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Removal of Phthalates from Aqueous Solution by Semiconductor Photocatalysis: A review

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Removal of Phthalates from Aqueous Solution by Semiconductor Photocatalysis: A review.

3

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10 **Abstract:**

11 While phthalate esters are commonly used as plasticizers to improve the flexibility and
12 workability of polymeric materials, their presence and detection in various environments has become
13 a significant concern. Phthalate esters are known to have endocrine-disrupting effects, which affects
14 reproductive health and physical development. As a result, there is now increased focus and urgency
15 to develop effective and energy efficient technologies capable of removing these harmful compounds
16 from the environment. This review explores the use of semiconductor photocatalysis as an efficient
17 and promising solution towards achieving removal and degradation of phthalate esters. A
18 comprehensive review of photocatalysts reported in the literature demonstrates the range of materials
19 including commercial TiO₂, solar activated catalysts and composite materials capable of enhancing
20 adsorption and degradation. The degradation pathways and kinetics are also considered to provide the
21 reader with an insight into the photocatalytic mechanism of removal. In addition, through the use of
22 two key platforms (the technology readiness level scale and electrical energy per order), the crucial
23 parameters associated with advancing photocatalysis for phthalate ester removal are discussed. These
24 include enhanced surface interaction, catalyst platform development, improved light delivery systems
25 and overall system energy requirements with a view towards pilot scale and industrial deployment.

26

27 Key words: phthalate esters; photodegradation; photocatalyst; advanced oxidation processes; pollutant
28 removal

29

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Abbreviations:

AOP	advanced oxidation process
BBP	butyl benzyl phthalate
CA	carbon aerogels
CA- α -Fe ₂ O ₃	citric acid- α -Fe ₂ O ₃
CB	conduction band
CB-TiO ₂	carbon black modified nano-TiO ₂
CMCD	carboxymethyl- β -cyclodextrin
CNT	carbon nanotube
CPI	controlled periodic illumination
DAP	diamyl phthalate
DBP	dibutyl phthalate
DEHP	di-(2-ethylhexyl) phthalate
DEP	diethyl phthalate
DiBP	di-isobutyl phthalate
DMP	dimethyl phthalate
DOP	di- <i>n</i> -octyl phthalate
E _{bg}	energy band gap
EEO	electrical energy per order
EU	European Union
HAT	hydrogen atom transfer
HGM	hollow glass microsphere
IQ	intelligence quotient
LDH	layered double hydroxide
LED	light emitting diode
L-H	Langmuir-Hinshelwood
MEHP	mono-2-ethylhexyl phthalate
MMP	monomethyl phthalate
mPMMA	magnetic poly (methyl methacrylate)
MWCNT	multiwalled carbon nanotube
NHE	normal hydrogen electrode
NT	nanotube
PA	phthalic acid
PAE	phthalate esters
PANi	polyaniline
PET	polyethylene terephthalate
RAF	radical adduct formation
ROS	reactive oxygen species
SET	single electron transfer
TRL	technology readiness level
UV	ultraviolet
VB	valence band
WWTP	wastewater treatment plant

55 1. Introduction

56 1.1 Overview of phthalate esters

57 A particular and damaging consequence of industrialization has been the proliferation of toxic
58 industrial compounds that have been released into the environment (Gogoi *et al.*, 2018). Phthalate
59 esters (PAEs) are among some of the most important industrial chemicals and are commonly used as
60 plasticizers to improve the flexibility and workability of polymeric materials (Staples *et al.*, 1997). The
61 structure of typical phthalate compounds is shown in Fig. 1.1, which can vary in physical and chemical
62 properties depending on the different alkyl chains present. High molecular weight phthalates, such as
63 di-(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DOP), are generally used in building
64 materials and furniture while lower molecular weight phthalates, such as dimethyl phthalate (DMP),
65 diethyl phthalate (DEP), and dibutyl phthalate (DBP) are widely used in personal care products,
66 coatings, and varnishes (Schettler, 2006). The global production of phthalates was estimated to be
67 around 5 million tons in 2010 (Guo *et al.*, 2012).

68

69 Fig. 1.1; Structures of typical phthalate molecules.

70

71 Recently, the amount of plastics in the marine environment has been found to be increasing at an
72 alarming rate and as result has been subject to extensive media coverage (Lebreton *et al.*, 2018).
73 Plastics and PAEs are not chemically bonded so they can migrate from plastics into the marine
74 environment relatively easily (Hahladakis *et al.*, 2018). According to the European Union (EU)
75 definition, DMP belongs to volatile organic compounds and other PAEs are classified as semi-volatile
76 organic compounds, and consequently such PAEs may be emitted to the atmosphere as particulates
77 and vapours (Weschler *et al.*, 2008). Phthalates have endocrine-disrupting effects as they can mimic,
78 compete with or disrupt the synthesis of endogenous hormones (McLachlan *et al.*, 2006). In addition,
79 phthalates are known to affect reproduction in invertebrates and fish; the development of crustaceans
80 may also be impaired, and they can induce genetic aberrations (Ye *et al.*, 2014). Due to these
81 detrimental effects, EU restrictions have been imposed on five phthalates, namely DBP, DEHP, butyl
82 benzyl phthalate (BBP), di-isononyl phthalate and di-isodecyl phthalate, which specifies the scope of
83 use that is permitted and the maximum permitted specific migration limit for each compound (Ventrice
84 *et al.*, 2013).

85

1.2 Occurrence of PAEs in the environment.

PAEs can leach, migrate or evaporate into the surrounding environment (Chen *et al.*, 2008; Moreira *et al.*, 2015) and as a result are often detected in soil, air, and water all over the world, with some key examples highlighted in Fig. 1.2. Subsequently, there have been several studies which have focused on the detection of PAEs in different environmental surroundings. Researchers from Serbia detected the occurrence of six PAEs in soil in the urban zone of Novi Sad and found that PAE concentrations ranging from 0.0002 mg/kg to 4.82 mg/kg, with the highest level obtained for DEHP and the highest total PAE samples obtained from city parks (Škrbić *et al.*, 2016). Similarly, DBP and DEHP have been detected as dominant compounds in soil in China with obvious spatial distribution (Lü *et al.*, 2018) and also in Denmark (Laturnus and Grøn, 2007). Zhang *et al.*, (2014) investigated the occurrence of indoor PAEs from 10 families from Tianjin, China with results showing the presence of a total of six PAEs in indoor PM₁₀ (particulate matter with a size generally less than 10 µm) and PM_{2.5} (particulate matter with a size generally less than 2.5 µm) were in the range of 13.878-1591.277 ng/m³ and 7.266-1244.178 ng/m³, respectively with DBP as the most abundant compounds followed by DEHP. Wang *et al.*, (2008) determined that the total concentration of six gas-phase PAEs in the urban area of Nanjing, China were 3.5-fold higher than that detected in suburban stations. Fromme *et al.*, (2013) investigated the presence of PAEs in indoor air of 63 German day-care centres and confirmed that di-isobutyl phthalate (DiBP), DBP, and DEHP were detected, with median values of 468, 227, and 194 ng/m³, respectively. High DBP concentrations were also found close to deep and bottom water located in waters off the shore of France (Paluselli *et al.*, 2018). Eight different PAEs were found in urban lakes in Guangzhou, China, with DEHP and DBP detected at higher levels than the other compounds (Zeng *et al.*, 2008). Peijnenburg and Struijs (2006) reported that DBP and DEHP were found in freshwater, marine water, sediment and even fish. Moreover, PAEs were capable of moving between phases (Gao and Wen, 2016) (Fig. 1.3), which presents a series of additional challenges when attempting to monitor, track and even remove the pollutants.

Fig. 1.2; Occurrence of PAEs reported in the literature, which were detected in soil (brown text), water (blue text) and air (green text) samples in (a) Europe and (b) Asia (Škrbić *et al.*, 2016; Li and Fu, 2006; Laturnus and Grøn, 2007; Peijnenburg and Struijs 2006; Paluselli *et al.*, 2018; Zeng *et al.*, 2008; Fromme *et al.*, 2013; Wang *et al.*, 2008; Teil *et al.*, 2006).

Fig. 1.3; Occurrence and transfer of phthalate esters (PAEs) between phases in environment.

(Reprinted with kind permission from Gao and Wen, 2016. Copyright (2020) Elsevier.)

The occurrence of PAEs in effluent and sludge from wastewater treatment plants (WWTPs) has also been investigated by several groups around the world. Salaudeen *et al.*, (2018) revealed that in South Africa, six PAEs were detected in almost all of the WWTPs influent and effluent of which DBP was the most abundant compound followed by DEHP. Cai *et al.*, (2007) selected sewage sludges from eleven WWTPs from nine different cities in China to analyse the occurrence of semi-volatile organic compounds and they found that PAEs (DMP, DEP, DBP, BBP, DEHP, and DOP) were the most abundant compounds. In addition, the study found that DEHP was the most abundant PAEs in most cities with a percentage ranging from 24 to 95% (mean: 70%). Çifci *et al.*, (2013) detected the occurrence of five PAEs (DMP, DEP, DBP, BBP, and DEHP) in sludges in Istanbul, Turkey and found that concentrations of these compounds in sewage sludge ranged from 1.4 to 2.7 mg/kg dry weight with DEHP as the most abundant compound. DMP, DEP, DBP, BBP, DEHP and DOP were detected in nearly all WWTP effluent samples and in all road runoff samples in Austria, with DEHP being the most abundant compound (Clara *et al.*, 2010).

1.3 Human exposure to PAEs

The threat PAEs and other environmental pollutants present is often driven by the frequency and method of exposure to humans and animals. As phthalates are omnipresent, it has been found that people have been exposed to phthalates *via* many different routes (Fig. 1.4). Initially, people may be exposed by direct contact with the products containing PAEs. Koniecki *et al.* (2011) investigated the occurrence of eighteen PAEs in 252 Canadian products, including baby products, cosmetic and personal care products. It was reported that DEP was the most frequently used phthalate, followed by DBP and DEHP. Xu *et al.*, (2020) collected plastic express packaging bags from major delivery companies in China and confirmed that leaching of phthalates after 48 h ranged from 181.44 to 5320.64 ng/g, indicating that plastic express packaging bags could be a potential source of phthalates. Paluselli *et al.* (2019) found that DiBP and DBP were the main PAEs released from the polyethylene bags, with the highest values of 83.4 ± 12.5 and 120.1 ± 18.0 ng/g of plastic, respectively while DMP and DEP were the main PAEs released from Polyvinyl Chloride-cables, with mass fractions as high as 9.5 ± 1.4 and 68.9 ± 10.3 ng/g, respectively.

