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Review Article

Degrading Endocrine Disrupting Chemicals from Wastewater by TiO_2 Photocatalysis: A Review

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Widespread concerns continue to be raised about the impacts of exposure to chemical compounds with endocrine disrupting activities. To date, the percolation of endocrine disrupting chemical (EDC) effluent into the aquatic system remains an intricate challenge abroad the nations. With the innovation of advanced oxidation processes (AOPs), there has been a consistent growing interest in this research field. Hence, the aim of this paper is to focus one such method within the AOPs, namely, heterogeneous photocatalysis and how it is used on the abatement of EDCs, phthalates, bisphenol A and chlorophenols in particular, using TiO_2-based catalysts. Degradation mechanisms, pathways, and intermediate products of various EDCs for TiO_2 photocatalysis are described in detail. The effect of key operational parameters on TiO_2 photocatalytic degradation of various EDCs is then specifically covered. Finally, the future prospects together with the challenges for the TiO_2 photocatalysis on EDCs degradation are summarized and discussed.

1. Introduction

Disruption of the endocrine system in wildlife and humans by synthetic organic chemicals has recently received considerable attention worldwide due to the recognition of that the environment is contaminated with various endocrine disrupting chemicals (EDCs) that exert hormonal imbalance activity [1]. An endocrine disruptor is defined by the European Commission (1996) as an exogenous substance or a mixture that alters the function of the endocrine system and consequently causes adverse health effects in an organism or its progeny or (sub)populations [2]. The causative chemicals of endocrine disruption in wildlife populations are wide ranging and include a plethora of industrial chemicals such as polycyclic aromatic hydrocarbons (PAHs), brominated flame retardants, several pesticides, dioxins, parabens, bisphenol A, phthalates, organic solvents, and some heavy metals as well as the naturally occurring phytoestrogens [2–6].

EDCs can be classified according to the mode of their endocrine actions. The most commonly reported EDCs in the environment are estrogenic, antiestrogenic, antiandrogenic, androgenic, and thyroidal [8]. The EDCs may function via modes of action such as mimicking endogenous hormones, antagoniting of hormone receptors, disrupting hormone secretion or metabolism, or disrupting natural hormone production pathways [9, 10]. Endocrine disruptors are also hypothesized to play a role in the pathogenesis of various disorders including male and female infertility, sexual underdevelopment, birth defects, endometriosis, and malignancies [2, 6, 11]. In fact, some EDCs have been shown to have multiple modes of action, which can lead to deleterious effects on the earth ecosystems [12]. Enormous examples of reproductive and developmental abnormalities have been reported over the years in a broad spectrum of wildlife including invertebrates, fish, amphibians, birds, and mammals [3, 5, 13], many of which are associated with EDCs exposure.

Enormous examples of endocrine disruption in wildlife involve animals that are living in or closely associated with the aquatic environment. This is perhaps not surprising considering that surface water acts as a sink for both natural and anthropogenic chemicals discharged into the environment [8, 14]. Sources by which EDCs contaminated the surface water are via sewage effluents from domestic and industrial facilities and industrial effluent discharges [15].

The quantity of chemicals within the aquatic environment together with the inherent susceptibility of aquatic life to the effects of EDCs, leads to significant impacts on the biota of aquatic ecosystems. In certain water bodies with large inputs of anthropogenic chemicals, aquatic life could be continually exposed to a huge range of EDCs at different concentrations. Concentration of EDCs in surface water has been reported in the ranges of $\mathrm{ng}\cdot\mathrm{L}^{-1}$ for alkylphenols and bisphenols [16, 17]. Despite their low concentration present in the aquatic environment, the hormone-like chemicals have been listed as hazardous pollutants by both the US Environmental Protection Agency (USEPA) and the European Union (EU) due to the fact that even a trace amount of them is adequate to initiate estrogenic activity.

Various chemical, physical, and biological treatment processes are currently proposed for the removal of EDCs. However, conventional water and wastewater treatment plants using activated sludge and/or charcoal adsorption systems are ineffective and nondestructive for many EDCs including BPA and chlorophenols [19, 20]. In the recent years, an alternative to the conventional methods is "advanced oxidation processes" (AOPs) based on the in situ generation of nonselective and highly reactive species such as hydroxyl radicals ($^{\bullet}\mathrm{OH}$), superoxide anion radicals ($O_2^{\bullet -}$), and hydrogen peroxide (H_2O_2) as initiators of the oxidative degradation. Among AOPs, heterogeneous photocatalysis using titanium dioxide (TiO_2) has become the focus of intense interest, owing to its chemical and photostability, able to efficiently catalyze reactions and superior ability for the removing a large variety of organic and inorganic pollutants in aqueous media, even form the gaseous environment [21–24]. Since AOPs rely on the generation of highly reactive radicals to react with pollutants, there are many operational parameters such as light intensity and wavelength; initial substrate concentration, catalyst loading, solution pH, reaction temperature, and the presence of oxygen can affect the efficiency of these processes. Consequently, understanding the roles of various operational parameters is crucial from the perspective of efficient design and application of photocatalysis processes to ensure sustainable operation in wastewater treatment. This paper aims to address the fundamentals of heterogeneous photocatalytic degradation of common endocrine disruptors, namely, phthalates, bisphenol A and chlorophenols using TiO_2-based catalysts. This paper also describes the degradation pathways that EDCs undergo with some of the intermediates that are generated during their degradation. Moreover, the effect of key operational parameters on TiO_2-photocatalyzed degradation of EDCs is then presented. Finally, the future prospects together with the challenges for the TiO_2 photocatalysis on EDCs degradation are summarized and discussed.

2. Overview of Industrial Endocrine Disruptors

Among numerous EDCs used in industrial processes, the three potential disruptors that have recently received scientific and public interest are phthalates, bisphenol A, and chlorophenols. The common feature of all is that they are produced in huge quantities, and a substantial fraction is discharged into the environment.

2.1. Phthalates. Phthalates or phthalic acid esters (PAEs) have been widely used as plasticizers for polyvinyl chloride (PVC) resin, cellulose film coating, styrene, adhesives, cosmetics, pulp and paper manufacturing [15, 25–28]. Other important usages of PAEs are in plumbing, nonionic surfactants, pesticide formulations, construction materials, and vinyl upholstery, to impart flexibility and softness to plastics [29]. About 60 different phthalates are produced worldwide and consumed for diverse purposes. During product manufacturing and wasteland filling, many phthalates-based chemicals are easily transported to the environment, in which they are bonded noncovalently to allow the required degree of flexibility. The PAEs such as dimethyl phthalate (DMP) and diethyl phthalate (DEP) are among the most frequently identified in diverse environmental samples including surface marine waters, freshwaters, and sediments [30, 31]. In Malaysia, studies focusing on concentrations of PAEs in highly industrialized Klang Valley have found varying concentrations of PAEs ranging from 0.1 to $64.3\,\mu\mathrm{g}\cdot\mathrm{L}^{-1}$ in the river water and 0.49 to $15.0\,\mu\mathrm{g}\cdot\mathrm{L}^{-1}$ in sediments [32]. The estrogenic activity of eight PAEs such as dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), dihexyl phthalate (DHP), diisoheptyl phthalate, di-*n*-octyl phthalate, diiso-nonyl phthalate, and diisodecyl phthalate was discovered by Zacharewski et al. [33]. Further studies in fish have shown that both BBP and DEP induced vitellogenin (VTG) at an exposure to low concentration in the range of $\mu\mathrm{g}\cdot\mathrm{L}^{-1}$ via the water [34, 35]. Numerous in vivo screens and tests have demonstrated that PAEs mediated their effects through binding to the estrogen receptor [33, 36]. In addition to these estrogenic effects, some PAEs are also considered to be toxic to microorganisms, aquatic life, and human beings [37]. Recent studies have indicated that phthalate metabolites such as monoethyl phthalate (MEP), mono-(2-ethylhexyl) phthalate (MEHP), mono-*n*-butyl phthalate (MBP), and monobenzyl phthalate (MBzP) can induce DNA damage in human sperm [38, 39].

