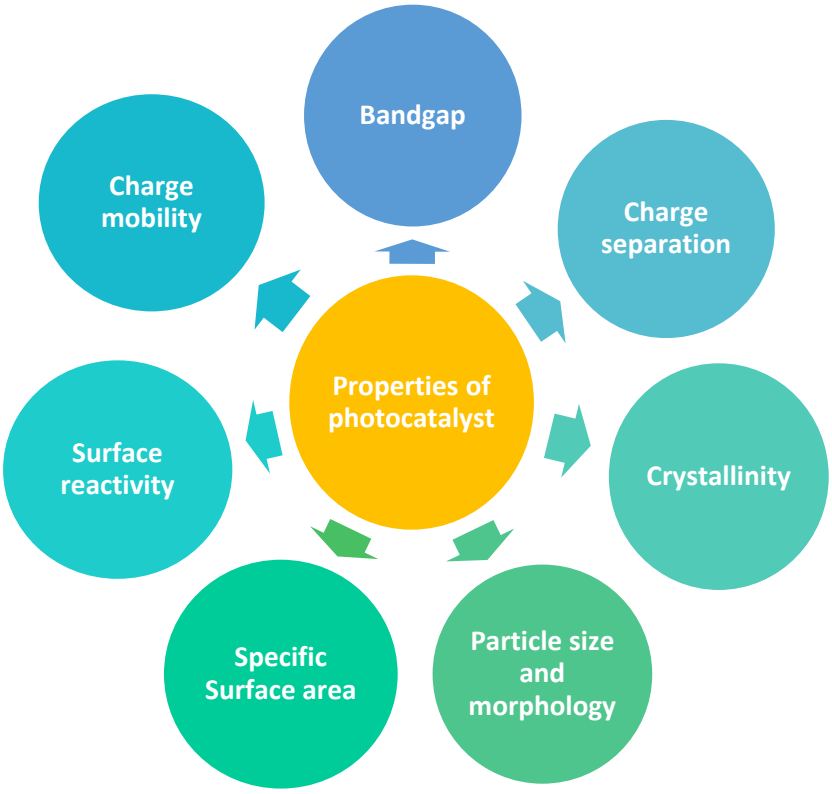


Figure 7 Physicochemical properties of a photocatalyst material

Photocatalytic performance of TiO_2 is controlled by its electronic properties, as well as by its morphology and surface chemistry. The key physicochemical properties of photocatalysts determining their photocatalytic efficiency are summarised in Figure 7. The crystal structure of the material determines the bandgap, while the bandgap determines the material's ability to absorb light. For example, crystalline rutile has the bandgap of 3.0 eV, whereas anatase has the bandgap of 3.2 eV. Particle size also affects the bandgap, e.g., mixed phases composed of TiO_2 nanoparticles have the bandgaps between 3.3-3.4 eV (Table 2). These bandgaps correspond to the UV region of the spectrum, therefore TiO_2 is able to absorb UV light but not visible light.

High charge mobility and efficient charge separation, as seen in the P25 TiO_2 material, are essential for delivering photogenerated electrons and holes to the surface (Hurum et al., 2003). High crystallinity improves both charge mobility and charge separation and allows charge carriers (free electron and hole) to diffuse to the surface of the photocatalyst, where they are able to react with adsorbed molecules. Conversely, charge recombination centres, such as defects or amorphous regions in the crystal structure, act as sites for charge recombination, resulting in annihilation of electrons and holes and loss of photocatalytic efficiency (Kudo & Miseki, 2009).

Particle size also impacts on the photocatalytic efficiency: in small particles, electrons and holes need to diffuse across shorter distances to reach the surface, with smaller probability of recombination on the way; small particles size also results in high surface area per mass, and therefore many surface-active sites for interaction with adsorbed molecules. However, thermal treatment to increase crystallinity often results in increased particle size and agglomeration. Ideally, photocatalyst materials should contain small but highly crystalline particles (Khataee & Kasiri, 2010; Kudo & Miseki, 2009).

