Insights into the Titania (TiO$_2$) Photocatalysis on the Removal of Phthalic Acid Esters (PAEs) in Water

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Abstract

In this era of globalization, plastic is regarded as one of the most versatile innovations, finding its uses ranging from packaging, automotive, agriculture, and construction to the medical and pharmaceutical industries. Unfortunately, the single-use nature of plastics leads to ecological and environmental problems. Among conventional disposal management of plastic waste are landfilling dumping, incineration, and recycling. However, not all plastic waste goes into disposal management and ends up accumulating in lakes, rivers, and seas. In the aquatic environment, the action of photochemical weathering plastics has resulted in the release of chemical additives such as phthalic acid esters (PAEs), an important plasticizer added to plastic products to improve their softness, flexibility, and durability. Nowadays, PAEs have been ubiquitously detected in our environment and numerous organisms are exposed to PAEs to some extent. As PAEs carry endocrine disruptive and carcinogenicity properties, an urgent search for the development of an efficient and effective method to remove PAEs from the environment is needed. As a viable option, titania (TiO$_2$) photocatalysis is a promising tool to combat the PAEs contamination in our environment owing to its high photocatalytic activity, cost-effectiveness, and its ability to totally mineralize PAEs into carbon dioxide and water. Hence, this paper aims to highlight the concerning issue of the contamination of PAEs in our aquatic environments and the summary of the removal of PAEs by TiO$_2$ photocatalysis. This review concerning the significance of knowledge on environmental PAEs would hopefully spark huge interest and future development to tackle this plastic-associated pollutant.

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1. Introduction

In the year 2019, the production of plastics almost surpassed 368 million tons and this figure is expected to increase in the following years [1]. A wide range of industries demands an increase in the production of plastic-based materials owing to the excellent advantages of plastic products, such as low cost, good durability, and convenience [2]. Plastic products find their uses in various industries such as packaging, automotive, agriculture, and construction [3,4]. Plastic products are also widely used in the medical and pharmaceutical industries, for instance, one-time-use syringes, tubes, and medicine bottles [5,6]. In fact, it is undeniable that plastic products are an essential part of people's daily lives.
Once used, plastic products will have to be discarded. Plastic products have become plastic waste and go to plastic waste management, either to be dumped into landfills, incinerated, or recycled [7]. It is undebatable that landfill dumping took ample land space, limiting land use for better purposes [8,9]. Plastic waste is contained and buried in the dumping site; hopefully, it does not release into the wider environment. Here, plastic waste is either burned or degraded in the natural environment [10]. The burning activity at the landfill emitted fine particulate matter and black carbon, deteriorating the air quality in the surrounding areas [11]. While the degradation of plastic waste usually is done by sunlight radiation and microorganisms but not all plastic waste is degradable [12]. As a precautionary step in order to site landfills, it is vital to keep a certain distance from any form of water source [13]. This precaution taken is due to the high probability of leakage of landfill leachates into soils that would be polluting the groundwater. Studies have shown that landfill leachates such as PAEs, bisphenol A, polycyclic aromatic hydrocarbon compounds, and heavy metals are detected at dangerous concentrations that have been originating from the landfill dumping site [14,15,16]. This is a concerning phenomenon wherein landfill dumping has negatively affected not only the soil but the groundwater quality.

Apart from soil and water, landfill dumping has become the source of microplastic pollution in the environment, which is likely due to transportation by air. Through micro-Raman analysis, Loppi et al. [17] have identified microplastics accumulating in lichens that grew close to the landfill dumping site. This analysis leads to an insight that the air is also polluted by microplastics that come from landfill dumping sites. Plastic waste management through landfill dumping needs further studies on its facilities to avoid soil, water, and air contamination. In addition, geophysical studies on soil structure and groundwater systems call for better investigations in order to effectively implement a controllable dumping site.

Besides landfill dumping, a huge amount of plastic waste is incinerated. This method operates at a high temperature in a high-maintenance incinerator, which is not cost-effective. In addition, hazardous by-products such as carbon dioxide, acidic gases, dioxins, furans, heavy metals, and particulate matter have been discharged into the air [18,19]. This will cause air pollution, global warming, and several health complications, such as respiratory difficulties, decreased lung function, and high cancer risk [20,21]. Several catalysts are implemented to mineralize the hazardous by-products before it is discharged into the air to eliminate or minimize the emission of toxic gases [22,23,24,25]. Incineration with energy recovery technology is also introduced, wherein the generated heat is to be converted into electricity [26]. However, such incinerators are still in the development stage and trials. Furthermore, there is a lack of skilled workers to do this dangerous job [27].