2.2. Bisphenol A. Bisphenol A (BPA) was first discovered as an estrogen in the mid of 1930s, when it was used as an estrogen for clinical use [8]. Then, in the 1950s, BPA was used to react with carbonyl dichloride to produce polycarbonate polymer and subsequently to synthesize epoxy resins, which are now used widely including as lacquer preservatives in the lining of food cans, in automotive parts, and in compact discs [1]. In addition, BPA is consumed as a resin in dental fillings, as powder paints, as additives in thermal paper, as a developer in dyes, optical lenses, and for encapsulation of electrical and electronic parts. BPA is currently produced at a rate about 2.5 million ton/yr worldwide with a significantly increasing trend [40, 41]. Due to its large-scale production and extensive applications, BPA has become an integral part of wastewater streams. The contaminant may also be transferred from different sources to food via (i) food processing by contact with resins, plastics, lacquers, gaskets, and containers and (ii) migration from packaging and bottling materials. One of the first reports of the estrogenic activity of migrating BPA from polycarbonate flasks during autoclaving was documented in 1993 [42]. BPA has also been shown to be estrogenic via in vivo screenings [43, 44]. In vivo effects in rat, a low-dose effect of BPA was observed [45]. Whereas, in vivo studies in fish, a concentration of $16\,\mu g\cdot L^{-1}$ BPA in the water can affect the progression of spermatogenesis [46]. Furthermore, BPA has also been found to have the paradoxical effect to block the beneficial effects of estradiol on neuronal synapse formation and the potential to disrupt thyroid hormone action [47–49]. More extensive reviews on endocrine effects of BPA can be found in the literatures [50–52].

2.3. Chlorophenols. Of all the nineteen chlorophenols, only seven of these compounds include monochlorophenols, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4,5-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol have been used by the industry [54]. 2,4-dichlorophenol (DCP) and pentachlorophenol (PCP), in particular, have been shown to have endocrine disrupting effects [55, 56]. In general, compound with a higher substituted chlorine atom appears to be rather more resistant to biodegradation—the half life in water can reach 3.5 months in aerobic waters for PCP and some years in organic sediments [57]. The occurrence of these compounds in drinking water can cause objectionable taste and odour at concentration below $10\,\mu g\cdot L^{-1}$ and affecting adversely the environment [54, 58, 59]. Due to broad-spectrum antimicrobial properties, these compounds have been used in wood preservation, disinfectants, leather, paints, agricultural seeds (for nonfood uses), and pulp and paper manufacturing. In addition, they have been widely employed in many industrial processes as synthesis intermediates in the production of pesticides, herbicides, fungicides, insecticides, pharmaceuticals, and dyes. The presence of DCP and PCP have reported to induce VTG synthesis in fish at concentrations of $1.0\,mg\cdot L^{-1}$ for 21-day exposure and $200\,\mu g\cdot L^{-1}$ for 28-day exposure, respectively, [60, 61]. PCP has also been demonstrated to affect pituitary function and the release of gonadotrophins in fish at concentration of $750\,\mu g\cdot mL^{-1}$ for 48-h exposure [62]. As for many other EDCs, longevity of exposure affects both the threshold and the magnitude of the response; PCP and DCP have shown bioconcentration factor values of $(4.9 \pm 2.8) \times 10^3$ and $(3.4 \pm 3.0) \times 10^2$, respectively, at their low concentrations around $\mu g\cdot L^{-1}$ [63].

3. Degradation of EDCs in Wastewater by TiO_2 Photocatalytic Reactions

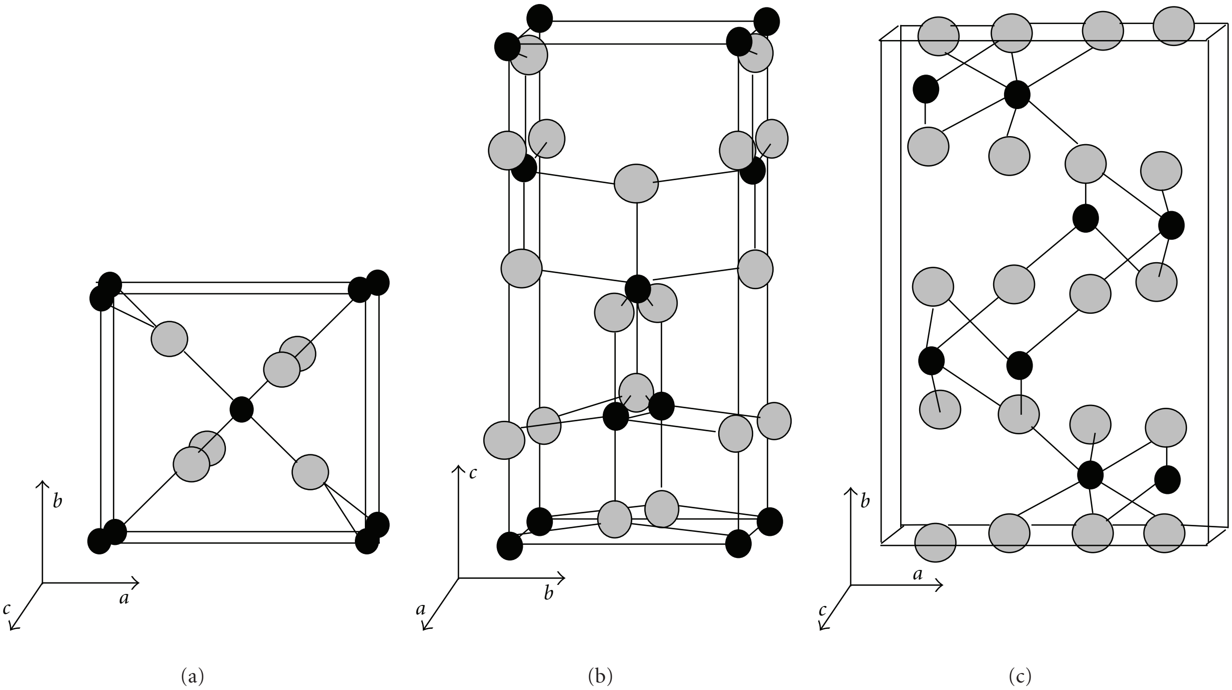
3.1. Titanium Dioxide Photocatalyst. Titanium dioxide (TiO_2), also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium. In nature, TiO_2 exists in three different polymorphs that are rutile, anatase, brookite. TiO_2 is typically extracted from minerals such as ilmenite, leucoxene ores, or rutile beach sand and commercially produced using sulphate route—the ground slag or ilmenite is digested with strong sulphuric acid to produce titanium oxysulphate and iron sulphate. The titanium oxysulphate is then subjected to selective thermal hydrolysis to produce hydrated TiO_2. This is further washed and calcined to produce TiO_2 (1) and chlorine route—rutile is converted to titanium tetrachloride by chlorination in the presence of petroleum coke. The titanium tetrachloride is then condensed to a liquid and reacted with hot oxygen to form TiO_2 (2) [65, 66]:

$$\begin{gathered} FeTiO_3 + 2H_2SO_4 \longrightarrow TiOSO_4 + FeSO_4 + 2H_2O \\ TiOSO_4 + H_2O \xrightarrow{\text{heat}} TiO_2\,nH_2O + H_2SO_4 \\ TiO_2\,nH_2O \longrightarrow TiO_2 + nH_2O \end{gathered} \tag{1}$$

$$\begin{gathered} TiO_2\ (\text{impure}) + C + 2Cl_2 \longrightarrow TiCl_4 + CO_2 \\ TiCl_4 + O_2 \longrightarrow TiO_2\ (\text{pure}) + 2Cl_2 \end{gathered} \tag{2}$$