Besides the size, photocatalyst morphology (e.g. nanoparticles, nanosheets, nanofibers and nanotubes) affects physicochemical properties, such as charge recombination, surface area and reactivity (Nakata & Fujishima, 2012). Targeted synthesis of high-energy surface facets, such as the (001) facet of anatase, enables higher reactivity and therefore high photocatalytic efficiency (Yang et al., 2009).

Overall, a variety of interconnected properties determine the efficiency of TiO_2 photocatalysts. While TiO_2 has favourable properties and is a highly efficient photocatalyst, the largest unresolved issues are charge recombination, and the large band gap resulting in the lack of visible light absorption.

Modifications of TiO_2

To address the shortcomings and improve the photocatalytic efficiency of pure TiO_2, strategies for modifying the TiO_2 material have been developed. These include doping, surface modification and formation of heterostructures (nanocomposites), as summarised in Figure 8.

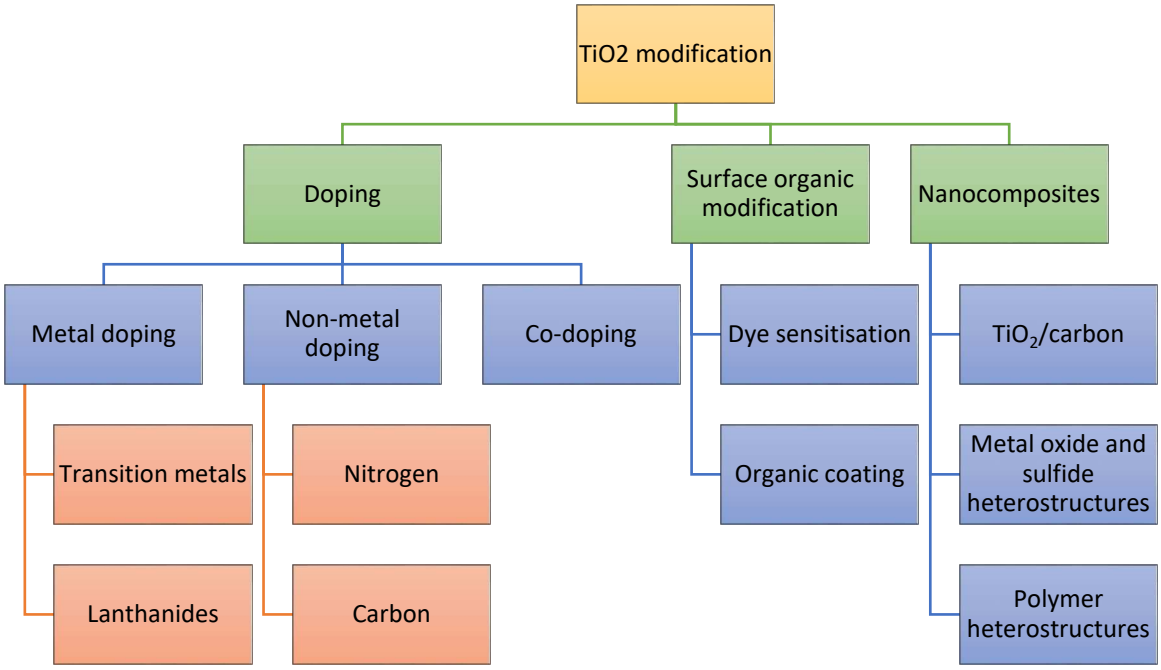


Figure 8 Strategies for modification of TiO_2

The most common modification of TiO_2 photocatalyst involves doping, i.e., introduction of impurity atoms. Doping with cations such as noble metals, transition metals and lanthanides, and with non-metals such as nitrogen and carbon, was found to improve the photocatalytic performance (Daghrir, Drogui, & Robert, 2013; Dong et al., 2015; Fujishima et al., 2008; Pelaez et al., 2012). Doping creates defect states in the band gap (below the conduction band minimum for metal doping, and above the valence band maximum for non-metal doping), which effectively narrow the band gap and allow visible light absorption. Defect states also act as trap states for electrons or holes, and therefore minimise the detrimental electron-hole recombination. Surface dopants can also create surface active sites, such as oxygen vacancies, which facilitate water adsorption to create more reactive hydroxyl radical, and thus improve the surface reactivity of the photocatalysts. At the same time, doping can have negative effects: dopants can create defect sites which increase electron-hole