In view of human health, ecotoxicity, and environmental burdens imposed by landfill dumping and incineration methods, recycling is more environmentally preferable [28]. In recycling activity, informal recyclers, or collectors whose job of collecting plastic waste will be collecting the plastic waste to be sent to registered facilities [29]. Furthermore, it will be segregated, shredded into small pieces, and go through a series of washing steps [30]. The washing steps are to eliminate contaminants attached to the plastic waste, such as labels, inks, and dirt. This is a vital step wherein such recycled plastic with traces of impurities would only be recycled into low-value products such as chairs, tables, and buckets [31,32]. At the end of the process, fine and high-quality plastic granules are reproduced and will be further processed into plastic products. The quality of recycled plastic granules close to virgin ones could be a promising result that discarded plastic waste can be recycled and commercialized [33]. Indeed, the action of recycling has economic value along with conserving the environment wherein researchers utilized plastic waste as a replacement for cement in the production of building bricks and concrete blocks [34,35]. In other studies, plastic waste is employed as an alternative material for road construction [36,37,38]. However, not all countries impose strict regulations on the practice of recycling [39,40]. Moreover, the lack of collection, sorting, and processing machines have hindered the recycling of plastic waste to some extent [41,42]. Also, the process of recycling is expensive and time-consuming, thus, only a small percentage of plastic waste is recycled [43].

Apart from the aforementioned plastic waste disposal management, landfill dumping, incineration, and recycling, they are still regarded to be inefficient in tackling plastic pollution. Plastic wastes still enter any parts of water bodies because of inadequate disposal.
that comes from some community which tends to take the easiest way to handle their plastic waste by dumping their plastic waste into nearby water bodies, especially rivers [44,45]. As a consequence, a huge amount of plastic waste accumulates in any form of water bodies such as rivers and lakes [46,47,48]. As time passed, plastic waste reached the oceans through inland waterways or was transported by the tides or windblown [49,50,51].

Under natural factors such as light irradiation and mechanical stress (water flow, waves, and bubble bursting), plastic particles break down into smaller pieces called plastic debris [52,53]. Plastic debris continuously undergoes weathering process, and they eventually reduce its sizes to less than 5 mm, categorized as microplastics, and smaller than 100 nm, categorized as nano plastics [54]. The concern due to the presence of micro- or nano plastics in aquatic ecosystems has been highlighted in many recent studies [55,56,57]. They are regarded as hazardous materials that can contain chemical additives resulting in an ecotoxicological impact on marine organisms [58]. Larger plastic debris is generally removed by a physical removal process, including filtration [59,60], but the treatment of micro- or nano plastics suspended in water is relatively limited due to their small size [61].

In a wider perspective, these untreated microplastics have been suspected to be the main source of chemical additives, in particular, PAEs, the common choice of plasticizers that are intentionally added to plastic products in order to increase their flexibility, elasticity, durability, and make the processing of plastic products easier [62,63,64,65]. PAEs are esters of phthalic acid (1,2-benzene dicarboxylic acid), which are composed of one benzene ring and two ester groups. The ester groups (R1 and R2) depict their individual names and specific characteristics such as density and solubility [66]. The general chemical structure of PAEs is shown in Figure 1. The global market of PAEs is expected to increase annually, corresponding to the high demand for industrial production or import due to the fact of the popular choice among plasticizers because it is relatively cheap and has excellent functionality in terms of workability during plastic manufacturing and better quality of plastic products [67,68].

More importantly, PAEs are not covalently bonded to the plastic polymer thus, there is a high possibility for the leaching of PAEs from the plastic to the environment to happen [69]. Paluselli et al. [70] studied the potential release of PAEs from plastic fragments into the surrounding seawater. They incubated two commercially available plastic materials, an insulation layer of electric cables and plastic garbage bags in glass bottles that were filled with filtered seawater. Within the first month of incubation, they found that dimethyl phthalate and diethyl phthalate were the main PAEs released from the electric cables, while diisobutyl phthalate and dibutyl phthalate were the main PAEs released from the plastic garbage bags. Their study proved that PAEs are likely to leach out from plastic into the surrounding environments even after a longer period of time. Figure 2 illustrates the intercalation of PAEs into plastic polymers where the PAEs and plastic polymers were denoted as the orange sphere and grey lines, respectively.

Recently, Tun and co-workers [71] revealed a high concentration of PAEs has been derived from microplastics in their study on soil pollution in 6 Asian countries. In 2021, Jebara et al. [72] detected maximum concentrations of PAEs during the tourism season (May–October) in Tunisia, most likely as a result of accidentally left plastic items such as food packaging, bags, and sunscreen containers. According to Ramzi et al. [73], the production of tonnes of plastic waste from small-scale industries gave rise to PAEs contamination in the estuary. On a note, there is a correlation between plastics or microplastic and PAEs, thus concluding that plastic waste significantly causes the accumulation of PAEs in our environment [74].