In general, TiO_2 structures of rutile, anatase, and brookite can be described in terms of (TiO_6) octahedral. These three crystal structures differ from one another by the distortion of each octahedral and by the assembly patterns of the octahedral chains. Anatase is built up from octahedrals which are mainly connected by their vertices. Octahedral structures in rutile are mostly connected by the edges. Both vertical and edge connections are found in the octahedral structure of brookite [7, 67]. Even though both anatase and rutile are the same tetragonal system, anatase has longer vertical axis of the crystals than rutile. Meanwhile, brookite has an orthorhombic crystalline system (Figure 1). Among these crystal structures, only anatase and rutile are photocatalytically active. Moreover, rutile is the thermodynamically most stable phase of TiO_2. It is by about 1.2 to $2.8\,kcal\cdot mol^{-1}$ more stable than anatase with temperature ranges from 700 to 1000°C. Based on optical absorption spectra, 3.2 eV is the band gap energy of anatase and in rutile 3.0 eV is its energy, implying the rutile has an aggressive excitation of solar radiation [67, 68]. Calcinated TiO_2, especially in the rutile form, is very stable and insoluble in water; it is also insoluble or partly soluble in concentrated and hot acids.

According to historical documents, TiO_2 was first discovered in the form of black sand in 1791 on the beaches of Cornwall, England, by William Gregor, who recognized the presence of a new element in ilmenite. The potential use of TiO_2 was not established until earlier in the last century, when the Norwegian chemists, Jebsen and Farup, worked on TiO_2 extraction from ilmenite. They revealed that the extracted TiO_2 has a very high refractive index and thus, enabled its potential as a pigment. Independently of Jebsen and Farup, Rossi and Barton in the United States have also started with the extraction of TiO_2 from minerals of ilmenite, titaniferous iron ores, and rutile their researches eventually led to the establishment of production site at Niagara Falls towards the end of the First World War. Until the turn of the 1930s, gradually growing of uncoated



(a)

(b)

(c)

Figure 1: Crystal structures of rutile (a), anatase (b), and brookite (c) [7].

anatase and rutile pigments manufacturing activities have been evidenced, driving to the full scale of TiO_2 production [65].

The revolution of TiO_2 was started when Fujishima and Honda [71] discovered the possibility of water splitting by photochemical cell having an inert cathode and rutile TiO_2 anode in 1972. This event marked the beginning of a new era in heterogeneous photocatalysis. As a consequence, the application of TiO_2 photocatalysis extended to environmental frontiers. Frank and Bard [72] for the first time reported the possibilities of using TiO_2 to degrade cyanide in aqueous medium under solar irradiation. Subsequent reports of photocatalytic reduction of CO_2 by Inoue et al. [73] attracted more interest in TiO_2 photocatalysis. In addition to environmental remediation, TiO_2 is also an inorganic chemical widely used in paints, plastics, inks, paper, personal care products, and electronic components. These widespread applications of TiO_2 are attributed to the stability of its chemical structure, biocompatibility, physical, optical, and electrical properties [74].

3.2. Mechanism of TiO_2 Photocatalysis. Heterogeneous photocatalysis is an increase in the rate of a thermodynamically allowed ($\Delta G < 0$) reaction in the presence of photocatalyst with the increase originating from the creation of some new reaction pathways involving photogenerated species and a decrease of the activation energy [67]. Generally, there are five essential key steps in the heterogeneous photocatalysis on the surface of TiO_2, namely, the (1) photoexcitation, (2) diffusion, (3) trapping, (4) recombination, and (5) oxidation [75–80].

3.2.1. Photoexcitation. Upon irradiation of TiO_2 with light energy equivalent to or greater than its band gap energy, the electron is excited from the valence band (vb) to the conduction band (cb). Figure 2 illustrates the mechanism of electron-hole pair generation when the TiO_2 particle is irradiated with sufficient light energy ($h\nu$). The photoexcitation leaves behind a positive hole in the valence band and, therefore, creating the electron-hole pair:

$$\mathrm{TiO_2} + h\nu \longrightarrow e_{\mathrm{cb}}{}^{-} + h_{\mathrm{vb}}{}^{+} \tag{3}$$

$$\begin{gathered} e_{\mathrm{cb}}{}^{-} \longrightarrow e_{\mathrm{tr}}{}^{-} \\ h_{\mathrm{vb}}{}^{+} \longrightarrow h_{\mathrm{tr}}{}^{+} \end{gathered} \tag{4}$$

3.2.2. Diffusion. In this step, water molecules (H_2O) and organic pollutant (R) are diffused to the interface of TiO_2 surface, forming spatial bonding with the TiO_2 solid:

$$\begin{gathered} \mathrm{Ti^{IV}} + \mathrm{H_2O} \longrightarrow \mathrm{Ti^{IV}} - \mathrm{H_2O} \\ \mathrm{TiO_2} + R_1 \longrightarrow R_{1\mathrm{ads}} \end{gathered} \tag{5}$$

3.2.3. Trapping. Water molecules and hydroxyl ions (OH^-) are available as electron donors and react with the photogenerated holes to form highly reactive and strong oxidizing hydroxyl radicals ($^{\bullet}OH$). On the contrary, oxygen molecules (O_2) are efficient electron acceptors. Through the reduction of O_2 with photogenerated electron, reactive superoxide radical anions ($O_2{}^{\bullet -}$) are produced. This reaction would