recombination, and therefore reduce the number of electrons and holes available for photocatalysis. Non-metal dopants, such as nitrogen, involve energy intensive processing and create oxygen vacancy defects in large quantities. Doping with previous metals has high costs, which limit their large-scale commercial applications. The co-doping approach, involving synergistic doping with a metal and a non-metal, resolves some of these problems and results in higher photocatalytic activities compared to pure TiO_2 and single metal or non-metal dopants (Dong et al., 2015).

TiO_2 surface modification by dye sensitisation, similar to the approach used in dye-sensitised solar cells, is an effective way to extend light absorption to the visible range. Here, the dye molecule absorbs visible light and then donates a photoexcited electron to TiO_2. Surface coating with organic adsorbates is also explored as a route to enhance photocatalytic degradation efficiency by strengthening the interaction of TiO_2 particles with hydrophobic pollutants. The dye sensitisation and organic coating are carried out in relatively mild conditions compared to doping; however, the stability of the adsorbed dye sensitiser is poor, as dye molecules desorb with increased number of photocatalytic cycles (Daghrir et al., 2013; Dong et al., 2015).

Nanocomposites are mixtures that involve chemical coupling of two phases, e.g. TiO_2 with narrow-gap semiconductors, such as CdSe (Daghrir et al., 2013; Pelaez et al., 2012), or with carbon-based materials, such as graphene and nanotubes (Morales-Torres, Pastrana-Martínez, Figueiredo, Faria, & Silva, 2012). Here, the narrow-gap semiconductor of graphene material acts as a photosensitiser which absorbs visible light and transfers electrons or holes to TiO_2. Nanocomposites also enable charge separation between the two phases and thus reduce recombination. These two effects, visible light absorption and charge separation, result in higher photocatalytic efficiency of composites compared to pure TiO_2. For example, chemical coupling of TiO_2 with reduced graphene oxide was found to be more efficient than a simple mixture, attributed to effective charge separation and enhanced surface adsorption of pollutants (Nawaz, Miran, Jang, & Lee, 2017). Lower-cost nanocomposites of TiO_2 with organic agricultural waste products have also been explored, for example, the nanocomposite of TiO_2 with coconut shell powder found to have a significantly higher degradation efficiency compared to pure TiO_2 (Khraisheh et al., 2013).

Photocatalytic reactors and process parameters for pollutant degradation

In addition to the nature and physicochemical properties of the photocatalyst, photoreactor design and process parameters have significant impact on the efficiency of photocatalytic degradation of pollutants.

Photocatalytic reactor designs include microfluidic, fixed bed and fixed film, membrane based, and foam based (Odling & Robertson, 2019). TiO_2 photocatalyst can be employed either in the powder form or by immobilising it on a substrate. Suspension of TiO_2 particles in water provides higher reaction efficiencies than immobilised TiO_2 (Dong et al., 2015). However, small particles tend to agglomerate to form large particles, reducing the number of active sites available for reaction. Difficulty in separating TiO_2 particles from the treated water raises further economic and safety concerns. To avoid these problems, TiO_2 particles in photocatalytic reactors are typically immobilised on substrates, such as glass, polymer or metal surface (Frederichi, Scaliante, & Bergamasco, 2020;

Odling & Robertson, 2019). Figure 9 depicts a continuous-flow fixed film reactor with immobilised TiO_2 for photocatalytic degradation of micropollutants (Carbonaro, Sugihara, & Strathmann, 2013).