Figure 1. General chemical structure of PAEs

Figure 2. The possible interaction between PAEs and plastic polymers (where the PAEs and plastic polymers were denoted as the orange sphere and grey lines, respectively).
The toxicological effects of PAEs on aquatic life and human being called for removal technologies of PAEs from the environment. Zhang et al. [75] summarized the removal technologies of PAEs in water through physical, biodegradation, and chemical methods. However, the advancement in TiO$_2$ photocatalysis for PAEs removal is not adequately discussed in terms of the possible mechanism of TiO$_2$ photocatalysis for the photodegradation of PAEs and the modification of TiO$_2$ photocatalysts to overcome the existing limitations. In this article, the development of TiO$_2$ photocatalysts for the photodegradation of PAEs is reviewed. It includes the modification of TiO$_2$ photocatalysts by surface or structurally, doping with metals and non-metals, and semiconductor coupling to achieve optimum photocatalytic performance. First, the occurrence of PAEs in our environment is presented to raise awareness of the existence of this toxic chemical. In the following section, an overview of TiO$_2$ photocatalysis dedicated to the photodegradation of PAEs is comprehensively reviewed. Most importantly, this article intends to increase research interest in TiO$_2$ photocatalysis for the removal of PAEs as an essential approach to water remediation.

2. Occurrence of PAEs in Our Aquatic Environment

At the present time, PAEs are ubiquitously detected in various environments, as presented in Figure 3. We have presented the occurrence of PAEs detected in soils and aqueous media across the Asian countries that are extracted from 14 studies. With the rapid growth of the human population and industrial development to satisfy human needs, a variety of industries has bloomed, for example, construction, automotive, electronics, packaging, medical, and pharmaceuticals. Each year, roughly 5 million tonnes of PAEs are produced due to their large-scale manufacturing and widespread application in the aforementioned industries; therefore, PAEs will continuously be introduced into our environment, possibly during the manufacturing process, usage, and disposal of plastic products [90]. The PAEs are commonly detected near these industrial locations, most probably as a result of (1) little or untreated industrial waste flow into surrounding rivers, (2) a lack of expertise in installing proper wastewater treatment facilities, and (3) the high cost of wastewater treatment facilities. Therefore, we require a well-designed industrial zone with a centrally located wastewater treatment facility to keep track of factory discharges [88,89,91].

Besides the industrialized zone, landfill dumping sites have been the sink for PAEs, as documented in the literature works [86,78]. Consequently, landfill leachates have been contaminating the nearby water sources [92,93,94]. Lee et al. [85] found a significant amount of PAEs in the water, sediment, and fish of Asan Lake, South Korea. The main service of lakes has been for agriculture purposes and fishery, but with the accumulation of PAEs, this phenomenon calls for urgent removal technologies of PAEs from the aquatic environment [83,95].

Figure 3. The occurrence of PAEs detected in soils and aqueous media across the Asian countries from 14 studies
The occurrence of PAEs is not only found in wastewater samples and tap water but is also in bottled water [87,76]. Nowadays, the global bottling market is growing at a rate of 9% per year, with a variety of brands available for marketing both domestically and internationally, it should be given special attention to the drinking water treatment process before it proceeds to the filling and packaging processes [96]. Liu and colleagues [84] analyzed PAEs in the water samples taken from the waterworks and found that the removal rate of PAEs was 25.8–76.5 percent, with DMP and DOP having the lowest removal rate from the water samples. This study suggested that the present removal technologies in the drinking water system are working poorly; therefore, we need to explore more removal technologies, either physical, biological, or chemical techniques.

3. Photodegradation of PAEs by TiO₂ Photocatalysts

The established data on the occurrence of PAEs in a wide spectrum is definitely not a good reflection of PAEs production and usage levels worldwide. Concerned by the widely distributed PAEs contaminating our environments and their mutagenicity, carcinogenicity, endocrine disruptive characteristics, resistance to traditional water purification processes, persistent accumulation in biotics, and long-term toxicity to life, the development of a removal method for PAEs is of great importance in environmental science.

Therefore, various techniques have been employed, including coagulation [97,98], adsorption [99], biodegradation [100,101], chlorination [102,103], photolysis [104], ozonation [105], Fenton process [106], and photocatalysis [107]. The coagulation and adsorption techniques, however, have shortcomings and constraints such as the generation of secondary pollutants, the sludge which requires filtration and will be eventually dumped in the waste area, while the used adsorbents that are no longer functional also create disposal problems. Meanwhile, biodegradation processes are very time-consuming and hardly degrade the toxic heavy metal that coexists in the contaminated area. The use of chlorine, especially in the water treatment system, is cost-effective, but it is carcinogenic, and some countries have banned the use of chlorine either for water treatment or in material production. The photolysis process has been reported to be inefficient in degrading PAEs, especially DMP, which is inert toward the photolysis process. The use of ozone as oxidants is technically more complex, dangerous, pricey compound, and not practical in developing countries. Furthermore, the Fenton process is a homogenous photocatalysis that only works efficiently at a strict and narrow pH range, and this process also generates sludge by the end of the reaction process [108].