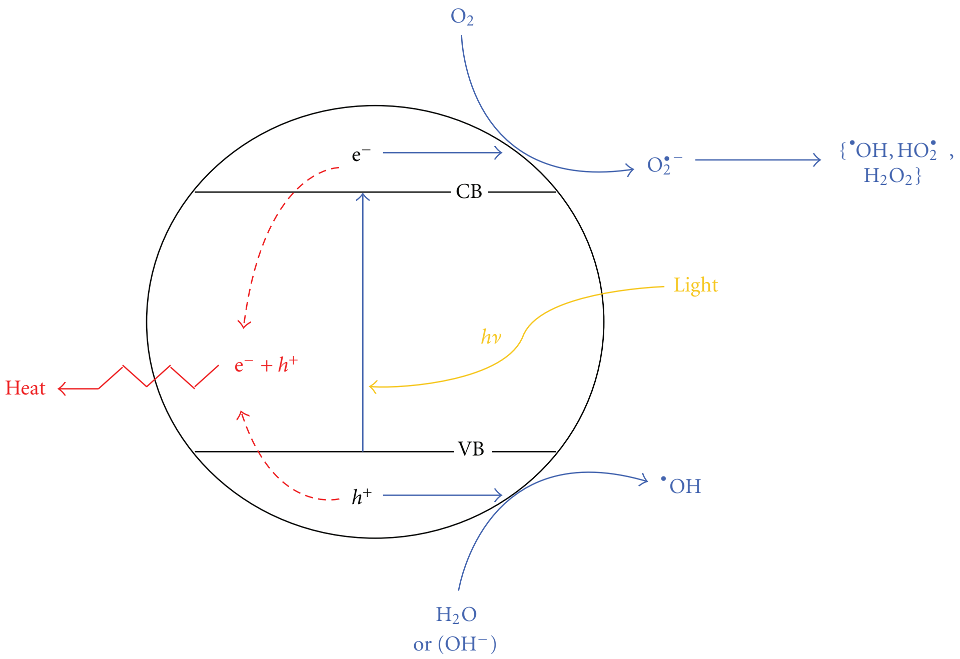


Figure 2: Schematic diagram illustrating the mechanism of photocatalysis on TiO_2 particles.

provide an additional pathway capable of totally mineralizing of the EDCs molecules:

$$\begin{gathered}
Ti^{IV} - OH^- + h^+ \longrightarrow Ti^{IV} - OH^\bullet \\
Ti^{IV} - H_2O + h^+ \longrightarrow Ti^{IV} - OH^\bullet + H^+ \\
R_{1ads} + h^+ \longrightarrow R_{1ads}{}^+ \\
Ti^{IV} + e^- \longrightarrow Ti^{III} \\
Ti^{III} + O_2 \longrightarrow Ti^{IV} - O_2{}^{\bullet -}
\end{gathered} \tag{6}$$

3.2.4. Recombination. In competition with charge transfer to diffused organic pollutants, there is the opportunity that both electron-hole pair recombination and trapped carrier recombination happen. These recombinations can occur either in the volume of the TiO_2 or on the surface of TiO_2, liberating input energy as heat:

$$e^- + h^+ \longrightarrow \text{heat} \tag{7}$$

3.2.5. Oxidation. The resulted $^\bullet OH$ radicals in the reacting system can initiate radical reactions, subsequently oxidizing the organic pollutants. Other radicals such as hydroperoxyl radicals ($HO_2{}^\bullet$) and hydrogen peroxide (H_2O_2) are also generated and involved in the reactions to degrade EDCs in water as follows.

(i) Reaction with radical attack on organic pollutants:

$$\begin{gathered}
Ti^{IV} - OH^\bullet + R_{1ads} \longrightarrow Ti^{IV} + R_{2ads} \\
Ti^{IV} - OH^\bullet + R_1 \longrightarrow Ti^{IV} + R_2 \\
OH^\bullet + R_{1ads} \longrightarrow R_{2ads} \\
OH^\bullet + R_1 \longrightarrow R_2
\end{gathered} \tag{8}$$

(ii) Other reactions with radical:

$$\begin{gathered}
e^- + Ti^{IV} - O_2{}^{\bullet -} + 2H^+ \longrightarrow Ti^{IV} + H_2O_2 \\
Ti^{IV} - O_2{}^{\bullet -} + H^+ \longrightarrow Ti^{IV} + HO_2{}^\bullet \\
H_2O_2 + OH^\bullet \longrightarrow H_2O + HO_2{}^\bullet \\
O_2{}^{\bullet -} + H^+ \longrightarrow HO_2{}^\bullet \\
2HO_2{}^\bullet \longrightarrow H_2O_2 + O_2 \\
H_2O_2 + e^- \longrightarrow OH^- + OH^\bullet
\end{gathered} \tag{9}$$

(iii) Nonproductive radical reactions:

$$\begin{gathered}
2OH^\bullet \longrightarrow H_2O_2 \\
2HO_2{}^\bullet \longrightarrow H_2O_2 + O_2 \\
2OH^\bullet \longrightarrow H_2O_2 \longrightarrow H_2O + O_2
\end{gathered} \tag{10}$$

$$OH^\bullet + HCO_3{}^- \longrightarrow CO_3{}^{\bullet -} + \mathrm{H2O} \tag{11}$$

The primary photoreactions (3) to (11) reveal the indispensable role of charge carriers (electron-hole pair) in the TiO_2 photocatalysis. Essentially, $^\bullet OH$, $HO_2{}^\bullet$, and $O_2{}^{\bullet -}$ radicals as well as photogenerated hole (h^+) are highly reactive intermediates that will attack repeatedly in the reacting system and ultimately lead to complete mineralization of the EDCs. The mediation of radical oxidative species in the photocatalytic reaction has been evidenced by electron paramagnetic resonance spectroscopy (EPR) using spin trap such as 5,5-dimethylpyrroline-N-oxide (DMPO). This process led to the formation of a stable free radical whose EPR spectra was the characteristic of the trapped

$^\bullet$OH radical [81]. Another analysis of the $^\bullet$OH radical formation on photocatalyst surface in solution has been performed through simple terephthalic acid-fluorescence (TA-FL) technique. Using this technique, the intensity of the peak attributed to 2-hydroxyterephthalic acid was known to be proportional to the amount of $^\bullet$OH radicals formed [82, 83]. More recently, the $^\bullet$OH radical produced on various photocatalysts has also been quantitatively investigated by Xiang et al. [84] via photoluminescence (PL) technique using coumarin (COU) as a probe molecule. Furthermore, electron spin resonance (ESR) has been used to study the radical oxidative species detection in solutions. This technique allowed to monitor the presence of $^\bullet$OH, $HO_2^\bullet$, and $O_2^{\bullet-}$ radicals in photocatalytic systems [18, 85–87].

4. Degradation Pathways of Various EDCs

Photocatalytic degradation reactions of organic pollutants usually take more than one elementary step to complete. An intermediate is the reaction product of each of these steps which eventually forms the final product in the last step. The desired final products for a complete photocatalytic degradation reaction are CO_2 and H_2O. Identification of these reaction intermediates would provide a further insight into the mechanism involved in the photocatalytic degradation process and will help to get a total picture of the degradation pathway. On this facet, the photocatalytic degradation schemes for some phthalates, bisphenol A, and chlorophenols suggested by researchers are given as below. For one thing, as to different types of organic pollutants, the degradation pathways are different. For another, as to a certain organic pollutant, the degradation pathway will be possibly different if different catalysts or different experiment conditions are applied.