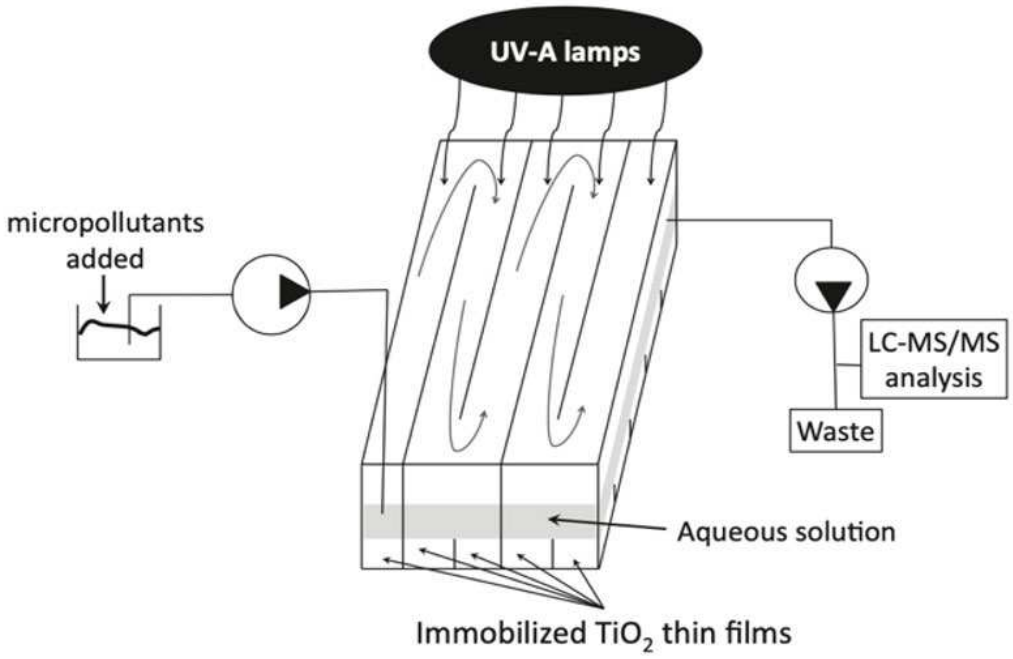


Figure 9 Continuous flow reactor for photocatalytic degradation of micropollutants (Carbonaro et al., 2013) reprinted with permission from Elsevier.

The choice of process conditions, such as pH, temperature, water hardness, light source and intensity, as well as the chemical structure of the micropollutants have a major effect on the efficiency of the degradation process (Gaya & Abdullah, 2008) (Malato et al., 2009) (Chong, Jin, Chow, & Saint, 2010). **Figure 10** summarises the key process parameters which affect photocatalytic degradation of micropollutants.