Apart from the aforementioned processes, photocatalysis is regarded as the most effective because it is environmentally friendly, energy-efficient, and totally mineralizes pollutants into carbon dioxide and water under ambient operating conditions. In photocatalysis, the choice of a photocatalyst is a vital step in driving the photocatalytic reaction to maximum performance at a minimum cost. A photocatalyst is a semiconductor with sufficient photoabsorption capacity to operate as a catalyst while remaining unchanged at the end of the reaction. Basically, the photocatalyst can work in two ways in a photocatalytic reaction: in the form of suspended powders or immobilized over a substrate. The suspended powders appeared to be more efficient due to the higher surface area of the photocatalyst’s active sites. However, they are often difficult to recover for subsequent usage. The recovering process frequently necessitates extra separation processes, which are both costly and time-consuming. Apart from that, they are easily suspended at the bottom of reaction media, necessitating frequent stirring to keep it unsuspended, making it challenging to apply in a continuous flow system. On that note, photocatalysts immobilized over a substrate had received special attention thanks to the ease of recovery and reusability, low operational cost, and achievement of complete mineralization of organic compounds to carbon dioxide and water under ambient operational conditions [109].

A wide range of photocatalysts has been employed in the photodegradation of PAEs, such as zinc oxide (ZnO) [110], α-iron(III) oxide (α-Fe₂O₃) [111], vanadium pentoxide/molybdenum trioxide (V₂O₅/MoO₃) [112], iron and silver codoped ZnO (Fe-Ag/ZnO) [113], and TiO₂ [114]. In particular, TiO₂ photocatalysis receives consistent growing interest for water treatment purposes owing to its high photocatalytic performance, non-toxicity, physiochemical stability, corrosion-resistant, availability, and remaining stable even after being repeatedly used [115,116].

3.1. Possible Reaction Pathways of TiO₂ Photocatalysis for Photodegradation

The discovery of the photocatalytic activity of TiO₂ by Fujishima and Honda in 1972 [117] has embarked on a new journey and vast explo-
ration of TiO$_2$, and in these recent days, TiO$_2$ is regarded as a prominent photocatalyst candidate in environmental science, particularly for the photodegradation of aqueous pollutants. Generally, activation of TiO$_2$ starts when it undergoes photoabsorption of light of sufficient energy, approximately 3.2 eV for anatase TiO$_2$, which results in the formation of electron-hole pairs [118]. Various names come upon these electron-hole pairs, such as photogenerated electrons, photogenerated holes, electrons, holes, negative electron, positive hole, charge carriers, or in symbols, $e^-$ and $h^+$. Upon $e^-$ formation, the reduction process takes place at the conduction band (CB) at the surface of TiO$_2$ photocatalyst, while upon $h^+$ formation, the oxidation process takes place at the valence (VB) edge at the surface of TiO$_2$ photocatalyst [119,120]. These reduction and oxidation processes drive the production of reactive oxygen species (ROS), superoxide anion radical (•O$_2^-$), and hydroxyl radical (•OH). The ROS then attack and mineralize the pollutant into carbon dioxide (CO$_2$) and water (H$_2$O) [121,122].

Figure 4 illustrates the photocatalytic reaction on the surface of TiO$_2$ photocatalyst wherein the dimethyl phthalate (DMP) is used as the representative for PAEs pollutant, with the following Equations (1) to (8) of the redox reactions during the photocatalytic reaction.

$$\text{TiO}_2 + h\nu \rightarrow e^- + h^+ \quad (1)$$
$$e^- + h^+ \rightarrow \text{heat} \quad (2)$$
$$e^- + O_2 \rightarrow •O_2^- \quad (3)$$
$$h^+ + H_2O \text{ (or } -OH) \rightarrow •OH \quad (4)$$
$$•O_2^- + \text{DMP} \rightarrow \text{intermediate products } \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (5)$$
$$•OH + \text{DMP} \rightarrow \text{intermediate products } \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (6)$$

According to the discovered intermediate products and the research done in the literature [123,124,125], the degradation pathway of DMP catalyzed by TiO$_2$ photocatalyst under light irradiation is proposed and presented in Figure 5. The •OH has been proven to play a key role in degrading organic compounds.
Generally, there are two possible positions for the attack of •OH radicals: the aromatic ring and the aliphatic chain of the DMP molecule.