4.1. Phthalates

4.1.1. Dimethyl Phthalate. Ding et al. [18] studied the photocatalytic degradation pathway of dimethyl phthalate (DMP) using TiO_2-pillared montmorillonite as catalyst under UV irradiation. The photocatalytic degradation pathway of DMP is presented in Figure 3. By GC-MS analysis, a total of twelve products were detected from the photocatalytic degradation of DMP. In the first pathway, $^\bullet$OH radicals added to the aromatic ring of the DMP and yielded hydroxylated DMP. With the further degradation of the intermediate, 2,3-dihydroxymethyl benzoate, 2,4-dihydroxymethyl benzoate and 2,6-dihydroxymethyl benzoate were observed. These three intermediates were reported to form by attack of another $^\bullet$OH radical on different positions in the benzene ring and removal of an ester group from hydroxylated DMP at the same position. Moreover, these three intermediates were also formed by the double attack of $^\bullet$OH radicals on the benzene ring of methyl benzoate. By ring-rupturing reactions, these aromatic intermediates were presumably further oxidized into aliphatic intermediates, such as 2,3-butanediol, 1,2-propanediol, and 1,2-glycol, and finally mineralized into CO_2 and H_2O. In the second pathway, a carbonyl group of DMP was excited after the photon absorption, and then cleavage of one C-C bond connecting the $COOCH_3$ group to the aromatic ring occurred; in succession, methyl benzoate was generated. Subsequently with further single β-cleavage of the ester group, removal of a $^\bullet CH_3$ radical occurred, and benzoic acid with a carbonic acid (COOH) structure was formed. The benzene ring of benzoic acid was demonstrated to attack by $^\bullet CH_3$ or $^\bullet$OH radicals alternatively generated 2,3-dimethyl-benzoic acid and 2-hydroxy-benzoic acid, respectively. The resulting intermediate of 2,3-dimethyl-benzoic acid further decomposed completely into CO_2 and H_2O, while 2-hydroxy-benzoic acid followed by a ring-cleaving process to give rise to 2-hydroxy-3-methyl-butyric acid, which oxidized also into CO_2 and H_2O at last.

4.1.2. 1,2-Diethyl Phthalate. Muneer et al. [53] identified the intermediates and degradation pathway of 1,2-diethyl phthalate (DEP) in aqueous suspensions of TiO_2 through GC-MS analysis. A proposed degradation pathway of DEP is shown in Figure 4. The GC-MS analysis of DEP at 195-min irradiated mixture showed the formation of three photoproducts $C_{12}H_{16}O_5$, $C_8H_4O_3$, and $C_{10}H_{10}O_4$ appearing at reaction times of 15.4, 16.8, and 26.8 min, respectively.

4.1.3. Dibutyl Phthalate. Xu et al. [64] investigated the photocatalytic degradation of dibutyl phthalate (DBP) catalyzed by polyoxotungstate/TiO_2 nanocomposites under simulated solar irradiation. The photocatalytic degradation intermediates and pathway are shown in Figure 5. Their findings revealed that DBP ($C_{16}H_{22}O_4$) was attacked by $^\bullet$OH radicals at aromatic ring and aliphatic chain to produce three different hydroxylated intermediate isomers of $C_{16}H_{22}O_5$ ((a), (b), and (c)). Under the oxidation of $^\bullet$OH radicals, isomers (a) and (b) lost butoxy groups to produce different isomers of $C_8H_6O_5$ ((e) and (f), resp.). Meanwhile, isomer (c) was converted to aldehyde of $C_{16}H_{20}O_5$ (g). $C_{12}H_{14}O_4$ (d) was formed by the cleavage of the alkyl-oxygen bond of DBP. Decarboxylation from intermediates (d) to (f) resulted in $C_{11}H_{14}O_2$ (h) and $C_7H_6O_2$ (i). In addition, cleavage of alkyl-oxygen bond in $C_{11}H_{14}O_2$ (h) also generated $C_7H_6O_2$ (i). With a further decarboxylation from $C_7H_6O_2$ (i), dihydroxybenzene and; quinine, were stated to form. Quinone was further oxidized, and thereby ring-opening reaction happened, leading to a series of aliphatic acids including butanedioic acid, formic acid, and acetic acid. Additionally, when $^\bullet$OH radicals attacked directly two carbon atoms in α-position of DBP, both of the positions were broken into a long chain structure of $C_{11}H_{16}O_2$ (j). In the end, all the intermediates were mineralized to CO_2 and H_2O.

4.1.4. n-Butyl Benzyl Phthalate. Xu et al. [69] examined the photocatalytic degradation of *n*-butyl benzyl phthalate (BBP) using TiO_2 as catalyst under UV light irradiation. With the identification of intermediates, a proposed pathway of the photocatalytic degradation of BBP is presented in Figure 6. The results in their investigation showed that monobutyl phthalate, monobenzyl phthalate, and phthalic acid were the main intermediates of BBP degradation. The

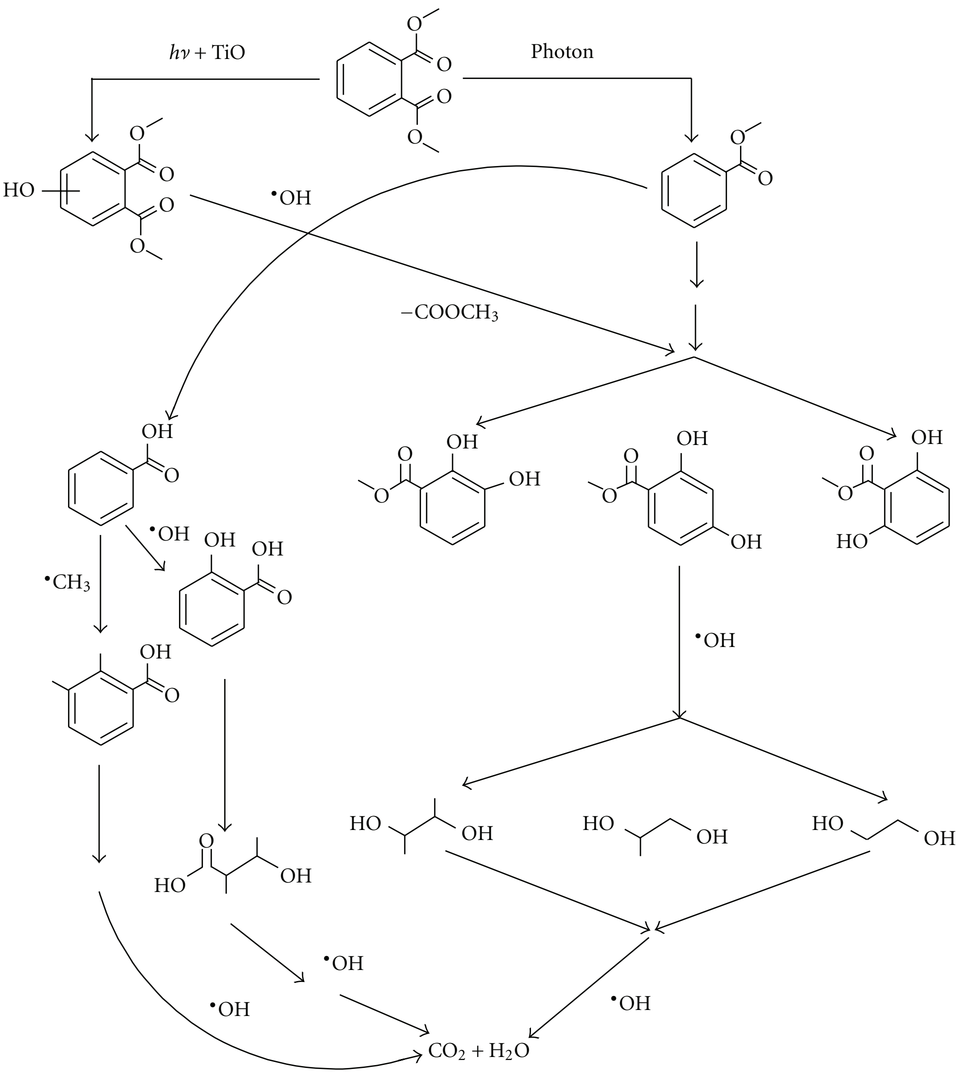


Figure 3: Photocatalytic degradation scheme for DMP [18].

formation of these three intermediates involved the electron transfer reactions and reactions with •OH radicals. The BBP upon the transfer of an electron was reported to form a radical anion, which was further attacked by •OH radicals forming the anionic species. By the loss of a butanol or benzyl alcohol, the species were converted to monobutyl phthalate and monobenzyl phthalate. Under the actions of electrons and then •OH radicals, both monobutyl phthalate and monobenzyl phthalate were converted to phthalic acid.