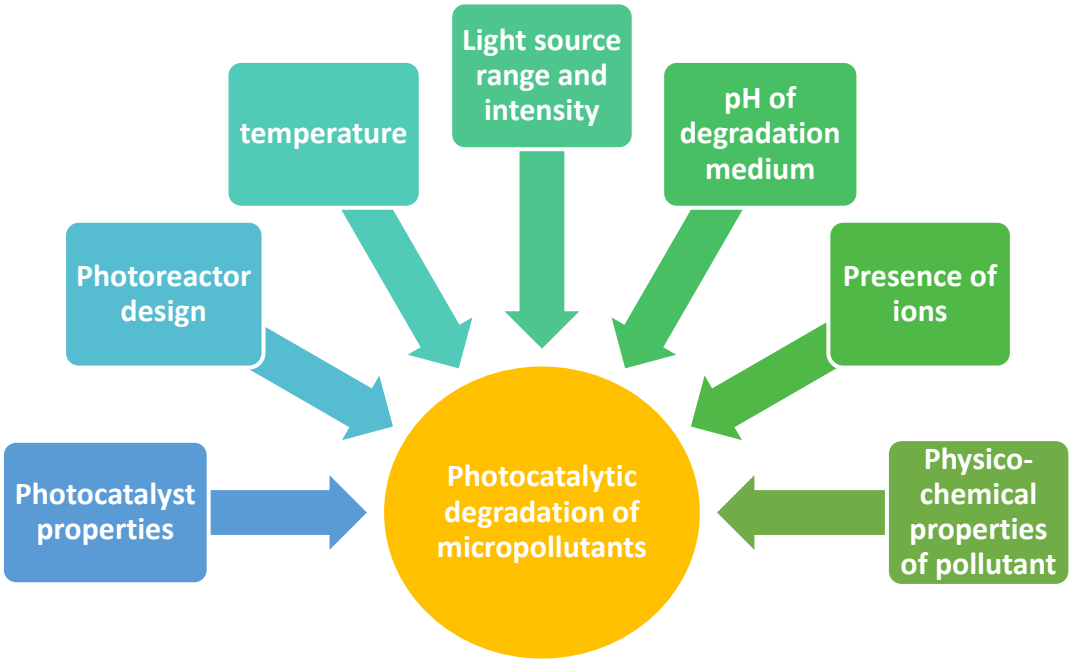


Figure 10 Process parameters influencing photocatalytic degradation of micropollutants

Photocatalytic degradation is typically carried out at moderate temperatures (room temperature, or between 20-80 °C), because the process is light-activated and does not require additional thermal activation. Elevated temperatures make the degradation less efficient because of increased electron-hole recombination and decreased adsorption of reactants; conversely, at low temperatures slow desorption of products becomes a problem, therefore the optimum range is between 20-80 °C (Malato et al., 2009). The amount of the photocatalyst, especially in the suspended powder form, also has a significant effect on micropollutant degradation; the optimum photocatalyst load needs to be determined for each pollutant and photoreactor (Malato et al., 2009).

The wavelength of the light source is an important factor, directly related to the band gap and therefore optical absorption of the photocatalyst. Unmodified TiO_2 absorbs UV light. The natural solar irradiation provides light in the UV-A (315-400 nm) and UV-B range (280-315 nm), while UV lamps also provide the more highly energetic UV-C light (100-280 nm, which is blocked by the Earth atmosphere). Higher light intensity, and therefore more photons adsorbed, increases the photocatalytic degradation yield (Chong et al., 2010).

The pH of the solution affects photocatalytic degradation because of the different surface charge states of the amphoteric TiO_2 photocatalyst at different pH (Chong et al., 2010) and different interactions of the pollutants with the photocatalyst and with the dominant oxidising species; therefore different preferred pH ranges have been observed for degradation of different pollutants (Luster et al., 2017).

Water bodies are dynamic entities, with a number of inorganic and organic species present at the same time, which have a strong influence on the micropollutant degradation. For example, the effect of ions such as Cu^{2+}, Cr^{3+}, Ca^{2+}, NO_3^-, SO_4^{2-} on the degradation of carbamazepine has been investigated, and varied trends were observed: some ions such as Cu^{2+} increased the degradation, while others such as Ca^{2+}, Cr^{3+} and SO_4^{2-} reduced it, while some ions such as bicarbonate ions in hard water inhibited the degradation process. This behaviour was attributed to the competing interactions of dissolved pollutants and ions with holes and reactive oxygen species (Carabin, Drogui, & Robert, 2016; Luster et al., 2017) (Rimoldi et al., 2017).

Moreover, the chemical structure of the micropollutants and their properties such as solubility, acidity and hydrophobicity have a major effect on the efficiency and the optimal conditions of the degradation process (Kanakaraju et al., 2013). For example, Figure 11 illustrates the degree of photocatalytic degradation of a range of micropollutants, including pharmaceuticals, dyes and UV blockers, pesticides, hormones and food additives (Kudlek, 2018). It is clear that some of the micropollutants have higher resistance to degradation than others.