Fig. 1.4; Human exposure to PAEs *via* different routes.

Furthermore, people may be indirectly exposed to PAEs through leaching of these compounds into other products, such as food and drinking water. For example, H. Li *et al.* (2019) confirmed the occurrence of twenty one PAEs in polyethylene terephthalate (PET) bottled drinking water samples in Beijing, with DBP, DiBP, and DMP being the main compounds detected. The correlation analysis in the study suggested that the PET bottles may be one of the primary sources of PAEs in these samples. Similar research also suggested diet may be a significant source of human exposure to DEHP (Wormuth *et al.*, 2006). In addition, clothing also appeared to play an important role of exposure to phthalates (Gong *et al.*, 2016).

Exposure to PAEs may also occur *via* general environmental contamination, such as through contaminated air and water along with indoor dust as another potential source (Subedi *et al.*, 2017). It was reported that DEHP was the most common compound detected in indoor dust samples in the bedroom and living room with mean concentration of 455 and 462 $\mu\text{g/g}$, being detected for each compound, respectively (Y. Li *et al.*, 2019). The profiles of the compounds detected in indoor dust is shown in Fig. 1.5 and it is obvious that DEHP is frequently detected as the most abundant PAE in door dust (Albar *et al.*, 2017).

Fig.1.5; Comparative profile of phthalates in indoor dust in different countries (Reprinted with kind permission from Albar *et al.*, 2017. Copyright (2020) Elsevier.)

Based on various exposure mechanisms, including the ingestion of food, drinking water, dust/soil, air inhalation and dermal exposure, the daily intake of PAEs in humans has been suggested to reach values as high as 70 $\mu\text{g/kg/day}$ (Net *et al.*, 2015). Ji *et al.*, (2014) estimated the daily intake (DI) of PAEs *via* ingestion, inhalation and dermal absorption from five sources (food, water, air, dust and soil) in Tianjin and found that diet was the main source of DEP, BBP, DEHP and DOP, whereas water ingestion led to the greatest exposure to DBP, DEHP and DOP. Contaminated air was another major source of DMP, DEP and DBP contributing up to 45% of the overall exposure (Ji *et al.*, 2014) (Fig. 1.5). Similarly, Koch *et al.*, (2003), tested the daily intake of PAEs in the German population and revealed that 12% of the subjects (10 out of 85 samples) within the collective of the general population exceeded the tolerable daily intake value established by the EU Scientific Committee for Toxicity,

Ecotoxicity and the Environment, which was 37 µg/kg. Furthermore, Wormuth *et al.* tested the daily exposure of PAEs within different age groups and showed that the amount of exposure varied, with infants and children experiencing greater PAE exposure compared to adults (Wormuth *et al.*, 2006) (Fig. 1.6). This was partly believed to be due to most infants wearing garments made from cotton, which has been shown to adsorb phthalates more easily than other fabrics (H. L. Li *et al.*, 2019).

Fig. 1.6; Daily exposure to six phthalates (in µg/kg bodyweight/day) in seven consumer groups, with minimal, mean, and maximal estimates shown. (Reprinted with kind permission from Wormuth *et al.*, 2006. Copyright (2020) Elsevier.)

1.4 Toxicity of PAEs and the effect on environment.

As phthalates are produced as bulk chemicals worldwide and are toxic organic contaminants, there have been many studies on the effects of PAEs on organisms, including reproductive and developmental effects. PAEs have endocrine-disrupting effects, so they can compete with or disturb the synthesis of endogenous hormones, causing reproductive problems (Knez, 2013). For example, an investigation into the relationship between PAEs levels in the body and reproductive health has been conducted, which revealed that urinary phthalate metabolite levels were significantly associated with a decrease in sperm motility, testosterone level and an increase in sperm gene damage and sperm aneuploidy (Jurewicz *et al.*, 2013). In addition, PAE exposure for pregnant women may cause several problems for both the mother and baby. For example, the risk of delivering preterm may be increased for pregnant women as a result of exposure to phthalates during pregnancy (Ferguson *et al.*, 2014) and exposure to monomethyl phthalate monomethyl phthalate (MMP) and mono-2-ethylhexyl phthalate (MEHP) were also associated with a decrease in birth weight (Song *et al.*, 2018). These issues were more severe for male babies, with testicular development and Leydig cell development potentially being vulnerable to phthalates such as low androgen levels and short anogenital distance (Lottrup *et al.*, 2006; Main *et al.*, 2006). Toxicology studies also proved that prenatal exposure to high-molecular-weight phthalates increased the risk of asthmatic symptoms and respiratory tract infections throughout childhood (Gascon *et al.*, 2015).

Behavioural traits were also confirmed to be adversely associated with prenatal exposure to phthalates, with evidence suggesting children were clinically diagnosed with conduct or attention deficit hyperactivity disorders as a result of exposure (Engel *et al.*, 2010). Furthermore, PAEs have also been linked to developmental problems. Cho *et al.*, (2010) enrolled 667 children at nine

elementary schools in South Korea and tested the concentration of urine phthalate concentrations along with the scores on neuropsychological tests from both the children and their mothers. The authors stated that controlling for maternal intelligence quotient (IQ) and other covariates, the results showed an inverse relationship between phthalate metabolites and IQ scores. Similarly, Olesen *et al.*, (2018) conducted an experiment to reveal the relationship between the prenatal phthalates exposure and language development. They proposed that high phthalate exposure in utero may have a negative effect on early language development for both males and females and low prenatal phthalate exposure could have an adverse effect on male early language development but no adverse effect on female.

Given the frequency at which PAEs are occurring in environmental samples, coupled with the significant health risk they pose to humans, there is now increased focus on developing technology that can efficiently achieve degradation and removal of these compounds. Therefore, this review explores the use of semiconductor photocatalysis as a viable option for PAE removal. An overview of photocatalyst development is provided which covers a broad range of materials that have been reported in the literature. In addition, the degradation pathways and kinetics are reviewed to provide the reader with a detailed insight into the photocatalytic removal mechanism. While reviewing previously published literature is important, it is also crucial to consider the key parameters which are fundamental to the advancement of the technology. Therefore, this review also considers the challenges that photocatalysis must overcome in order to achieve continued development with a view towards pilot scale and potential industrial deployment. This was achieved by using the technology readiness level (TRL) scale and electrical energy per order (EEO) value as platforms to identify and evaluate the key factors which could facilitate the transition of photocatalysis from ‘lab’ to ‘real world’.

2. Oxidation Methods for PAEs removal

The previous sections have highlighted the significant issues and threat associated with PAEs regarding both toxicity and routes of human exposure. As people can be exposed to PAEs, without knowledge and by a range of methods that are considered part of ‘*everyday life*’, there is now an increased focus and urgency to develop effective and preferably low energy technologies capable of removing the compounds from the environment. Traditional drinking water treatment focuses on removing the particles and colloids *via* physical processes. Since PAEs are stable and often recalcitrant organic chemicals, removing them from water using traditional methods can often be challenging. The removal rates of PAEs from two waterworks in Harbin, China were reported to be approx. 25.8 to 76.5 %, with DMP and DOP showing the lowest removal efficiencies at both waterworks, Fig. 2.1 (Liu *et al.*, 2013). These values indicate that traditional drinking water treatments may not be effective in

eliminating these micro-pollutants from potable water.

Fig. 2.1; PAEs detected in water samples from the two different Waterworks, a) Mopanshan Waterworks, b) Seven Waterworks (waterworks with the old water source of the Songhua River). (DNOP in this figure refers to DOP) (Reproduced with kind permission from Liu *et al.* (2013), open access).

As a result, an increasingly large volume of research has now focused on the development of new methods to eliminate PAEs from water and soil, including, membrane processes (Bodzek *et al.*, 2004), sodium percarbonate activated by discharge plasma (Wang *et al.*, 2018a), bioaugmentation (Jianlong *et al.*, 2004) and a range of advanced oxidation processes (AOPs) such as photolysis (Lau *et al.*, 2005), ozonation (Li *et al.*, 2009) Fenton process (He *et al.*, 2009) and photocatalysis (J. C. Sin *et al.*, 2012). A number of detailed and informative reviews have previously covered some of these remediation approaches (Gao and Wen, 2016; Abdel daiem *et al.*, 2012; Gani *et al.*, 2017; Gani and Kazmi, 2016). Among these processes, AOPs are promising candidates to remove refractory organic contaminants with a range of examples being effectively deployed for environmental remediation applications, including water treatment processes (Gmurek *et al.*, 2017). Many AOPs utilize ultraviolet (UV) light or visible light and a selective reagent that facilitates a chemical reaction, the breaking of chemical bonds and forming breakdown products of the targeted chemicals (Fig. 2.2). Even the direct absorption of light may result in photodegradation, although many molecules are resistant to direct photolysis. Consequently, there is a requirement for an additional oxidant or catalyst, which usually results in the formation of highly reactive and short-lived reactive oxygen species (ROS), such as hydroxyl radicals ($\cdot\text{OH}$).

Fig. 2.2; Oxidation processes included in the AOPs for PAE degradation.

Although AOPs are effective in removing PAEs from aqueous solutions, the cost of these processes is relatively high because of the need for expensive reagents such as H_2O_2 and O_3 and electrical energy when far UV radiation is applied. A review by Gmurek *et al.* (2017) provided an overview of photochemical approaches to the decomposition of endocrine disrupting compounds, investigating the use of photocatalysis, photochemical reactions with Fenton's reagents and H_2O_2 and

direct photolysis. An interesting alternative option is the use of semiconductor photocatalysis, which has been proven to be an efficient and promising solution towards eliminating refractory organic contaminants in water (Zhang *et al.*, 2019). Photocatalysts, such as TiO₂ are nontoxic and leave no hazardous reagents in the system following treatment. Another significant advantage of semiconductor photocatalysis for the removal of PAEs is the potential to simultaneously remove heavy metal contaminants. Xu *et al.* (2007) showed that when using TiO₂ photocatalysis for the degradation of DBP, the simultaneous photocatalytic reduction of Cr(VI) to the less toxic Cr(III) also occurred. Similarly, You *et al.*, (2018) succeeded in removing Cr(VI)/Pb(II)-DBP mixed pollutants by Bi₂O₃-TiO₂ under visible light, where Pb(II) was reduced to Pb⁰ and DBP was mineralized to CO₂. In wastewater treatment, it is common to have a varied range of pollutants present, therefore the ability to deploy a technology capable of removing more than just one compound is highly desirable.