4.1.5. Di(2-ethylhexyl)phthalate. Chung and Chen [70] studied the degradation of di(2-ethylhexyl)phthalate (DEHP) by TiO_2 photocatalysis. The possible degradation pathway of DEHP is demonstrated in Figure 7. In their photocatalytic degradation process, •OH and •H radi-cals initially attacked the aliphatic chain of DEHP and yielded the intermediates such as benzoic acid, phthalic acid, 2-(butoxycarbonyl)benzoic acid, mono (2-ethylhexyl)phthalate, octyl 4-hydroxybenzoate, and 2-[(octyloxy)carbonyl]benzoic acid. With a further attack from the reactive radicals, the aromatic opened products were formed and finally mineralized to final products of CO_2 and H_2O.

4.2. Bisphenol A. Tao et al. [88] tested the photocatalytic degradation of bisphenol A (BPA) using TiO_2-loaded mesoporous MCM-41 under UV irradiation (λ = 365.0–366.3 nm). Through the GC-MS analysis, the photocatalytic degradation intermediates and the pathway of bisphenol A are shown in Figure 8. Their results noticed that 4-(1-hydroxy-1-methyl-ethyl)-phenol (HMEP) and phenol were initially produced via the photocleavage of phenyl groups by •OH radicals attack. 4-vinyl phenol was then generated by dehydration from HMEP and subsequently oxidized to 4-hydroxyacetophenone. Additionally, 2-methyl-2,3-dihydrobenzofuran was reported to be produced from phenol. These single aromatic intermediates were further oxidized through ring rupturing reactions into aliphatic intermediates containing $C_4H_{10}O$, $C_5H_{10}O$, and $C_6H_{14}O_2$, which were mineralized into CO_2 and H_2O ultimately.

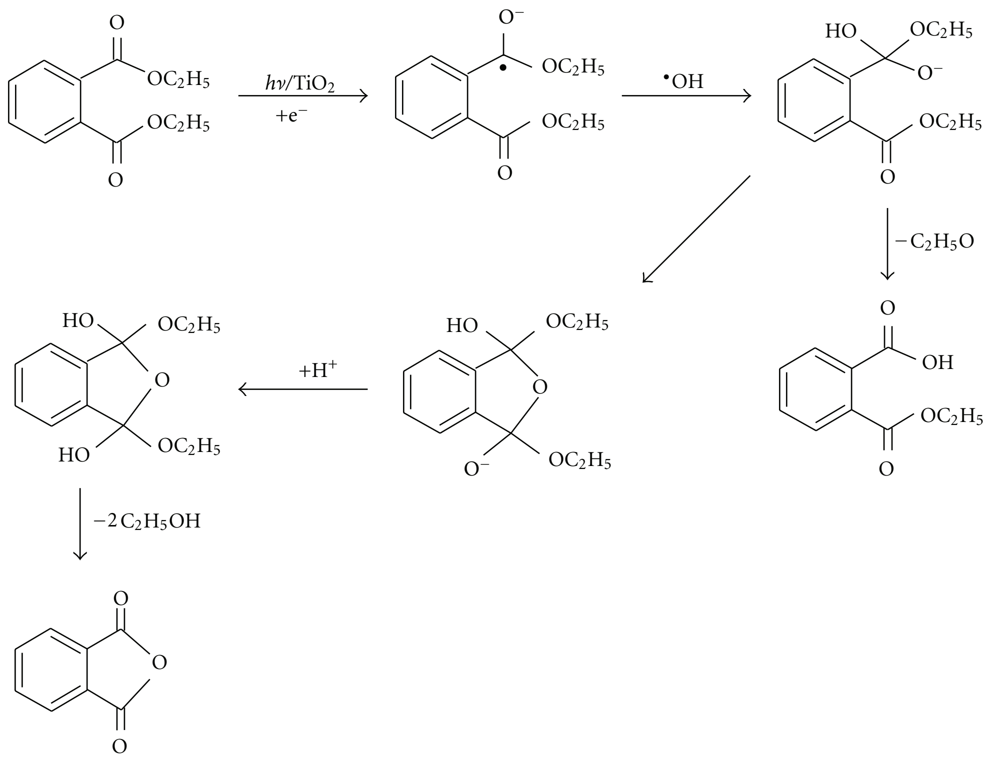


FIGURE 4: Photocatalytic degradation scheme for DEP [53].

4.3. Chlorophenols

4.3.1. 2,4-Dichlorophenol. Zang et al. [89] investigated the photocatalytic degradation of 2,4-dichlorophenol (DCP) catalyzed by TiO_2 suspensions. The proposed photocatalytic degradation pathway of DCP is presented in Figure 9. Their study noted that DCP was firstly converted to chlorohydroquinone, which was converted to chlorobenzoquinone and hydroxybenzoquinone. Then, hydroxybenzoquinone was reported to convert into acidic intermediates. Subsequently, the formed acidic intermediates were oxidized to final products of CO_2 and H_2O.

4.3.2. Pentachlorophenol. Jung et al. [90] studied the photocatalytic degradation of pentachlorophenol (PCP) using TiO_2 thin films coated on stainless steel cloth. The photocatalytic degradation pathway of PCP is shown in Figure 10. In the primary photocatalytic degradation process, $^\bullet OH$ radicals attacked the PCP and yielded intermediates such as tetrachlorocatechol, tetrachlorohydroquinone, and tetrachlororesorcinol. With the further degradation of the intermediates, 1,2,4,5-tetrachloro-*p*-benzoquinone, 1-hydro-2,4,5-trichloro-*p*-benzoquinone, and hydroxyhydroquinone were formed. Eventually, an oxidative aromatic ring-opening reaction happened and rendered the formation of short-chain carboxylic acids, such as tartaric, oxalic, malic, hydroxymalonic, and glycolic, followed by oxidation to CO_2.

5. Operating Parameters in Photocatalytic Processes

The rate and efficiency of a photocatalytic reaction depends on a number of operating parameters that govern the degradation of EDCs in wastewater such as light intensity and wavelength, initial substrate concentration, catalyst loading, solution pH, reaction temperature, and dissolved oxygen.