In the first pathway, in which the addition of •OH at the aromatic ring of the DMP molecule forms compound (1). Accordingly, compound (1) possessed two possible hydroxylated derivatives ((2) & (3)) of DMP. Next, compound (2) underwent the subsequent removal of two methoxy groups forming the final compound (4), containing two aldehyde functional groups. Meanwhile, compound (3) cleaved the −COOCH₂ group to generate compound (5). In the second pathway, in which the addition of •OH at the aliphatic chain of the DMP molecule forms compound (6). Next, compound (6) decayed to compound (7). Under the reductive conditions, compound (8) was reduced to form compounds (9) and (10). The compounds (4), (5), (9), and (10) could be further decomposed to CO₂ and H₂O. It should be noted that the intermediates of monomethyl phthalate and phthalic acid have been reported to be much less toxic than DMP [128]. However, more research into the toxicity and risk assessment of these intermediate compounds is needed because they still pose a considerable risk to the environment.

3.2. Research Overview of TiO₂ Photocatalysis Dedicated to Photodegradation

So far, TiO₂ is the most promising semiconductor that has been researched. However, TiO₂ photocatalyst has suffered from its poor ability to absorb the wide spectrum of solar light due to its relatively large bandgap. TiO₂ photocatalyst works well under ultraviolet light but limited use of visible light as the light source [129]. Alongside that, the fast recombination of photogenerated charge carriers is also a drawback of TiO₂ photocatalyst, which would decrease the quantum efficiency of the overall reaction. The Tables 1, 2, 3, and 4 summarized several works of degradation of PAEs, such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), and benzyl butyl phthalate (BBP), by using TiO₂ based photocatalyst. Modification by surface or structural, doping with metal and non-metal, and semiconductor coupling of TiO₂ are done in the direction to improve the photocatalysis in the visible light and the recombination rate of electron-hole pairs can be stymied.

Kaneco et al. [130] reported the effect of photocatalyst dosage, initial substrate concentration, and temperature on the photocatalytic degradation of dibutyl phthalate. The photocatalyst should be optimally used because an excessive photocatalyst dosage is quite inefficient, wherein the light penetration to reach the active site of the photocatalyst will be reduced. The more unfavourable phenomenon is the particles start to agglomerate, which resulted in a reduced surface area in addition to wasting the photocatalyst. In line with Kaneco et al. [130], other studies also suggested that an increase in the initial substrate concentration gave a decrease in the degradation efficiency due to the interruption of light from reaching the photocatalyst’s surface [145,146]. The effect of temperature on the degradation efficiency gave no significant changes as well as not energy-effective. Thus, most reaction operates at room temperature [146].

Xu et al. [131] studied the photocatalytic degradation of benzyl butyl phthalate and concluded that the photocatalyst dosage appeared to be optimum at 2 g/L. From 3 to 5 g/L, the efficiency slightly decreased and was almost constant due to the agglomeration problem. Besides that, they observed an optimal degradation of benzyl butyl phthalate is achieved at pH 7.0, whereby there is no chemical treatment is needed. In 2011, Jing and colleagues [132] successfully prepared TiO₂ powder through hydrothermal and sol-gel methods. The photocatalytic activity of TiO₂ prepared through the hydrothermal method gave higher degradation efficiency as compared to TiO₂ prepared through the sol-gel method owing to better crystallinity, less agglomerate, and larger specific surface area. This study suggested the choice of preparation methods is quite important to obtain such photocatalysts with better properties.

Jing et al. [133] carried out an experiment on the photocatalytic degradation of dimethyl phthalate under the illumination of ultraviolet light. In their study, they discover the vital species responsible for the degradation of dimethyl phthalate. They believed that the •OH had accounted for about 86 percent of the whole reaction. This study is quite valuable to drive more exploration of photocatalysts comprised of abundant external hydroxyl groups to favour the production of •OH. In 2019, Wang and co-workers [134] investigated two systems: UV/TiO₂ and UV-Vis/Bi₂WO₆ systems, to degrade three types of PAEs, dimethyl phthalate, diethyl phthalate, and dibutyl phthalate. From their observations, the UV/TiO₂ system gave better degradation efficiency as compared to the UV-Vis/Bi₂WO₆ system. In addition, the UV-Vis/Bi₂WO₆ system hardly degrades dimethyl phthalate and diethyl phthalate. While, the UV/TiO₂ system showed the strongest deg
Table 1. Photocatalytic degradation of PAEs using TiO$_2$