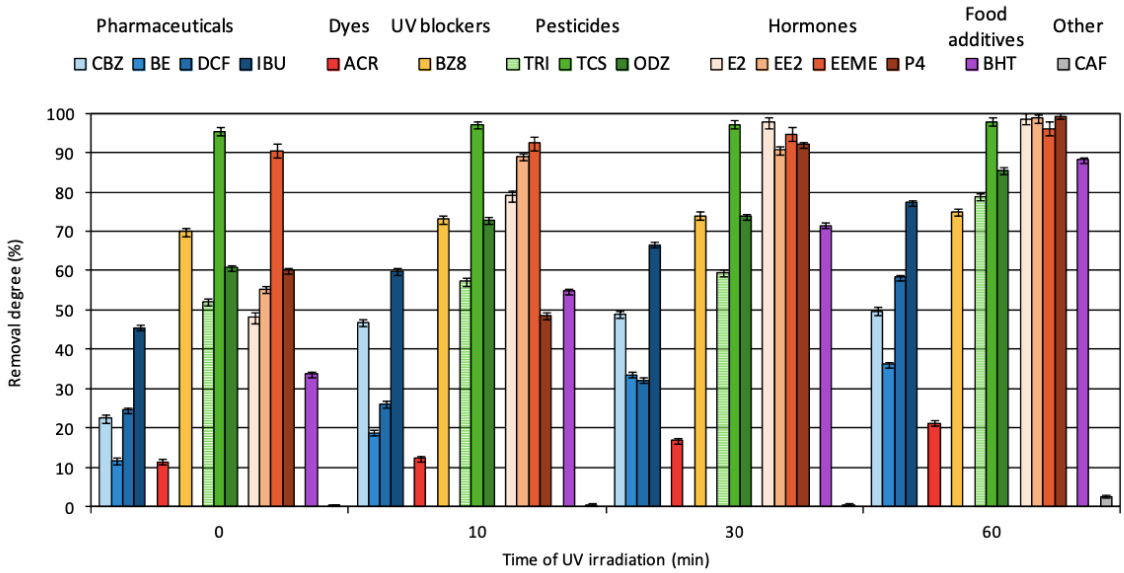


Figure 11 UV based photocatalytic degradation of various micropollutants: pharmaceuticals such as carbamazepine (CBZ), benzocaine (BE), diclofenac sodium salt (DCF), ibuprofen sodium salt (IBU); dyes and UV blockers such as acridine (ACR) and dioxybenzone (BZ8); pesticides such as triallat (TRI), triclosan (TCS), oxadiazon (ODZ); hormones such as β-estradiol (E2), 17α-ethinylestradiol (EE2), mestranol (EEME), progesterone (P4); food additives such as butylated hydroxytoluene (BHT) and caffeine (CAF), with 50 mg L^{-1} of TiO_2 under UV irradiation, after (Kudlek, 2018)

Challenges and Future Scope

While TiO_2 is an efficient and widely used photocatalyst, some challenges still remain. Table 3 lists the key limitations and corresponding strategies for overcoming these limitations.

The large bandgap of TiO_2 allows it to absorb light only in the UV region, and thus limits the fraction of the solar light that can be utilised for photocatalysis. Loss of photogenerated electrons and holes due to recombination before producing reactive species for photocatalysis is another challenge. Both issues are being addressed to some extent through doping, dye sensitisation and formation of nanocomposites.

An important economic and safety concern about dispersed photocatalyst particles in water is separating them from treated water. Agglomeration of photocatalyst nanoparticles to larger less active particles causes reduction in efficiency. These problems can be mitigated by using immobilised photocatalyst and improved design of photocatalytic reactors.

The efficiency of photocatalytic degradation of organic pollutants in water using TiO_2 photocatalysts is restricted by poor adsorption of hydrophobic pollutants on the TiO_2 photocatalyst, which may be addressed by surface modification of TiO_2 using organic coatings.