5.1. Effect of Light Intensity and Wavelength. Light irradiation plays a significantly important role in all of photocatalytic reactions and generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst. The energy of a photon is related to its wavelength, and the overall energy input to the photocatalytic process is dependent on the light intensity. Therefore, the effects of both intensity and wavelength have been studied in numerous investigations for various organic pollutants including phthalates, bisphenol A, and chlorophenols. It has been reported that at low light intensity (catalyst dependent, surface reaction limited) the rate was linearly proportional to the light intensity, while at medium-high intensity, the rate became proportional to the square root of the light intensity, and, at higher light intensity, the rate was independent of the light intensity [91–93]. This variation is likely due to the recombination of photogenerated electron-hole pairs under different irradiation intensities. Huang and

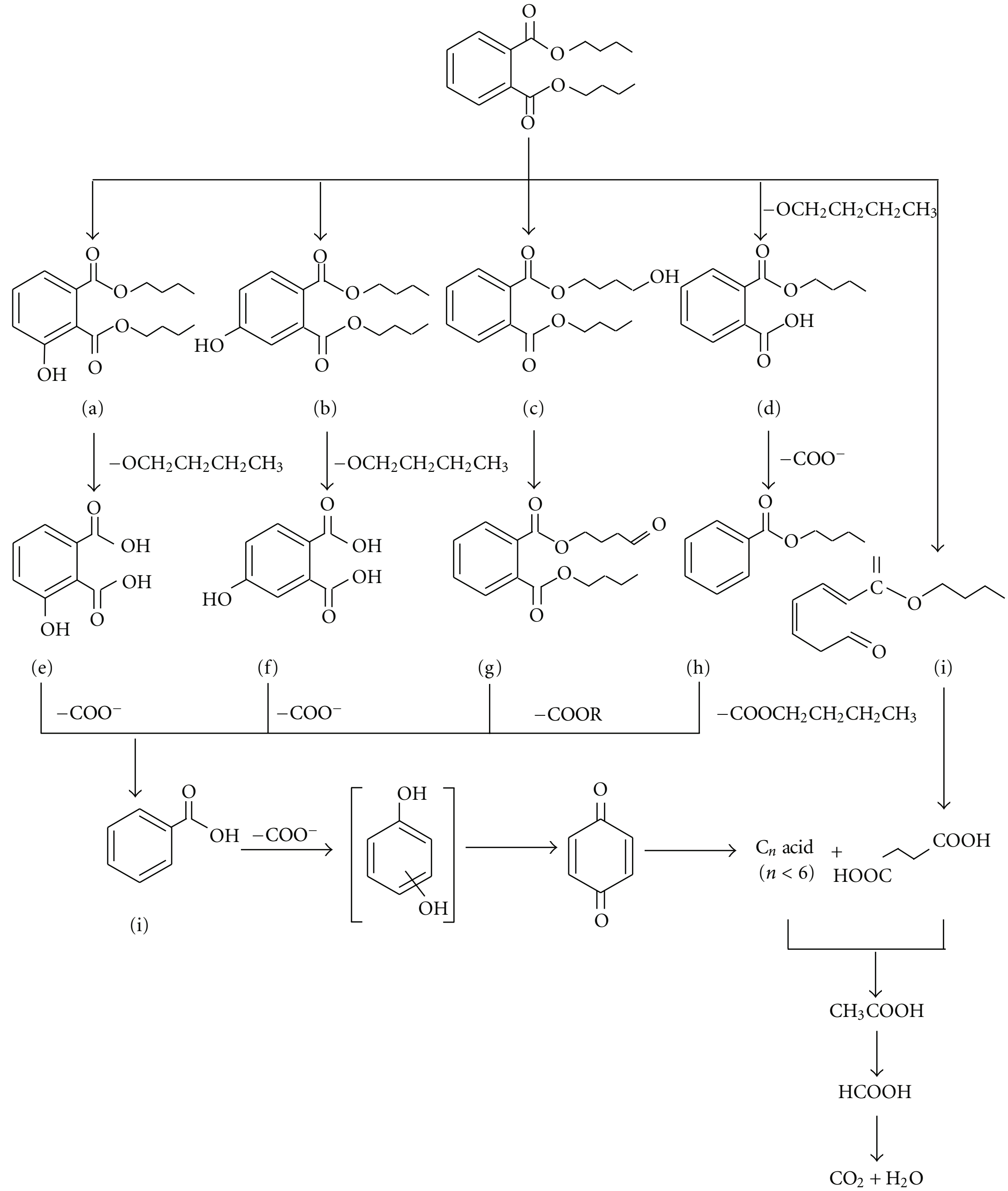


Figure 5: Photocatalytic degradation scheme for DBP [64].

Chen [94] examined the effect of light intensity on the photocatalytic degradation of diethyl phthalate (DEP) using TiO_2 as catalyst. The degradation efficiency of DEP was observed to increase linearly with UV radiation intensity up to 2.50×10^{-6} Einstein$\cdot l^{-1}\cdot s^{-1}$ and then only smaller changes when the light intensity increased from 2.50×10^{-6} to 4.00×10^{-6} Einstein$\cdot l^{-1}\cdot s^{-1}$. Their study explained that, at lower UV intensity, the photocatalytic degradation was limited. As the UV intensity increased, more $^{\bullet}OH$ radicals were formed, thus, resulted in the increase of DEP degradation. Above certain UV intensity, the reaction rate went from first order of pollutant concentration to one-half order. Bayarri et al. [95] compared the degradation and mineralization efficiencies of 2,4-dichlorophenol (DCP) using lamps of UV-A and UV-ABC over TiO_2. The degradation and mineralization efficiencies using UV-ABC were reported to be more efficient than using UV-A. This improvement was related to the combined use of photolysis, photocatalysis, and synergistic effects due to associated photolysis and photocatalysis. Chan et al. [96] tested the effect of UV intensity on the photocatalytic degradation of di(2-ethylhexyl)phthalate (DEHP), and the TiO_2 degradation efficiency increased rapidly from 0 to about 40% with increasing of light intensity from 0 to $8.4\,W\cdot m^{-2}$. After that, the increase in degradation efficiency gradually slowed and reached a maximum of about 72% at $33.6\,W\cdot m^{-2}$. The influence of