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>PAEs</th>
<th>Experimental conditions</th>
<th>Results</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial TiO$_2$ powder</td>
<td>DBP</td>
<td>Light source: Xenon lamp (990 W) Substrate concentration: 5 mg/L Photocatalyst dosage: 0–30 mg pH: 1–10 Illumination time: 60 minutes Temperature: 10–40 °C</td>
<td>The photocatalyst dosage appeared to be optimum at 5 mg, above 10 mg, and the efficiency decreased due to the agglomeration problem. The temperature is directly proportional to the efficiency, but the changes are not significant; therefore, the reaction proceeds at 20 °C due to operating cost. For the pH of the reaction solution, the authors selected pH 6 as the optimal experimental condition to avoid unnecessary chemical treatment.</td>
<td>[130]</td>
</tr>
<tr>
<td>Commercial TiO$_2$ powder</td>
<td>BBP</td>
<td>Light source: Sixteen 350 nm black blue fluorescent UV lamps (8 W) Substrate concentration: 1 mg/L Photocatalyst dosage: 0–5 g/L pH: 7.0 Illumination time: 120 minutes Temperature: Maintained at ~24 °C (installation of the cooling fan in the photoreactor)</td>
<td>The photocatalyst dosage appeared to be optimum at 2 g/L, the efficiency slightly decreased and was almost constant from 3 to 5 g/L due to the agglomeration problem.</td>
<td>[131]</td>
</tr>
<tr>
<td>TiO$_2$ powder (prepared by hydrothermal and sol-gel method)</td>
<td>DMP</td>
<td>Light source: UV lamp (15 W) Substrate concentration: 10 mg/L Photocatalyst dosage: 1 g pH: 5.5 Illumination time: 60 minutes Temperature: 25 °C</td>
<td>The authors investigated two approaches for the preparation of TiO$_2$ powder: hydrothermal and sol-gel methods. TiO$_2$ prepared through the hydrothermal method gave higher degradation efficiency (2.5 times better) as compared to TiO$_2$ prepared through the sol-gel method owing to better crystallinity, less agglomeration, and larger surface area.</td>
<td>[132]</td>
</tr>
<tr>
<td>Commercial TiO$_2$ powder</td>
<td>DMP</td>
<td>Light source: Hg lamp (300 W) Substrate concentration: 5.16 µM Photocatalyst dosage: 0.2 g/L pH: 5.0 Illumination time: 75 minutes Temperature: Not stated</td>
<td>The addition of scavengers, such as CH$_3$OH, KI, and CHCl$_3$, has come to conclude that •OH is 86 percent responsible for the reaction.</td>
<td>[133]</td>
</tr>
<tr>
<td>TiO$_2$ (prepared by sol-gel method)</td>
<td>DMP, DEP, DBP</td>
<td>Light source: UV/TiO$_2$: Mercury lamp (500 W) Vis/Bi$_2$WO$_6$: Xenon lamp (500 W) Substrate concentration: DMP (6 mg/L), DEP (6 mg/L), DBP (4.128 mg/L) Photocatalyst dosage: 1 g/L pH: No pH adjustment Illumination time: 300 minutes Temperature: ~20 °C</td>
<td>The authors investigated two systems: UV/TiO$_2$ and UV-Vis/Bi$_2$WO$_6$ system to degrade three types of PAEs and they observed that UV/TiO$_2$ system gave better degradation efficiency as compared to the UV-Vis/Bi$_2$WO$_6$ system. The UV-Vis/Bi$_2$WO$_6$ system also hardly degrades two types of PAEs, DMP and DEP.</td>
<td>[134]</td>
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Table 2. Photocatalytic degradation of PAEs using TiO$_2$ (surface or structural modification).

<table>
<thead>
<tr>
<th>Photocatalyst</th>
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<th>Results</th>
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</tr>
</thead>
<tbody>
<tr>
<td>{001}TiO$_2$</td>
<td>DMP, DEP</td>
<td>Light source: Xenon lamp (300 W) Substrate concentration: 50 µM Photocatalyst dosage: 100 mg pH: Not stated Illumination time: 120 minutes Temperature: Not stated</td>
<td>The {001}TiO$_2$ portrayed a higher degradation rate as compared to that of pure TiO$_2$.</td>
<td>[135]</td>
</tr>
<tr>
<td>Mesoporous TiO$_2$ nanotube</td>
<td>DBP</td>
<td>Light source: Mercury lamp (125 W) Substrate concentration: 5 mg/L Photocatalyst dosage: 20 mg pH: Not stated Illumination time: 60 minutes Temperature: Not stated</td>
<td>The mesoporous TiO$_2$ nanotube gave the highest efficiency as compared to the TiO$_2$ nanoparticles, Degussa P25, and TiO$_2$ nanotubes.</td>
<td>[136]</td>
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Table 3. Photocatalytic degradation of PAEs using TiO\(_2\) (elemental doping).