2.1 Photocatalytic mechanism

Despite the varying and growing number of photocatalytic applications, the core mechanism often remains the same. Photocatalysis is a light driven chemical process which is primarily dictated by the electronic structure of the active photocatalyst material. The principle of photocatalysis is illustrated in Fig. 2.3 (and supported by Eq. 1-10), which demonstrates the formation of ROS utilised for the degradation of PAEs. Semiconductors such as TiO₂ are characterised by an occupied valence band (VB) and vacant conduction band (CB), separated by an energy band gap (E_{bg}). The E_{bg} value dictates the energy and wavelength of light required to promote an electron (e^-) from the VB to the CB, *via* photoexcitation. Therefore, in the example of TiO₂, the $E_{bg} = 3.2$ eV, which can be provided by a photon at a wavelength of ~ 387 nm. Therefore, upon irradiation with light of an appropriate wavelength, an electron-hole pair are generated by producing a positive hole in the VB (h^+_{VB}) and an electron in the CB (e^-_{CB}) (Eq. 1). These charged species can react with surface adsorbed molecules to facilitate redox reactions. The h^+_{VB} can react with surface adsorbed H₂O, and titanol groups to generate $\cdot OH$ (Eq. 3), which are often the primary radical associated with photocatalytic degradation due to a high oxidative potential of 2.8 eV vs NHE (normal hydrogen electrode) (Fang *et al.*, 2013; Nagarajan *et al.*, 2017a). Simultaneously, the e^-_{CB} can react with O₂ which has been adsorbed onto the surface of the catalyst, generating a superoxide anion radical ($\cdot O_2^-$) (Eq. 5). There are additional ROS generated *via* the subsequent reduction of $\cdot O_2^-$, which is due to the redox potential of the TiO₂ electron-hole pair thermodynamically supporting the formation of H₂O₂. The generation of H₂O₂ occurs *via* a peroxide radical (Eq. 6-7) and can also result in additional $\cdot OH$ formation as a result of scavenging an e^-_{CB} (Eq. 8). While still debated, the rate-limiting steps in photocatalysis have been proposed to be the factors which are capable of preventing recombination (Eq. 2) such as the adsorption of O₂ onto the

308 photocatalyst surface (Eq. 4) and/or the transfer of e^-_{CB} to the adsorbed O_2 molecules (Eq. 5)
 309 (Sczechowski *et al.*, 1995).

310

311

312 Fig. 2.3; Principle of photocatalytic degradation of PAEs by semiconductor.

313

314 2.2 An overview of photocatalyst materials deployed for PAEs removal

315 While a range of photo-active materials have frequently been reported as photocatalysts in the
 316 literature, TiO_2 remains one of the most utilised materials (Fujishima *et al.*, 2000). With respect to PAE
 317 removal, researchers have demonstrated that TiO_2 can be employed to degrade PAEs in wastewaters
 318 (Huang and Chen, 2010), with $\cdot OH$ and $\cdot O_2^-$ found to be capable of degrading DMP by 91.9 and 78.1%,
 319 respectively (Wang *et al.*, 2018b). As a result, most materials investigated for the photocatalytic
 320 degradation of PAEs have focused on titania based compounds. An excellent review by Sin *et al.* (2012)
 321 also highlighted the use of TiO_2 photocatalysis for the degradation of endocrine disrupting chemical
 322 from wastewater. To provide a more extensive overview of materials used however, a broader range of
 323 catalysts are discussed here, which have been divided into three groups of catalytic materials; single
 324 metal oxide, doped and composite photocatalysts.

325 Single metal oxide semiconductors such as ZnO , Fe_2O_3 and TiO_2 have frequently been reported
 326 in the literature for photocatalytic applications, primarily due to their availability as commercial

products. TiO₂ is available as a photo-active material in a range of platforms such as pellets, paints and powders with varying crystal morphologies. This coupled with advantages such as being inexpensive, non-toxic and chemically inert has resulted in much of the early work in any photocatalytic applications beginning with TiO₂. Interestingly for PAEs removal, despite most of the work beginning around the early 2000's, which was due in part to the increasing concern of the presence of PAEs in water, one of the earliest reports was in the late 1980's. In 1988, Hustert and Moza monitored the photocatalytic breakdown of DMP, DEP, DBP and DEHP in an aqueous system using TiO₂ (Hustert and Moza, 1988). The authors concluded it was the generation of [•]OH by TiO₂ that facilitated the degradation and subsequently resulted in the formation of hydroxyphthalates and dihydroxyphthalates as intermediate products. Moreover, they found the degradation process was accelerated by the addition of O₂. Shortly after this, in 1992, Halmann reported the photodegradation of di-n-butyl-ortho-phthalate and found the addition of H₂O₂, Fe³⁺ and NaIO₄ enhanced the photocatalytic degradation process (Halmann, 1992). Following these initial reports, which demonstrated the feasibility of photocatalytic technology to remove PAEs, it was the work of Muneer *et al.*, (2001a) and Kaneco *et al.*, (2006), that provided a more detailed insight in the potential mechanisms and the impact of varying parameters. Subsequently, these studies provided an excellent platform for further work to be conducted that focused on both visible light photocatalysis and enhanced activity through the development of composite materials. As early as 2005, there were reports of modified TiO₂ films being used for the improved removal of DBP (Li *et al.*, 2005) along with doped materials in 2012 for BBP degradation (Wang *et al.*, 2012). Development in these key areas has continued to date, with a range of papers published from 2005 onwards that have attempted to develop materials that can achieve rapid rates of PAE removal under visible light irradiation. Within this period and in more recent years (~2017 onwards), papers have also been published that have investigated PAE removal at pilot scale and under solar irradiation (Vela *et al.*, 2018a; Vela *et al.*, 2018b).

Table 2.1 provides a summary and overview of single metal oxide photocatalysts to be used for the degradation of PAEs.

353

Table 2.1 An overview of single metal oxide photocatalysts for PAE degradation

354

Pollutant	Structure	Catalyst	Light source	Experimental conditions	Key results and observations
DEP		TiO ₂ (anatase) (Huang and Chen, 2010)	Xenon lamp: 254 nm.	DEP initial concentration: 20 mg/L Catalyst loading: 0.2 g/L Temperature=25°C pH=4.0 Luminous intensity: 2.5×10^{-6} Einstein/L·s.	DEP was eliminated after 50 mins irradiation.
		ZnO (Liao <i>et al.</i> , 2010)	Hg lamp (15 W): 254 nm	DEP initial concentration: 50 mg/L Catalyst loading: 1 g/L UV light intensity: 9.79 mW/cm ² pH: 5.61 Microwave power: 400 W.	The authors reported the time required to achieve 50 % DMP removal was 18.1 and 30.3 min for TiO ₂ P25 and ZnO, respectively.
DMP		Hydrothermal (h-t) and sol-gel (s-g) prepared TiO ₂ (Jing <i>et al.</i> , 2011)	UV lamp (15 W): 365nm.	DMP initial concentration: 10 mg/L pH: 5.5 Catalyst loading: 1 g/L.	The photocatalytic activity of h-t TiO ₂ (62.1 % DMP removal) was 2.5 times higher than that of s-g TiO ₂ (33.6 % DMP removal).
DBP		TiO ₂ (P25) (Kaneco <i>et al.</i> , 2006)	Xe lamp (990 W): 320-410 nm.	DBP initial concentration: 5 mg/L Catalyst loading: 0-30 mg (100 ml) pH:1-10 Light intensity: 1.8 mW/cm ² .	Complete degradation of DBP was achieved in < 3 h, with moderate amounts of TiO ₂ (5 mg in 100 ml). The final degradation product was observed to be CO ₂ .
		α-Fe ₂ O ₃	High-pressure	DBP initial concentration: 13mg/L	The maximum degradation

		nanoparticles (Liu <i>et al.</i> , 2018)	mercury lamp (250W).	pH:6.5.	achieved was 94% under optimum conditions; 300 mg/L α -Fe ₂ O ₃ , 50 μ l of 30% H ₂ O ₂ , pH =6.5 and an initial DBP concentration of 13 mg/L. The study reported that DBP and subsequent intermediates were mineralized to CO ₂ and H ₂ O.
BBP		P25 TiO ₂ (Xu <i>et al.</i> , 2009)	UV lamp (8 W): 350nm.	BBP initial concentration: 1 mg/L Catalyst loading: 2.0 g/L Temperature: 24 $\pm$ 1 $^{\circ}$ C Light intensity: 3 mW/cm ² .	80% photocatalytic degradation of BBP was recorded after 2 hrs irradiation.

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Photocatalytic research is typically dominated by materials synthesis and the development of novel photocatalysts, which is often driven by the desire to overcome the apparent limitations associated with the use of single oxide materials such as TiO₂. Firstly, TiO₂ is hindered by a wide E_{bg} (3.2 eV for anatase and 3.0 eV for rutile), which means UV light is required to promote electron excitation from the VB to the CB. Secondly, the recombination rate of the electron-hole pair is high, which subsequently leads to low photonic efficiencies for many photocatalytic degradation reactions. Therefore, early research focused on the modification of TiO₂ with a view towards producing a visible light absorbing material with a high photonic efficiency. This has typically been achieved *via* the addition of co-catalysts either through doping elements into the matrix of the catalysts or by the addition of small nanoparticles onto the surface. Element doping with metal and non-metals has been demonstrated to be a potential way to reduce the E_{bg} of photocatalysts and increase the absorption of visible light as dopants are capable of introducing intermediary energy levels (Hassan *et al.*, 2016). The addition of co-catalysts can also significantly suppress recombination by improving electron-hole charge separation, which subsequently can lead to enhanced degradation of PAEs.

Within the literature, TiO₂ has been successfully doped with co-catalysts such as Ni, Cl, N, Mn and Co for both improved PAEs degradation and visible light absorption (Table 2.2) (Wang *et al.*, 2012; Singla *et al.*, 2016). While Cl and N doped catalysts have been reported to have improved photocatalytic degradation of and BBP and DEHP over unmodified TiO₂ respectively, it is worth noting that both studies used Xe lamps with $\lambda \geq 400$ nm. Under these conditions, TiO₂ would not be expected to have a high photocatalytic activity and therefore it could be debated as to whether a comparison of activity using a broader spectrum light source would be more suitable. In contrast however, the work by Singla *et al.* and Kaur *et al.* showed the impact of transition metal doping on TiO₂ for DEP degradation (Kaur *et al.*, 2018; Singla *et al.*, 2016). In both studies a mercury lamp with a peak emission of 365 nm was used, which demonstrated all the doped samples (Ni, Mn and Co) achieved enhanced DEP degradation over that of undoped TiO₂. While a pure visible light study was not conducted, the authors did determine that Mn-doped TiO₂ produced the lowest optical band gap at 2.47 eV, which would be suitable for visible light activation.