Photocatalytic degradation typically does not proceed completely to form the end products (CO_2 and water), but instead may produce molecular intermediates. These intermediates can have two detrimental effects. First, they can accumulate on the photocatalyst surface and make the photocatalyst inactive towards reactant adsorption; this is known as surface poisoning of the

catalyst, which is detrimental to the performance and needs to be minimised through the choice of process parameters and the reaction environment. Second, the intermediates themselves may be toxic and cause secondary water pollution. Studies into the toxicity of these intermediates are needed, as well as approaches to achieve complete degradation (Dong et al., 2015). For example, aerobic conditions minimised formation of the harmful intermediate acridine during carbamazepine degradation (Im, Son, Kang, & Zoh, 2012).

One of the limitations of the laboratory studies of photocatalytic degradation of micropollutants to date is that they typically addresses one pollutant at a time and thus do not give a full picture of complex real water systems where multiple pollutants are present simultaneously (Schröder et al., 2016).

Interestingly, degradation efficiency of advanced oxidation processes is affected by the toxicity content (nature and concentration of the pollutants) of the water to be treated. For example, ozonation was more effective in the higher toxicity water whereas TiO_2 photocatalysis was efficient when the toxicity was relatively moderate and for removing more persistent pollutants (Mahy et al., 2020). Thus, hybrid technologies such as combination of photocatalytic degradation with ozonation and with conventional water treatment methods are likely to be most effective.

Table 3 Limitations of TiO_2 photocatalyst and strategies to mitigate these limitations

Limitation	**Mitigation strategy**
Lack of light absorption in the visible range	Doping, sensitisation, nanocomposites
Loss of charges due to recombination	Doping, sensitisation, nanocomposites
Agglomeration of photocatalyst particles	Synthesis methods, surface modification, immobilisation of particles
Separation of powdered photocatalyst from treated water	Immobilisation of particles, reactor design
Poor adsorption of aromatic organic pollutants	Surface modification with organic modifiers
Catalyst poisoning	Surface modification, optimisation of process parameters
Energy intensive manufacturing methods	Green synthesis of TiO_2

Other important factors in evaluating technologies for pollutant degradation are the cost and the environmental impact. The cost including capital, operation and maintenance was found to be higher for UV based TiO_2 photocatalytic degradation, compared to the Fenton and photo-Fenton process and hydrogen peroxide treatment (Saritha, Aparna, Himabindu, & Anjaneyulu, 2007). A recent study (Pesqueira, Pereira, & Silva, 2021) investigated the environmental impact of various solar based advanced oxidation processes based on life cycle analysis, and found solar photolysis to have the lowest impact, followed by solar photolysis with H_2O_2, TiO_2 photocatalysts, TiO_2/H_2O_2 photocatalysts, and photo-Fenton having the worst environmental impact. The environmental impact of TiO_2 photocatalyst can be further reduced by re-use of the photocatalyst.

Concluding remarks

In summary, micropollutants originating from human activity (industrial, agricultural and household usage) are present in surface and ground water, as well as in drinking water, with varying concentrations. Water pollution has significant environmental impacts, as well as impacts on the quality and safety of drinking water. The presence of micropollutants is thought to lead to health and environmental damage; further research is required to investigate potential hazards associated with micropollutants. A number of technologies for purification of wastewater are currently in use, but the current technologies cannot completely eliminate the problem of water pollution. In order to achieve the SDG6 goal of ensuring availability and sustainable management of water by 2030, policies are needed that regulate the purification treatment of wastewater, encourage reuse of wastewater, and support the development and implementation of water treatment technologies. TiO_2 based photocatalytic degradation is one of the most promising and rapidly developing technologies, which offers high efficiency in removing persistent pollutants compared to conventional technologies. It is challenging to simultaneously address multiple issues such as complete elimination of pollutants, costs and a low environmental impact with a single technology. Hybrid technologies or combinations of several processes are promising, whereby the advantages of each method can be strategically combined to tackle the degradation of key persistent pollutants.

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