<table>
<thead>
<tr>
<th>Photocatalyst</th>
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<th>Results</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition metals (Mn, Ni, Co) doped TiO(_2)</td>
<td>DEP</td>
<td>Light source: Mercury lamp (125 W)</td>
<td>Among these transition metals, Ni-doped TiO(_2) gave better performance owing to its smaller crystallite size and higher surface area.</td>
<td>[137]</td>
</tr>
<tr>
<td>Cu doped TiO(_2)</td>
<td>DBP</td>
<td>Light source: 340 nm light source (taking place in a quartz cell)</td>
<td>Cu doped TiO(_2) gave a better performance (approximately 20%) in the photodegradation of DBP as compared to the unmodified TiO(_2).</td>
<td>[138]</td>
</tr>
<tr>
<td>Zn doped rutile TiO(_2)</td>
<td>DEP</td>
<td>Light source: Mercury lamp (125 W)</td>
<td>Zn doped TiO(_2) exhibited better photocatalytic activity as compared to undoped TiO(_2).</td>
<td>[139]</td>
</tr>
<tr>
<td>P doped TiO(_2)</td>
<td>BBP</td>
<td>Light source: Xenon lamp (300 W)</td>
<td>The authors successfully prepared P-doped TiO(_2) thin film coated onto glass plates through the sol-gel method. They tested their photocatalyst in the degradation of BBP. From their observation, the P-doped TiO(_2) thin film, pure TiO(_2) thin film, and commercial Degussa P25 reached 98, 28, and 17% photodegradation rates, respectively.</td>
<td>[140]</td>
</tr>
<tr>
<td>Cl doped TiO(_2)</td>
<td>BBP</td>
<td>Light source: Xenon lamp (300 W)</td>
<td>Upon 240 minutes of visible light irradiation, the Cl doped TiO(_2), pure TiO(_2), and commercial Degussa P25 reached 92, 16, and 30% photodegradation rates, respectively.</td>
<td>[141]</td>
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</table>

Table 4. Photocatalytic degradation of PAEs using TiO\(_2\) (semiconductor coupling)

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>PAEs</th>
<th>Experimental conditions</th>
<th>Results</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>CdS-TiO(_2)</td>
<td>DMP</td>
<td>Light source: Sunlight irradiation</td>
<td>Upon 180 minutes of sunlight irradiation, the photocatalytic degradation of DMP reached 81%. The optical properties of CdS-TiO(_2) showed strong photoresponse under the visible light region.</td>
<td>[142]</td>
</tr>
<tr>
<td>Tungsten oxide doped TiO(_2)</td>
<td>DEP</td>
<td>Light source: Blue LED lamp</td>
<td>The authors observed a decrease in the bandgap value, which significantly improved the degradation rate of DEP of the modified TiO(_2).</td>
<td>[143]</td>
</tr>
<tr>
<td>8-cyclodextrin-functionalized FeO(_x)@TiO(_2) core-shell nanoparticle</td>
<td>DBP</td>
<td>Light source: Mercury vapor lamp (400 W)</td>
<td>The authors highlighted the specialty of their photocatalyst: (1) the anchored cyclodextrins are for the capturing of the organic pollutants, (2) the TiO(_2) is for degradation and mineralization of the organic pollutants, and (3) the FeO(_x) allows for easier separation and recovery of the photocatalyst.</td>
<td>[144]</td>
</tr>
</tbody>
</table>
radiation ability on dimethyl phthalate, diethyl phthalate, and dibutyl phthalate, with the removal efficiencies reaching 93.03, 92.64, and 92.50%, respectively.

Taking advantage of the high surface energy of facet {001} of TiO₂ with promising better oxidation ability, Gu et al. [135] prepared the TiO₂ coated on fluorine-doped tin oxide (FTO) conductive glass through the hydrothermal method, and they successfully achieved TiO₂ dominated by {001} facet. They observed that the prepared {001} TiO₂ portrayed a higher degradation rate as compared to that of commercially TiO₂. This study suggested that surface modification of TiO₂ by highly exposing facet {001} of TiO₂ is able to give better photocatalytic performance due to its better adsorption and oxidation ability. Compared to the TiO₂ nanoparticles, Degussa P25, and TiO₂ nanotubes, the mesoporous TiO₂ nanotube gave the highest efficiency in the degradation of dibutyl phthalate [136]. Structural modification into the mesoporous structure allows the greater mass transfer and light entry as well as provides a larger surface area for significantly improved photocatalytic performance.

In most studies, TiO₂ is modified by elemental doping to optimally absorb the light energy to drive the photocatalytic reaction [137,138,139,140,141]. Kaur et al. [137] studied the transition metal-doped TiO₂ for the photocatalytic degradation of diethyl phthalate. They observed a narrower bandgap value in the doped TiO₂ as compared to undoped TiO₂, which resulted in a better photocatalytic performance. Sathasivam et al. [138] proposed the presence of Cu as the dopant in TiO₂ gave improved photocatalytic activity in the degradation of dibutyl phthalate. Similarly, Singh et al. [139] observed that Zn-doped TiO₂ showed better photocatalytic activity than the undoped TiO₂ in the photocatalytic degradation of diethyl phthalate. Basically, elemental doping would introduce a transition band in the bandgap that led to a narrower bandgap for better photocatalytic performance under visible light. Besides that, Mohamed & Aazam [140] has concluded that P doping is advantageous in the crystallization process as well as preventing the agglomeration problem. In some cases, with an excessive dopant amount, the transition band introduced would act as the recombination centres that negatively affect the photocatalytic performance [141].