In addition to TiO₂ based catalysts, Table 2.2 also shows doped ZnO, Fe₂O₃ and SrTiO₃ have all been deployed as active materials for the photodegradation of PAEs under visible light irradiation. In 2017 Jamil and colleagues investigated PAEs removal using SrTiO₃ (Jamil *et al.*, 2017), which is a material that has gained a lot of interest due to the activity the perovskite structured metal oxide has demonstrated for water splitting (Lo *et al.*, 2010; Xu *et al.*, 2011; Yu *et al.*, 2011). The authors reported the synthesis of Bi doped and BiCu co-doped SrTiO₃ *via* two methods: the citric acid gel method and

389 the Pechini method. The prepared materials displayed visible light responsive photo activity as a result
390 energy levels inserted by Bi^{3+} and Cu^{2+} ions. Under both synthesis methods, an E_{bg} of 1.78 eV was
391 achieved for BiCu co-doped SrTiO_3 , which equates to ~ 695 nm. The co-doped materials were also
392 observed to be the most active under photocatalytic conditions, achieving $\sim 70\%$ DBP removal after 2
393 hrs of visible irradiation.

394 The more recent development of novel photocatalytic materials has often been coupled with
395 attempting to demonstrate activity using either natural or low power irradiation sources. Solar driven
396 photocatalysis remains one of the most desirable approaches for advancing the technology, however
397 low efficiencies remain a significant challenge. Advancements in light emitting diode (LED)
398 technology has also resulted in numerous photocatalysis studies now adopting LED based light arrays
399 as an alternative to solar driven work. Eslami *et al.*, (2017) and Akbari-Adergani *et al.*, (2018a) used
400 Fe, Ag co-doped ZnO along with visible LEDs to ‘*simulate sunlight*’ irradiation for the degradation of
401 DEHP and DBP respectively. In both studies, more than 90% PAEs degradation was achieved with
402 Akbari-Adergani and colleagues using central composite design to model and determine optimum
403 conditions of $\text{pH}=3$, a photocatalyst concentration of 150 mg/L and DBP starting concentration of 15
404 mg/L (Akbari-Adergani *et al.*, 2018).

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Table 2.2 An overview of doped photocatalysts for PAE degradation

Pollutant	Structure	Catalyst	Light source	Experimental conditions	Key results and observations
BBP		Cl-doped TiO ₂ (Wang <i>et al.</i> , 2012)	Xe lamp (300 W): 400 nm.	BBP initial concentration: 10 mg/L Catalyst loading: 1 g/L Temperature: 30±2 °C.	Photodegradation rates of BBP by pure TiO ₂ and P25 were 16 and 30 %, respectively. In contrast (under the same conditions), more than 92% BBP was removed by Cl-TiO ₂ .
		P-doped TiO ₂ thin-films (Mohamed and Aazam, 2013)	Xe lamp (300 W): 400 nm.	BBP initial concentration: 20 mg/L Temperature: 30 °C.	The photodegradation rates of BBP was 17 and 98 % using P25 TiO ₂ and PTIO-0.03 (P-doped TiO ₂ with 0.03 % P) catalyst, respectively. Moreover, photocatalytic activity increased when the P content increased from 0.01 to 0.03 %. At concentrations greater than 0.03 %, the photocatalytic activity decreased with increasing P content.
DEHP		N _x -TiO _{2-x} (Anandan <i>et al.</i> , 2013)	Xenon lamp (55 W): $\lambda \geq 440$ nm.	DEHP initial concentration: 5.0×10^{-4} M Catalyst loading: 0.1 g/L pH: varying from 8.44 to 4.35 Temperature: 25 °C	A higher rate of DEHP degradation was achieved using N-doped TiO ₂ over that of TiO ₂ Degussa P25.
		Fe-Ag@ZnO (Eslami <i>et al.</i> , 2017)	Visible-LED lamp: 430-500 nm.	Catalyst loading: 20 mg/L.	DEHP was removed by 90 % within 120 min of visible irradiation. The authors reported that photocatalytic degradation of DEHP increased when operated at a higher and lower pH (as a result of acidic and basic catalytic

					hydrolysis).
DMP		Sonically fabricated N-doped TiO ₂ (U-N/TiO ₂) and non-sonically fabricated N-doped TiO ₂ (N/TiO ₂) (Zhou <i>et al.</i> , 2013)	Visible light.	DMP initial concentration: 15 mg/L Temperature: 22±2 °C Catalyst loading: 0.5 g/L.	After 5 hrs irradiation, the removal rate of DMP with N/TiO ₂ and U-N/TiO ₂ was 41% and 58%, respectively. The study reported that U-N/TiO ₂ possessed a larger surface area, smaller particle size, and better dispersion than N/TiO ₂
DEP		Ni/ TiO ₂ (Singla <i>et al.</i> , 2016)	Mercury lamp (125 W): 365 nm.	DEP initial concentration: 30 mg/L Catalyst loading: 1 g/L.	Ni doped TiO ₂ samples showed improved photocatalytic activity compared to undoped TiO ₂ .
		Mn/ TiO ₂ ; Ni/ TiO ₂ ; Co/ TiO ₂ ; (Kaur <i>et al.</i> , 2018)	Hg lamp (125 W): 365 nm.	Catalyst loading: 1g/L.	Metal doping was observed to decrease the E _{bg} of TiO ₂ . The lowest optical band gap was observed in Mn doped TiO ₂ (2.49 eV). Ni doped TiO ₂ achieved the highest rate DEP degradation, however, due to a lower crystallite size and higher surface area. All the doped TiO ₂ showed improved photocatalytic performance over pure TiO ₂ .

		WO ₃ /TiO ₂ (Ki <i>et al.</i> , 2018)	UV LED and blue LED.	DEP initial concentration: 10 mg/L Catalyst loading: 5 g/L Temperature: 20 °C pH: 6.17.	Low concentrations of WO ₃ loaded onto the surface of TiO ₂ enhanced photodegradation of DEP under visible light. In contrast, the authors also reported decreased photocatalytic activity under UV light.
DBP		(Fe, Ag) co-doped ZnO (Akbari-Adergani <i>et al.</i> , 2018)	Visible LED lamp (7 W): 450–500 nm.	DBP initial concentration: 15 mg/L pH: 3 Catalyst loading: 0.15 g/L.	95% removal of DBP was achieved under optimum conditions; pH=3, a photocatalyst concentration of 150 mg/ L and an initial DBP concentration of 15 mg/L.
		Bi, Cu co-doped SrTiO ₃ (Jamil <i>et al.</i> , 2017)	Metal halide lamp: 82 lm/W.	DBP initial concentration: 10 mg/L Catalyst loading: 1 g/L.	The photocatalytic activity of nano- sized Bi, Cu co-doped SrTiO ₃ samples were higher than that of Bi doped SrTiO ₃ samples.
		m-TiO ₂ -NTs (Mesoporous TiO ₂ nanotubes) (He <i>et al.</i> , 2019)	High pressure mercury lamp (125 W): 365 nm.	DBP initial concentration: 5 mg/L Catalyst loading: 0.2 g/L Light intensity: 1.5 mW/cm ² .	The m-TiO ₂ -NTs possessed a multiple channel tubular structure which provided a higher specific surface area than TiO ₂ nanoparticles (TiO ₂ -NPs). Therefore, the degradation rate constant for DBP removal for m-TiO ₂ - NTs was 7.7 times higher than that of TiO ₂ .

In addition to catalyst doping, material development has also focused on the formation of composites by combining semiconductors with various materials and support structures that can facilitate enhanced light harvesting and charge separation along with improved downstream filtration capabilities. These composite materials for PAEs degradation are summarized in Table 2.3. The formation of composite materials is often done with a view towards achieving increased excitation across a broader wavelength range along with achieving increased charge species separation through efficient electron transfer (Zhang *et al.*, 2010). Carbon nanomaterials are promising candidates to be combined with TiO₂ to form composites, as they can act as effective electron transfer units and prompt electron transfer from the CB of TiO₂ nanoparticles towards the carbon surface due to their lower Fermi level (Chen *et al.*, 2011). Carbon aerogels (CA), with high porosity, low electrical resistivity, and large surface area, have been shown to be effective for DMP degradation when combined with TiO₂ (Cui *et al.*, 2016). In addition, multiwalled carbon nanotubes (MWCNTs) have also been shown to be effective when used in photocatalytic composite materials. When coupled with TiO₂, a higher photocatalytic activity than pure TiO₂ for the removal of DMP was reported (Tan *et al.*, 2018).

Composite materials can also be formed by combining two or more photoactive semiconductors, which can allow for both efficient charge separation and improved light harvesting capabilities. Examples for PAE removal include V₂O₅/MoO₃ (Chuai *et al.*, 2015), ZrO_x/ZnO (Liao *et al.*, 2010) and Pt-In₂O₃/TiO₂ (Ma *et al.*, 2012). The formation of such composites and subsequent activity is often dictated by the overall molar ratio of the elements present along with structures which form at the interface. In 2015, Chuai *et al.* determined a molar ratio of 1:2 for V to Mo was optimal for DMP degradation using V₂O₅/MoO₃. Furthermore, the authors observed that the composite catalyst was capable of improved visible light driven activity when compared to pure V₂O₅ and MoO₃ as a result of a V 3d impurity energy level along with the formation of a heterostructure at the interface between the compounds (Chuai *et al.*, 2015). The authors suggested that both V₂O₅ and MoO₃ were simultaneously excited by visible irradiation and capable of injecting e⁻_{CB} and h⁺_{VB} into lower and higher energy levels respectively i.e. e⁻_{CB} were injected into MoO₃ from V₂O₅ while, h⁺_{VB} were transferred to the VB of V₂O₅ from MoO₃. The transfer of charged species in this way is an effective way of suppressing recombination and has also been reported in other studies that have deployed composite materials. Liao *et al.* in 2010 reported a ZrO_x/ZnO composite to have greater efficiencies for the removal of DMP when compared to pure ZrO_x, ZnO and TiO₂ P25 (Liao *et al.*, 2010). The authors suggested that interfacial charge transfer, which resulted in electrons being injected into ZrO_x from ZnO, due to the relative binding energies, was responsible for the improved activity when conducting microwave-assisted photocatalysis. Interestingly, under pure photocatalytic conditions,

P25 and ZrO_x/ZnO had similar activity for DMP removal, however under microwave irradiation there was a notable improvement. Liao and colleagues stated that this was due to the existence of three different valence oxides in the composite (e.g. ZrO_3 , Zr_2O_3 and ZrO), which formed non-stoichiometric defect structures that exhibited strong dielectric relaxation under microwave irradiation.

In addition to improved charge separation and visible light responsiveness, composite materials can also improve substrate adsorption and catalyst recovery by using support structures to load the catalyst on to. The work by Jiang *et al.* (2013) and Chen *et al.* (2009) investigated the use of hollow glass microspheres (HGM) and magnetic poly (methyl methacrylate) (mPMMA), respectively, as catalyst support structures to improve filtration and catalyst recovery. Both studies successfully degraded DMP, with Jiang *et al.* observing a 20-60% improvement of removal upon the addition of Pt. Furthermore, the Pt- $\text{TiO}_2/\text{mPMMA}$ composite material was found to be active over multiple experimental runs after being recovered (Chen *et al.*, 2009). A study by Huang *et al.*, (2013) also utilized a support structure that could enhance the process *via* substrate adsorption using TiO_2 immobilised onto hydrophobic layered double hydroxides (LDHs). The LDHs were found to have excellent adsorption capabilities for the initial removal of DMP which was combined with photocatalytic degradation *via* TiO_2 .

Table 2.3 An overview of composite photocatalysts for PAE degradation

Pollutant	Structure	Catalyst	Light source	Experimental conditions	Key results and observations
DBP		Carboxymethyl- β -cyclodextrin- $\text{Fe}_3\text{O}_4@\text{TiO}_2$ (CMCD- $\text{Fe}_3\text{O}_4@\text{TiO}_2$) (Chalasani and Vasudevan, 2013)	Mercury lamp (400 W).	DBP initial concentration: 20 mg/L Light intensity: 17 mW/cm ² Catalyst loading: 1 g/L.	CMCD- $\text{Fe}_3\text{O}_4@\text{TiO}_2$ displayed enhanced degradation of DBP compared to $\text{Fe}_3\text{O}_4@\text{TiO}_2$, with complete degradation achieved within 60 mins. The particles were also stated to be easily recovered by magnetic separation.
DBP		g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{O}_2\text{CO}_3$; g- $\text{C}_3\text{N}_4/\text{BiOCl}$ (Shan <i>et al.</i> , 2016)	Halogen tungsten lamp (500 W): 420 nm	DBP initial concentration: 5 mg/L Light intensity: 1 mW/cm ² Catalyst loading: 1 g/L.	Approx. 60 % removal of DBP achieved within 300 min of irradiation, which was observed to be more efficient with the presence of composite materials g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{O}_2\text{CO}_3$ and g- $\text{C}_3\text{N}_4/\text{BiOCl}$, when compared to any single catalyst.
DBP		Carbon black modified nano- TiO_2 film (CB- TiO_2) (Li <i>et al.</i> , 2005)	low-pressure UV lamp (15 W): 254 nm.	DBP initial concentration: 15 mg/L pH= 6.4. (tubular photoreactor)	The photocatalytic activity of the CB- TiO_2 films was observed to be 1.4 times higher than that of TiO_2 films in degrading DBP.
		$\text{TiO}_2/\text{mPMMA}$ (Pt- $\text{TiO}_2/\text{mPMMA}$) (Chen <i>et al.</i> ,	Low-pressure mercury lamp: 365 nm.	DMP initial concentration: 29 mg/L (0.15 mM) Catalyst loading: 1 g/L	DMP was removed to over 99 % after 180 min irradiation. Improved activity was observed when using 0.90 and 1.50 wt%

DMP		2009)		(Pt: 1.50 wt%).	Pt-TiO ₂ /mPMMA.
		V ₂ O ₅ /MoO ₃ (Chuai <i>et al.</i> , 2015)	xenon lamp as (500 W): $\lambda > 420$ nm.	DMP initial concentration: 40 mg/L Catalyst loading: 100 mg/60 ml.	V ₂ O ₅ /MoO ₃ composites exhibited stronger photocatalytic ability than pure MoO ₃ and V ₂ O ₅ .
		MWCNTs/TiO ₂ (Multiwalled carbon nanotubes composites) (Tan <i>et al.</i> , 2018)	UV lamp (96 W)	DMP initial concentration: 1 mg/L Catalyst loading: 0.5 g/L.	The photocatalytic efficiency of MWCNTs/TiO ₂ nanocomposites (97% DMP removal) was observed to be higher than TiO ₂ (71 % DMP removal). The authors stated that MWCNTs were capable of enhancing light absorption across the UV–Vis range while reducing the charge recombination rate.
		ZrO _x /ZnO (Liao <i>et al.</i> , 2010)	Hg lamp (15 W): 254 nm.	DMP initial concentration: 50 mg/L Catalyst loading: 1 g/L pH: 5.61 Temperature: 25 °C Microwave power: 400 W.	TOC removal efficiency of DMP was 88 % after 30 min irradiation, which was observed to be approx. 15 % higher than that achieved with P25 TiO ₂ .
		LDHs/ TiO ₂ (Huang <i>et al.</i> , 2013)	UV lamp (8 W): 365 nm.	DMP initial concentration: 10 mg/L Catalyst loading: 2 g/L Temperature: 25°C. (annular quartz reactor)	Approx. 80 % of DMP was removed after 4 hrs irradiation. The LDHs/TiO ₂ composites showed higher photocatalytic reactivity than that of bare TiO ₂ nanoparticles.
		TiO ₂ /carbon aerogel (Cui <i>et al.</i> , 2016)	Xe lamp (300 W): filter used to	DMP initial concentration: 2 mg/L; Catalyst loading: 0.1 g/L.	After 3 hrs irradiation, the TiO ₂ /CA-composites degraded > 83 % of DMP, which was found to be significantly higher

DEP			remove infrared light.	(cylindrical glass reactor)	than the degradation efficiency of TiO ₂ and CA-9.3 when used separately.
		HGM-TiO ₂ (Hollow glass microspheres) (Jiang <i>et al.</i> , 2013)	Low-pressure mercury lamp: 350 nm.	DMP initial concentration: 10 mg/L. (Rayonet photochemical reactor)	After 20 mins irradiation, DMP was eliminated in presence of ≥8.0 g/L HGM-TiO ₂ .
		PANi/CNT/TiO ₂ (co-doping with polyaniline and two functionalized carbon nanotubes onto TiO ₂) (Hung <i>et al.</i> , 2017)	LED array (10 W): 410 nm and 455 nm.	DEP initial concentration: 1 mg/L pH: 3-9. Light intensity of each LED: 40 mW/cm ² .	DEP degradation under simulated sunlight was 41.5–59.0 % and 44.5–67.4 % after 120 min, with sol–gel hydrolysis PANi/CNT/TiO ₂ photocatalysts and hydrothermal synthesized ones, respectively. The optimum pH was found to be 5.0 and 7.0 for the two PANi/CNT/TiO ₂ photocatalysts.
		Nanorod ZnO/SiC nanocomposite (Meenakshi and Sivasamy, 2018)	Eight UV lamps (each 8 W): 254 nm. Visible light (500 W).	DEP initial concentration: 5, 10, 15 and 25 mg/L pH: ranging from 2 to 12.	DEP degradation was observed to be > 90% under UV and visible light irradiations with ZnO/SiC nanocomposites as photocatalyst.
		Pt/In ₂ O ₃ –TiO ₂ nanotubes	Xenon lamp: (350 W):	DEP initial concentration: 10 mg/L Temperature: 30 ± 2 °C	The authors reported the highest degradation of DEP was 99.8 % when

		(Metallic platinum and indium oxide codoped titania nanotubes) (Ma <i>et al.</i> , 2012)	320 nm to 680 nm.	Catalyst loading: 1 g/L.	using Pt/In ₂ O ₃ -TiO ₂ -NTs-(0.8, 9.4) (0.8 % Pt and 9.4 % In ₂ O ₃ loading) after 45 mins of illumination.
		CA- α -Fe ₂ O ₃ (citric acid- α -Fe ₂ O ₃) (Shuai <i>et al.</i> , 2018)	High pressure mercury lamp (500 W): 300-400 nm.	DEP initial concentration: 0.2 mg/L (0.89 mmol/L) pH: 5.5 Organic acids: 0.5 mmol/L Catalyst loading: 25 mg/L Light intensity (average): 2.5 mW/cm ² .	In the presence of CA and CA/ α -Fe ₂ O ₃ , the removal rate of DEP was 40 and 60 %, respectively within 5 hrs of UV irradiation.
		H ₃ PW ₁₂ O ₄₀ -titania (Li <i>et al.</i> , 2010)	Xe lamp (300 W)	DEP initial concentration: 13.5 mg/L Catalyst loading: 150 mg/100 ml Temperature: 35 $\pm$ 2 °C Light intensity (average): 5 mW/cm ² .	The rate of DEP mineralization was accelerated using H ₃ PW ₁₂ O ₄₀ /TiO ₂ over pure TiO ₂ . Following 480 mins of UV irradiation, > 80 % TOC reduction was achieved.

2.3 Pathways of degradation of PAEs

Due to the non-selective nature of radicals generated during photocatalysis, determining the exact mechanism can often be challenging. Despite this however, mechanistic studies are extremely valuable as they can provide key details on the overall process, which is particularly crucial when deploying the technology for environmental remediation work. It is essential that any process used to clean or remove pollutants from air or water, does not subsequently result in the formation of secondary pollutants through reaction intermediates. Typically, photocatalytic degradation reactions of organic materials can achieve mineralisation through to carbon dioxide and water. During this process however, a range of intermediates may be formed because of the redox reactions occurring. Furthermore, in the case of water treatment, it is desirable to also ensure these intermediates are not harmful and can be further oxidised if required. Identification and monitoring of these reaction intermediates can provide more insight about the photocatalytic mechanism during the degradation process and help to propose reveal pathways. Achieving this will also provide valuable information on the photocatalytic process, which can facilitate the continued development of the technology. As was recently discussed by Wang and colleagues the advancement of photocatalysis is reliant on not just technological enhancement such as improved reactor design but also on addressing a number of crucial and fundamental chemistry issues (Wang *et al.*, 2020).