Semiconductor coupling of TiO₂ has significantly improved the photocatalytic performance on account of the ideal heterojunction formed. Notably, the different positions of conduction and valence band between them favour the electron-hole separation, thus, extending the lifetime of electron-hole pairs. In addition, a narrower bandgap is observed upon semiconductor coupling, which is a favourable criterion for optimally absorbing the light energy [142,143]. As such, reusable photocatalyst is highly demanding, Chalasani & Vasudevan [144] incorporated crystalline Fe₂O₃ core to the TiO₂ shell allowing an easier separation and recovery process of the photocatalyst used. In the future, more research on film form TiO₂ by means of coating TiO₂ on a substrate can be explored to give added value to the photocatalyst, reusability, and convenience.

The TiO₂ photocatalyst has been regarded as a mature choice and to be the first one to be considered in the photodegradation of organic pollutants. It is also proven to synergistically reduce heavy metals together with the removal of PAEs, which are of great interest industrially [147]. The TiO₂ photocatalyst could be modified structurally, doping and coupling with other semiconductors to obtain a larger surface area, better absorption of solar light, and reduced recombination rate of electron-hole pairs to achieve enhanced photocatalytic performance.

3.3 Future Development of Photocatalysis for Degradation

Significant progress has been developed in the field of TiO₂ photocatalysis dedicated to the degradation of a wide range of organic compounds [148,149]. This huge devotion to TiO₂ photocatalysis is due to its excellent photocatalytic activity with strong oxidizing and reducing properties. But these properties can only be activated under ultraviolet light, which represents a mere 5% of the solar energy. Therefore, extensive research has been conducted in engineering the bandgap of TiO₂ in order to utilize a greater portion of solar light, such as the visible light region. Apart from that, it is highly appealing to explore possible metal oxide with a narrow bandgap to be added to the TiO₂ system, not only for improving light absorption towards the visible light region but also help to reduce the electron-hole pairs recombination rate, thus enhancing the photocatalytic activity of TiO₂ photocatalyst. In the exploration of potentially improved photocatalysts, computational modeling, and simulations could provide fundamental understanding and information on the relationship between structure and properties to facilitate the design and construction of photocatalysts with superior performance for practical use.
3.4 Prospective Utilization of Photocatalysis for Photodegradation using TiO2-based Catalysts

The application of TiO2 powder for photodegradation leads to several consequences such as being hardly suitable for continuous water flow systems and being in need of an additional separation system which is highly cost and complicated in terms of facility installation, maintenance, and waste management of the unactive photocatalysts [150]. In view of the authors, one way of solving this issue is by adopting the popular form of TiO2, by means of supported TiO2 films. Following this, it is of paramount importance to search for suitable deposition methods to obtain such supported TiO2 film with strong adhesion to the substrate, and highly durable, while maintaining their respective photocatalytic activity. This will be one step closer to connecting the laboratory work to the industrial sites and water or wastewater treatment plants in the near future.

4. Conclusion

As widely demanded plasticizers, PAEs have been utilized pretty much everywhere in our plastic-based products. To be concerned, PAEs are readily leached out into the environment and contaminate the aquatic environment. Therefore, extensive research is largely in need of efficient methods and technologies to degrade PAEs into nontoxic and safe final products. On that note, photocatalytic degradation of PAEs using TiO2 is deduced to be a greatly effective removal method to tackle these plastic-associated pollutants. However, it is still a long way to go for practical applications of TiO2-based photocatalytic materials; a couple of challenges need to be addressed, including the following: (1) powder form TiO2 limits the use of TiO2 in a continuous flow system because the tedious and high cost of recovering and separation of TiO2 from the treated solution. Thus, film form TiO2 by means of coating TiO2 on a substrate is a popular adoption to get rid of post-treatment of TiO2. Following this, the choice of deposition method is highly important for achieving the strong adhesion between TiO2 film and the substrate, (2) the activation of TiO2 is limited to UV light irradiation due to its relatively large bandgap, which is around 3.2 eV. Structure modification, elemental doping, or semiconductor coupling could alleviate this difficulty, allowing TiO2 to be visible light and sunlight-responsive photocatalysts. More research is needed on visible light harvesting photocatalysts with enhanced electron-hole pair lifetimes, high stability of TiO2, lower costs of dopants, and simple procedure in modification, and (3) the lack of sufficient fundamental understanding of the activation of modified TiO2. These challenges should be overcome to significantly improved the photocatalytic performance of TiO2-based photocatalytic materials for future practical applications.

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Distribution and contamination status of phthalic acid esters in the sediments of a tropical monsoonal estuary, Cochin India.

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