The photocatalytic degradation pathways for three common PAEs, namely DMP, DEHP, DBP, are discussed in the following section. It is important to highlight that for certain organic materials the degradation pathway may vary slightly when different catalysts or different experimental conditions are applied. PAE removal rates are reduced with an increase in the length of the alkyl side chains and the alkyl branch chain during photocatalytic reactions (Li *et al.*, 2006). Similar results have demonstrated that PAEs with shorter alkyl chains, such as, DMP and DEP could be degraded faster than DBP and DOP in bioaugmentation (Jianlong *et al.*, 2004).

2.3.1 Degradation pathway of DMP

The $\cdot\text{OH}$ has been proven to play a key role in degrading PAEs (Hung *et al.*, 2017), which is primarily a result of the aforementioned oxidative potential (2.8 eV vs NHE). This can be further confirmed by the range of techniques which generate $\cdot\text{OH}$, including plasma (Qi *et al.*, 2019) and Fenton process (Wongniramaikul *et al.*, 2007), which have been shown to effectively degrade PAEs. Usually, $\cdot\text{OH}$ oxidizes organic materials in aqueous solutions *via* three possible reaction mechanisms; the addition of the radical to an aromatic ring or other unsaturated bond leading to the radical adduct formation (RAF, Eq. 11), hydrogen atom transfer by $\cdot\text{OH}$ (HAT, Eq. 12), and/or single electron transfer

with $\cdot\text{OH}$ (SET, Eq. 13) (Naik *et al.*, 2005).

In the RAF mechanism, the $\cdot\text{OH}$ can easily react with aromatic and unsaturated molecules, especially in acidic environments. For example in the case of aromatic compounds the radicals may undergo an addition reaction to the benzene ring, producing OH-adducts (Mohan and Mittal, 1999). Song *et al.*, (2009) reported that there are more than 50 active sites in aliphatic alkyl chains within cyanotoxin such as microcystin-LR, which can react with $\cdot\text{OH}$ *via* the HAT reaction. The SET mechanism is also considered as a main pathway for $\cdot\text{OH}$ mediated degradation of some aromatic molecules (Tripathi, 1998).

It is suggested in DMP degradation, SET is insignificant in the $\cdot\text{OH}$ -mediated degradation and that RAF and HAT are the main pathways (An *et al.*, 2014). During the degradation, four stable degradation products, phthalic acid (PA), MMP, ortho-hydroxylated DMP and meta-hydroxylated DMP were identified along with a proposed initial reaction mechanism (An *et al.*, 2014; Graham, 2008) (Fig. 2.4). The final products of photocatalytic reactions are ultimately mineralisation products, CO_2 and H_2O , which would be expected if complete PAE removal was achieved.

Fig. 2.4; Degradation pathway of DMP.

2.3.2 Degradation pathway for additional PAEs

In DMP degradation reactions, the primary aromatic intermediates are MMP and PA. A similar trend can be seen in the photocatalytic degradation of other PAEs. For example, in the photocatalytic degradation of DEP, the two primary intermediates formed were PA and MEP (Ki *et al.*, 2018), while the photodegradation of DEHP resulted in the production of PA and MEHP (Anandan *et al.*, 2013). Thus, the degradation pathway of common PAEs can be summarized in Fig. 2.5.

Fig. 2.5; Degradation pathway of PAEs.

Fig. 2.5 illustrates the common primary photocatalytic degradation pathway of PAEs based on these two main intermediates. Initially, the degradation of the parent compound began with attack from various oxidants, such as $\cdot\text{OH}$. When $\cdot\text{OH}$ attacked aliphatic chain (marked red in the Fig.2.5), the original compound decayed to phthalic acid or mono-functional phthalate resulting from bond cleavage (Muneer *et al.*, 2001b). DEHP however, exhibits more toxic effects compared with MEHP (Ye *et al.*, 2014), so consequently if the photocatalytic degradation is not complete, the toxicity of the treated materials will have increased.

The mechanism of BBP photodegradation is slightly different, as there are two benzene rings in this compound, Fig. 2.6. Mono-butyl phthalate, mono-benzyl phthalate and phthalic acid were identified as primary intermediates products of BBP degradation (Xu *et al.*, 2009). They all subsequently degraded into phthalic acid before ultimately forming CO_2 and H_2O .

The implementation of AOPs in water treatment systems requires an accurate prediction of the fate and risk assessment of the target contaminants. It can be seen that during the photocatalytic degradation of every PAE compound, PA is the common intermediate. PA is not developmentally toxic in rats even at a dietary dose which induces maternal toxicity (Ema *et al.*, 1997).

Fig. 2.6; Degradation pathway of BBP. (Reprinted with kind permission from Xu *et al.*, 2009. Copyright (2020) Elsevier.)

2.4 Kinetics of removal of PAEs

The kinetic analysis of photocatalysed reactions has become a challenging area of research as the development of the field has revealed the processes and mechanism occurring are more complex than initially suggested. Catalytic processes in heterogeneous systems are often described by the kinetics of the Langmuir-Hinshelwood (L-H) model, which is described in Eq. 14. This model assumes products are formed as a result of the reaction between catalyst and adsorbed reactants, which often involves the participation of ROS. The popular use of the L-H model within photocatalysis research is likely a result of its versatility as researchers are frequently able to utilise it for experimental data.

$$r = -\frac{dC_t}{dt} = k\sigma = \frac{kKC_t}{1 + KC_t} \quad (14)$$

In this situation, r describes the reaction rate ($\text{mg/L} \cdot \text{min}$), t means the time (min), k represents the apparent reaction rate constant ($\text{mg/L} \cdot \text{min}$), σ is the fractional coverage of catalyst surface, and K

552 defines the dynamic equilibrium constant of PAEs' adsorption onto a photocatalyst (L/mg). When
 553 adsorption is relatively weak, or the reactant concentration is low ($KC_t \ll 1$), Eq. (15) can be simplified
 554 to a pseudo-first order kinetic model (Fu *et al.*, 2016):

$$555 \quad \frac{dC_t}{dt} = -kKC_t = -k_{app}C_t \quad (15)$$

556 where k_{app} is the apparent rate constant (/min). Integrating Eq. (16), it is

$$557 \quad \ln\left(\frac{C_t}{C_0}\right) = -k_{app}t \quad (16)$$

558 Where the value of k_{app} can be calculated from the slope of a plot $\ln\left(\frac{C_t}{C_0}\right)$ versus t .

559 The L-H model was used to describe the photocatalytic process, leading to the determination of
 560 the kinetic parameters, which are not directly related to constants of Langmuir adsorption isotherm.
 561 This indicates that the parameters of L-H kinetics in cases of photocatalytic reactions do not have real
 562 physical meaning. These parameters are experimental constants describing the degradation in assumed
 563 experimental conditions, including a specific range of substrate concentration.

564 While widely cited in semiconductor photocatalysis, flaws have been found within this model. For
 565 example, Turchi and Ollis, (1990) found the L-H parameters k and K had a negative correlation, which
 566 has not been shown in Eq. 14. It was observed that k and $1/K$ varied with light intensity to the same
 567 exponent, which may be 1.0 (very low intensity) or 0.5 (high intensity) (Emeline *et al.*, 2000). K is a
 568 parameter reflecting adsorptive affinity of a substrate onto catalyst surface so it should not vary with
 569 light intensity. As such, a research group carried out a series of experiments on the degradation of DMP
 570 with TiO_2 to clarify details of the process and establish a new kinetic model based on L-H model, (Eq.
 571 17-19) (Du *et al.*, 2009).

$$572 \quad \frac{1}{k} = \frac{489.5}{\sqrt{I}} + 3.22 \quad (17)$$

$$573 \quad \frac{1}{K} = \frac{12.13}{\sqrt{I}} + 1.43 \quad (18)$$

$$574 \quad K = \frac{1.299}{k} + 0.025 \quad (19)$$

575 Subsequent research has proven that PAE degradation follows the pseudo-first order kinetic
 576 models, such as that observed for BBP (Vela *et al.*, 2018a). Moreover, to date there are no examples in
 577 the literature that have reported photocatalytic PAE degradation which follows a second order kinetic

model. In the kinetic analysis of the photocatalytic degradation of a range of compounds including phthalates in a pilot scale reactor, Vela *et al.*, (2018a) used fluence units as opposed to time, which was the “the radiant energy received by a surface per unit area”. The authors considered this was more appropriate as time would be affected by the geometry of the photoreactor, while fluence units could be interchangeable between different investigations. Through this analysis Vela and colleagues found that the photocatalytic degradation of the compounds, including four PAEs, followed a pseudo first order process. Ollis, (2018) recently provided a detailed analysis of the key issues that needed to be considered with respect to kinetics of photocatalysed reactions. Ollis discussed that while the L-H model has been used extensively for photocatalytic processes, it should be noted that it was originally developed for simpler, non-light driven, heterogenous processes. Ollis concluded that a number of considerations should be taken into account when applying the L-H model to photocatalytic processes, particularly as there may be a range of mechanisms involved in these processes and the influence of light will also have an impact on the surface reactions. Ollis also concluded in his analysis that the photocatalytic rate constant k , is a property of the photocatalyst material rather than the structure of the chemical compounds undergoing the photocatalytic degradation process. In view of photocatalytic PAE removal, these are key factors which should be given consideration when attempting to develop the technology further.

3. Moving forward: key considerations for advancing the technology

This review has attempted to provide readers with key information and data on the frequency, occurrence and health risks associated with PAEs along with a broad overview of the potential for photocatalysis as an approach to degradation and removal. Despite the progress that has been made, photocatalytic technology for PAE removal remains predominantly at the research stage and is now faced with overcoming several crucial challenges with a view towards demonstrating efficiency at larger scale deployment. Interestingly, however, it should be noted that photocatalysis as a technology is faced with similar challenges that are not specific to a single application and can be linked to most photocatalytic processes. In heterogenous photocatalysis, uniform distribution of light, low efficiencies, high energy requirements, and mass transfer limitations all result in difficulties when scaling up in industry (Mukherjee and Ray, 1999). Overcoming these challenges, however, is only part of the solution to advancing photocatalytic technology, as the use of raw water when operating at pilot or industrial scale presents additional parameters that require consideration. The physiochemical composition of raw water can vary and furthermore factors such as pH, turbidity and the presence of

organic ions and other pollutants can significantly impact photocatalysis. In a reaction suspension where multiple organic species are present, competition for both active sites and ROS at the catalyst surface increases which could reduce the efficiency and rate of PAE removal. Moreover, a variation in pH could greatly influence the interaction between substrate and catalyst, which is already a potential limitation due to the chemical structure of PAEs. In addition, turbidity could also impair light penetration and distribution which would reduce the photo-excitation of the catalyst.

Despite the challenges however, photocatalysis has grown rapidly and continues to be one the more 'favoured' AOPs applications, especially for environmental remediation, on account of the ambient operating conditions and potential for coupling with low and/or renewable energy. As a result, the technology has now been applied to a range of applications, however very few of these have shown economic viability or efficiency at industrial level. There are a number of parameters and factors which have influenced the slow development of the field and while reviewing them independently wouldn't be appropriate, it is possible to consider them in relation to two key platforms; the TRL scale and the EU standard metric, EEO value. Using these approaches, photocatalytic technology can be evaluated on a broader scope which allows the assessment of more than just one individual parameter. Furthermore, this can be done for photocatalytic technology generally and at an application specific level, which in this case would be environmental remediation focused PAE removal.

Reviewing photocatalysis, based on the TRL scale can provide an initial evaluation of the technology while highlighting the key challenges faced with further development, Fig. 3.1. Emerging technologies considered at the concept development and academic research phase, have a TRL = 1-2. In contrast, when technologies are mature and deployed successfully at industrial level, the TRL = 7-9. The TRL for photocatalysis applications varies, with energy production typically at 1-3, environmental remediation at 3-5 and self-cleaning surfaces, which are based on the photocatalytic process, as the only example considered as established technology, at a TRL = 7-9. The degradation of PAEs *via* photocatalysis can be considered at TRL = 3-5, due to the majority of work being conducted at lab-scale with only a limited number of pilot scale tests reported. To date, the work by Vela *et al.* (2018a and 2018b) are some of the only studies to investigate photocatalytic PAE removal at pilot scale capacities. Experiments were carried out in a pilot plant in Murcia employing ZnO to degrade Diamyl phthalate (DAP) and BBP under solar irradiation (Vela *et al.*, 2018b). The solar pilot plant was used to degrade 100 L of pollutant water with 200 mg/L ZnO and 250 mg/L Na₂S₂O₈ under natural sunlight irradiation with an average daily capacity of 5000 m³ /day. Results showed that at pilot plant scale after 240 min sunlight irradiation, the remaining amount of DAP and BPP was 20.8 ± 6.5% and 24.3 ± 5.3%, respectively. In addition, Vela *et al.*, (2018b) also reported the use of P25 TiO₂ (200 mg/L) with

643 Na₂S₂O₈ (250 mg/L) in the same pilot plant to photodegrade DAP and BBP under natural sunlight. The
644 results showed that around 30-40% BBP and DAP remained after 240 min sunlight irradiation (Vela *et*
645 *al.*, 2018a). In addition, it was estimated that if the pilot plant operated for 8 hours per day and 365
646 days per year, 90% of PAEs could be removed. In addition, based on the facility being operational for
647 10 years, treatment cost would be 103 and 149 €/m³ for photocatalytic treatment with ZnO and P25
648 TiO₂, respectively. In contrast, if the plant was only operated for 240 days per year (which takes into
649 consideration variable weather conditions), the cost is noticeably higher at 144, 209 €/ m³ for ZnO and
650 P25 TiO₂, respectively (Vela *et al.*, 2018a).

651 While transitioning photocatalysis technologies to higher TRLs requires input across a varied
652 number of parameters, it is possible to broadly define them as:

653

- 654 • **Increased photocatalytic activity** – this can typically involve improved fundamental
655 understanding of the chemical processes including investigating the interaction between
656 the photocatalyst and the target pollutant (i.e. PAEs) and the crucial physio-chemical
657 parameters which influence this. This should also take into consideration the impact of
658 varying physio-chemical parameters of raw water on the photocatalytic process.
- 659 • **Enhanced reactor and system technology** – this is centred around reducing mass transfer
660 limitations while increasing photon delivery and distribution within reactor systems to
661 facilitate enhanced photocatalytic reactions. In addition, it also involves reviewing the
662 entire system which includes pre-treatment, substrate delivery, catalyst platform and
663 deployment and downstream filtration requirements
- 664 • **Efficient deployment at large scale** – this area focuses on the scaling up of photocatalytic
665 technology with a view towards achieving economic and industrial feasibility. A key
666 intermediate step in relation to this is increasing the number of pilot scale studies which
667 can demonstrate efficiency of the photocatalysis process when operating with increased
668 capacities.

669

670 Fig. 3.1; The TRL scale in relation to photocatalytic applications highlighting where the technology
671 gap lies, and the key challenges associated with bridging it.

672

673 These broad parameters highlight that it is engagement at both ends of the TRL scale that is

required for further advancement of the photocatalytic process. An improved understanding of the fundamental chemical challenges will facilitate increased photocatalytic activity, which must be supported by the design and construction of reactor systems, preferably at pilot scale, that provide ideal reaction environments. Therefore, it is essential to have engagement over multiple components of the development process in order to achieve a TRL = 9 or greater. In view of this, the EEO becomes an important parameter to consider when assessing photocatalytic processes, specifically for pollutant removal in water, as it measures activity based on multiple parameters. The EEO is defined as the electric energy required to degrade the initial concentration of pollutant by one order of magnitude in a unit volume of an aqueous solution (Eq. 20) (Bolton *et al.*, 2001). The EEO can be an extremely useful metric for photocatalytic activity, especially regarding the key parameters that are identified by the TRL scale when advancing the technology. Moreover, it provides an assessment tool for evaluating the performance of photocatalysis in relation to already established AOPs technologies for environmental remediation.

$$EEO = \frac{P \Delta t}{V \log \frac{C_{A0}}{C_A}} \quad (20)$$

Where P is rated power in kW power, Δt is reaction time in hour, V is the batch reactor volume in m³, C_A is the concentration of pollutant A at any time and the C_{A0} is the concentration of pollutant at the beginning. It is evident in Eq.16, in order to increase EEO, there are two main methods: increase the reaction rate and reduce the energy requirements.

Therefore, in reviewing the TRL scale and considering the EEO value, the following chemistry and engineering related parameters for photocatalytic PAEs removal can be considered as key:

- **Chemistry: Improved photocatalytic degradation** - including enhanced surface interaction through pH modification, substrate adsorption and the use of additives.
- **Engineering: Improved reactor design** - focusing on catalyst platform deployment, irradiation array development and overall system energy requirements.

3.1 Improving the chemistry; key considerations for PAE removal

There are a number of crucial fundamental chemical challenges that must be overcome in order to improve photocatalytic PAE degradation. Parameters which need to be taken into consideration

704 include the formation of reaction intermediates and their subsequent impact on the environment, the
705 ability to deal with varied concentrations of PAEs in real world samples along with the presence of
706 additional pollutants in environmental samples that may create a competitive system. Therefore, it is
707 the surface interaction between substrate and catalysts which requires consideration and along with it,
708 the parameters which can greatly influence this; surface interaction and catalyst hydrophobicity, pH
709 and system additives e.g. H₂O₂.

710 As was discussed in previous sections of this review, several materials have been developed and
711 used to degrade PAEs in water with more novel photocatalysts frequently being reported. As
712 photocatalysis is often considered as '*non-selective*', due to the nature of the radicals generated, there
713 is a challenge in developing catalysts which are selective for PAE removal. While absolute PAE
714 selectivity may not necessarily be required, as a technology that can remove a range of pollutants is
715 desirable, increasing surface adsorption of PAEs is beneficial. As PAEs are hydrophobic pollutants,
716 increasing the lipophilicity of photocatalysts can enhance adsorption of the compounds onto the
717 photocatalyst surface (Ooka *et al.*, 2004). For example, when TiO₂ was combined with hydrophobic
718 LDH, the photocatalytic efficiency of DMP was enhanced compared to pure TiO₂ due to the
719 hydrophobic flaky structure of LDH working as an effective adsorbent for DMP (Huang *et al.*, 2013).
720 With increasing the ratio of LDHs to TiO₂, a high concentration of DMP was observed to adsorb onto
721 the TiO₂ composite catalyst, which resulted in improved DMP removal efficiency, Fig. 3.2. Another
722 example is the application of TiO₂ pillared clay. The hydrophobicity of this material has been
723 demonstrated to have enhanced photocatalytic activity compared to unmodified TiO₂ for the
724 degradation of DBP, DEP and DMP in water (Ooka *et al.*, 2003). It was suggested that hydrophobic
725 interaction between the adsorbate (DMP, DEP and DBP) and interlayer surface of the TiO₂ pillared
726 clay was the predominant factor in PAE adsorption to the photocatalyst surface in water, which further
727 enhanced the performance of the photocatalytic degradation process. Therefore, while the development
728 of new photocatalysts is often done with a view towards achieving visible photon activation, careful
729 consideration should be given to substrate-catalyst interaction, which is the crucial initial stage of any
730 photocatalytic process.

731

732 Fig. 3.2; (a) Adsorption capacity by SDS-LDHs/TiO₂ composites and single TiO₂ nanoparticles
733 (under the same experiment conditions, in dark); and (b) the photocatalytic removal of DMP: (■)
734 ST42, (●) ST43, (◆) ST44, (▲) ST34, (▼) ST24, (★) nano-TiO₂, (*) photolysis. (The number after
735 ST is the ratio of amount of TiO₂ of amount of hydrophobic layered double hydroxides.) (Reprinted

The pH of the reaction solution is also an important parameter as it can impact the photocatalytic performance of PAE degradation through the electrostatic interaction at the catalyst surface. Kaneco *et al.*, investigated the role of initial pH on the degradation efficiency for DBP with TiO₂ within the range of 1 to 10 (Kaneco *et al.*, 2006). Improved photocatalytic degradation efficiency was observed when the pH levels were between 6 and 10, which the authors suggested was due to increased DBP adsorption onto the negatively charged TiO₂ surface through the positive hydrogen atoms on a DBP molecule. In addition to improved surface interaction, the increased presence of OH⁻ ions were found to be beneficial by Chalasani and Vasudevan, 2013 when CMCD-Fe₃O₄@TiO₂ was used to degrade DBP over the pH range of 7-10. The authors explained that at a high initial pH, the presence of increased OH⁻ in solution induced a higher generation of [•]OH, which were believed to be the dominant oxidizing species in the photocatalytic degradation of DBP. It is worth noting that the optimum pH conditions will differ with different photocatalyst and PAEs, which is due to two main factors; the adsorption mechanism of PAEs onto the catalyst surface and the formation [•]OH. Moreover, consideration must be given to the pH of samples detected in natural environments as this could significantly impact the ability to effectively deploy photocatalysis.

While potentially an effective method to remove PAEs from water, the efficiency of photocatalysis is relatively low compared to other AOPs (Mansouri *et al.*, 2019). As a result, the use of additives or hybrid systems are often used to enhance the formation of ROS at the catalyst surface or improve charged-species separation in the photocatalyst materials. For PAE removal, photocatalysis has been coupled with microwave irradiation (Ling *et al.*, 2019) and ultrasound (Na *et al.*, 2012), which were both proven to enhance the degradation rate. Chen *et al.*, (2012) demonstrated that the decomposition of DMP was greatly enhanced under microwave irradiation over Fe@Fe₂O₃ resulting from accelerated electron transfer and increased ROS formation. The addition of chemical additives can also promote increased photocatalytic activity. H₂O₂ was shown to accelerate the degradation efficiency of DEP as a result of the increased formation of [•]OH (Medellin-Castillo *et al.*, 2013). Similarly, the addition of electron acceptors can also accelerate the photocatalytic reaction by preventing the recombination of the electron-hole pair in the photocatalyst. The presence ferrate enhanced the photocatalytic degradation of DMP (Graham, 2008), while Na₂S₂O₈ was also used in a photocatalytic system to prevent recombination, enhancing the photodegradation of BBP and DAP under solar light (Vela *et al.*, 2018a). While the use of additives and hybrid systems are clearly capable

of enhancing the photocatalytic process, careful consideration must be given to the energy and cost requirements associated. The efficiency achieved at lab scale using such a system must be translatable at increased operating volumes to ensure the development of technology is both economically and technologically viable. Therefore, it is at this point the engineering aspects of photocatalytic PAE removal must all be considered.

3.2 Improving the engineering; key considerations for PAEs removal

Advancing the photocatalytic application of PAE degradation towards industrial scale is obviously a complex challenge and one that requires input across a broad number of key areas. Systems for water treatment based on semiconductor photocatalysis (including photodegradation of PAEs) face many challenges despite being extensively researched for over the past 40 years. There are still several crucial fundamental engineering challenges which must be overcome when attempting to improve photocatalytic PAE degradation including catalyst platform deployment, irradiation array development and overall system energy requirements.

Many photocatalytic reactors have been designed at lab-scale, with two main classifications: suspended and immobilised catalyst systems. It is common to deploy photocatalysts as suspended particles in solution, which often results in the scattering of light radiation and enhanced mass transfer. There are, however, challenges in separating the suspended powders from post water treatment. Therefore, it is often desirable to use immobilised photocatalyst systems. Chiou *et al.*, (2006) reported the use of a packed-bed photoreactor, which coated TiO₂ on glass beads to degrade DBP from water, which achieved a 75% degradation efficiency of DBP (5 mg/L) following 80 min irradiation. Another example utilised TiO₂ coated onto a Ti plate which resulted in the successful elimination of DMP from water (Ku *et al.*, 2017). Several supported photocatalyst systems have been developed, such as TiO₂ coated on glass (Chiou *et al.*, 2006); TiO₂-based films on glass substrate (Mahy *et al.*, 2019) which have been proven to be effective in degrading PAEs in water. In addition to immobilizing photocatalysts, another feasible method to facilitate post-treatment has been the development of composites with magnetic materials, such as Fe₂O₃, which can be easily removed from aquatic solutions using magnets (Dong *et al.*, 2013; Chang and Man, 2011).

The delivery of photons through artificial and natural sources to drive photocatalytic reactions is crucial and essential to the process. The source of irradiation also represents a key parameter in relation to both energy requirements, overall efficiency and the potential for scale up. The majority of photocatalytic research has now moved away from using traditional light sources such as mercury

lamps, which have several limitations for AOP use (Autin *et al.*, 2013), with low power LEDs more favoured. In addition, there remains a strong desire to utilise direct solar light as a potential renewable option to drive photocatalysis. Würtele *et al.* (2011) described LEDs as having a number of unique benefits for photocatalysis including being environmentally friendly, compact and robust, capable of faster start-up times, and potentially requiring less energy while having a longer lifetime. These are key advantages, especially in relation to the TRL scale and potentially improving the EEO value, as the deployment of LEDs could represent a crucial approach to lowering the energy requirements of a system. Furthermore, LEDs have the unique ability over traditional light sources of being capable to be deployed under controlled periodic illumination (CPI), which involves pulsing LEDs with high frequency (Tokode *et al.*, 2014). Not only does this present an approach to further reduce the energy requirement of the system, however it may also address low photoconversion efficiencies, which is considered a major challenge preventing photocatalysis transitioning from academia to practice. Compared to other AOPs, such as UV/H₂O₂, photocatalysis has a lower Φ for $\cdot\text{OH}$ production, which is considered as one of the most critical limitations for water treatment. Through deploying CPI, however, a higher Φ can potentially be achieved, which to some extent could address these drawbacks. The use of CPI for the photocatalytic degradation of DMP has been investigated where under the same 5 seconds of illumination, the calculated EEO was decreased by almost 40% for experiments conducted with the increasing dark period from 0.5 s to 5.0 s (Ku *et al.*, 2017). Despite the advantages of LEDs, they can also lead to non-uniform light distribution, which may decrease photonic efficiency for photocatalytic oxidation (Martín-Sómer *et al.*, 2017). Therefore, if LEDs are used in the reactor, it is imperative to optimize the light distribution, otherwise the efficiency of the process may not be improved compared to traditional mercury lamps.

With respect to reducing energy requirements, the development of self-powered photocatalytic units, which don't have any fossil fuel dependency, is an interesting field of study. One of the most promising and desirable energy supplies is sunlight. The low-energy density of sunlight (<1000 W/m²), however, can limit solar powered applications. When large land areas are available and an effective light-harvesting method is employed, photocatalysis can be an effective process for small-scale industrial waste stream treatment (Spasiano *et al.*, 2015). Additionally, photovoltaics have been successfully introduced to utilize solar radiation as an energy source for all devices, including UV-LEDs in Iran to photocatalytically remove organic contaminants. This photoreactor was proposed to be a sustainable, self-powered, and practical point-of-use decontamination system (Eskandarian *et al.*, 2016). In the case of photocatalytic reactors, two main parts that require energy supply is for stirring/pumping (if applicable) and powering light sources. Effective visible light activated

photocatalysts are another method to potentially reduce energy requirements in photocatalytic reactors and remains the primary area of photocatalysis research within the literature. As highlighted above, a major drawback of commercial TiO₂ materials as photocatalysts for industrial process are they cannot effectively harvest sunlight (Gupta *et al.*, 2013). It would be highly desirable if semiconductor photocatalyst materials that could be activated under sunlight were available on a large scale. Over the last two decades there has been extensive research on development of visible light activated catalysts. Their performance, however still falls short of UV activated catalysts with respect to the [•]OH generation rate, such as Evonik P25 TiO₂ (Nagarajan *et al.*, 2017). If UV light must be utilised in systems, significant advances in UV-LED technology needs to be utilised, which of course use less energy as mentioned above.

Once the technical challenges of producing a large-scale reactor have been overcome, the criteria for assessing the performance of photocatalytic water treatment toward PAE degradation must be considered. To attract commercial interest, researchers should ensure performance criteria include factors such as material cost, reusability of photocatalyst, the feasibility of large-scale deployment, tendency to foul in the proposed water matrix, and long-term stability and performance under typical operating conditions. Each of these are still issues that need to be addressed to demonstrate that the photocatalytic process is also economical. Moreover, a complete risk assessment of the process is an important initial consideration. Many intermediates of PAE degradation during photocatalytic process have been identified in lab, neglecting the presence of additional environmental dissolved organic materials that are found in real wastewater. Undesired by-products may be generated by oxidation processes, which are even more toxic than the original contaminant and can have a damaging effect on humans, which can be more detrimental than the original contaminant molecules. Complete risk assessment, therefore, is necessary in addition to research on technical issues to help realize this technology. It is also important to compare photocatalytic processes with other AOPs, such as UV/H₂O₂ and UV/O₃ to confirm the overall economic feasibility, which can be achieved through using the EEO value. Parameters such as the operational lifetime of typical photocatalytic system must be established to provide an overall understanding of the economic and environmental impacts of a complete process for photocatalytic degradation of chemical contaminants in water.

4. Conclusion.

This review has shown that PAEs are frequently being detected in the environment and can have

a damaging effect on human health. There are a number of exposure pathways, including direct contact *via* plastics and indirectly *via* exposure to contaminated soil, air and water. Many phthalates have endocrine-disrupting effects which can have significant, damaging and harmful physiological effects on humans. The risk posed by PAEs has resulted in increased focus on achieving removal and degradation of the harmful compounds. Semiconductor photocatalysis has been demonstrated to be an efficient and promising solution towards eliminating PAEs from the environment. This review explored the range of photocatalyst materials previously reported for PAE removal including the initial work using single metal oxides such as TiO₂ along with doped materials such as Fe, Ag co-doped ZnO which have achieved DEHP and DBP removal under low power visible irradiation. Composite materials were also reviewed including LDH-TiO₂ which could enhance the removal of PAEs through both adsorption and photocatalytic degradation. The mechanism of the photocatalytic process for PAEs removal together with a consideration of intermediates generated by the process was also discussed which identified the [•]OH as playing a key role in the degradation pathway. In addition to reviewing the literature, crucial recommendations that need to be considered with respect to developing photocatalytic technology for large scale PAE removal were also explored and discussed. While the technology has been demonstrated to be effective on a lab scale there are still challenges that need to be addressed before a practical large-scale process may be realised. In the view of the authors, the use of the TRL scale and EEO value can provide valuable platforms and evaluation tools for assessing photocatalytic activity while identifying factors which are key to achieving continued development of the technology. Addressing these parameters, which span both chemistry and chemical engineering, can aid in facilitating the transition of photocatalytic PAE removal from the lab to the real world.

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Conflict of interest

The authors declare no competing financial interest.

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