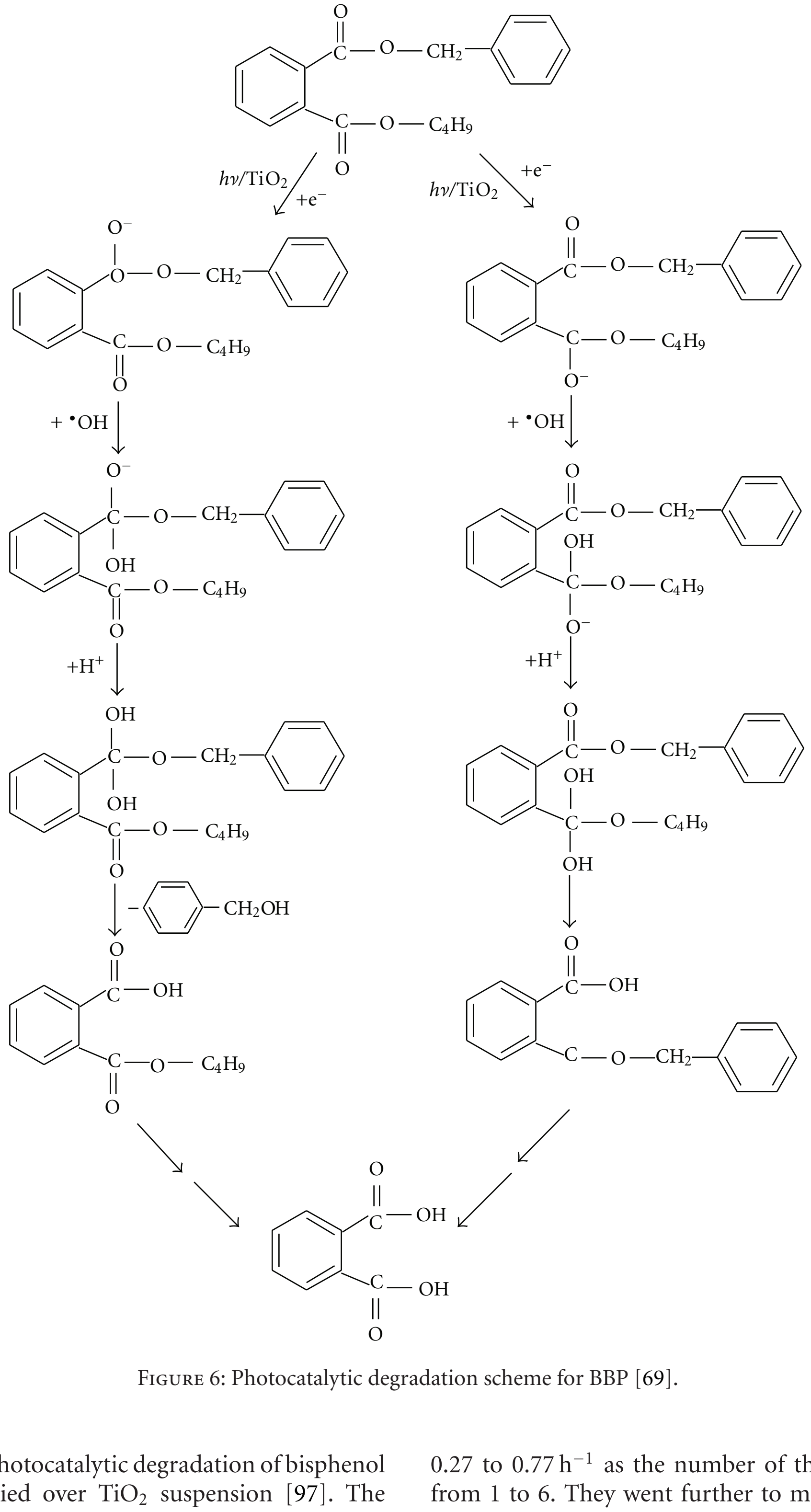


Figure 6: Photocatalytic degradation scheme for BBP [69].

light intensity on the photocatalytic degradation of bisphenol A has also been studied over TiO_2 suspension [97]. The degradation efficiency was reported to increase rapidly in the light intensity up to $0.35\,mW\cdot cm^{-2}$, and then the efficiency increased gradually. Lee et al. [98] investigated the effect of light intensity on the photocatalytic degradation of bisphenol A over immobilized TiO_2 by turning on different number of UV lamps ($\lambda = 365\,nm$). The results in their work indicated that the degradation rate constant increased from 0.27 to $0.77\,h^{-1}$ as the number of the UV lamps increased from 1 to 6. They went further to measure the photon rate of UV lamp and found that the rates were 2.8, 10.1 and $18.3\,\mu E\cdot s^{-1}$; respectively, as 1, 3, and 6 UV lamps were used in the reactor. The enhanced degradation rate was related to the increase of photon rate. Using TiO_2 as catalyst, Minero et al. [99] examined the effect of solar irradiation intensity on the photocatalytic degradation of pentachlorophenol (PCP). Their findings revealed that the PCP degradation and

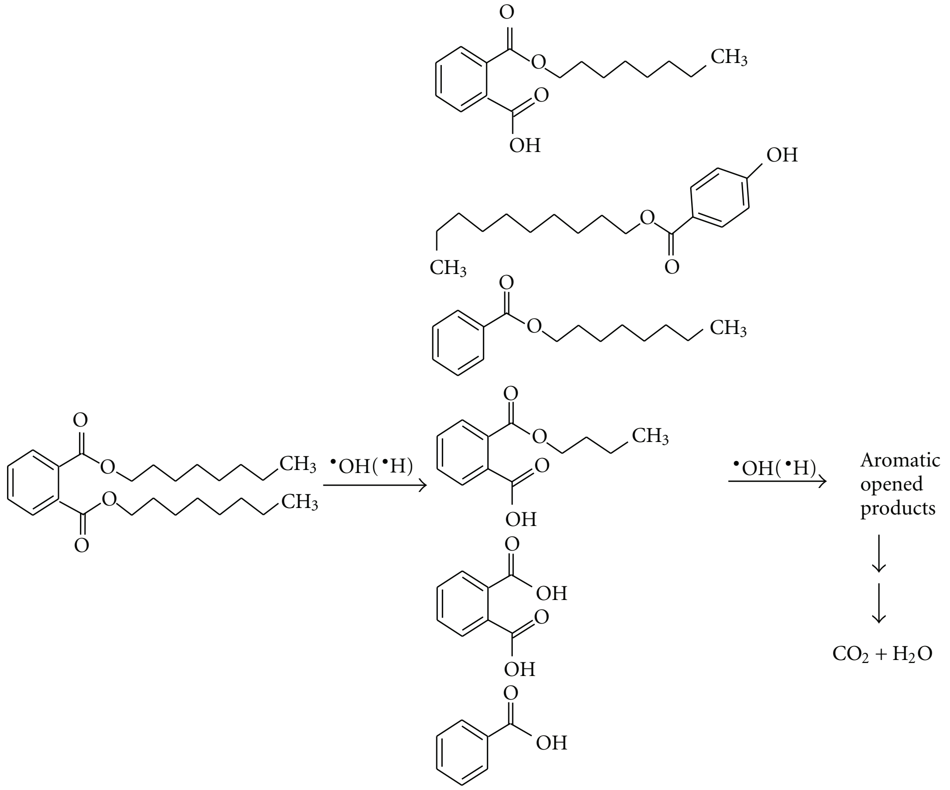


Figure 7: Photocatalytic degradation scheme for DEHP [70].

TOC disappearance rates increased linearly with increasing the solar light intensity. The effects of light intensity and wavelength on the photocatalytic activity of immobilized TiO_2 have also been investigated on the degradation of bisphenol A (BPA) [100]. In their work, three different light sources: germicidal lamp ($\lambda = 254\,nm$), blacklight lamp ($\lambda = 360\,nm$), and vita-lite lamp (visible region) were used to study the effect of light wavelength. The used of both UV lamps was shown to have higher efficiency for the degradation of BPA. The degradation rate constants were reported to be $0.00111\,min^{-1}$ and $0.0067\,min^{-1}$ for germicidal lamp and black-light lamp, respectively, compared to $0.0012\,min^{-1}$ for vita-lite lamp. This effect was ascribed to the insufficient energy of visible lamp to induce the photocatalytic degradation of BPA. On the other hand, the degradation of BPA was accelerated using the germicidal lamp at different light intensities. The degradation rate constant was noticed to increase from 0.0111 to $0.0268\,min^{-1}$ as the light intensity increased from 2 to $6\,W{\cdot}L^{-1}$. Liao and Wang [101] also observed an enhancement of dimethyl phthalate (DMP) degradation with increasing the UV light intensity. The enhanced degradation efficiency was attributed to the higher light intensity provided more light energy for the breaking of chemical bonds of DMP, and the reactions between the light and the TiO_2 catalyst improved the generation of $^{\bullet}OH$ radicals in the solution.

5.2. Effect of Initial Substrate Concentration. Due to the fact that, as the concentration of model pollutant increases, more and more molecules of the organic compound get adsorbed on the surface of the photocatalyst, the initial substrate concentration can influence the extent of reaction rate at the surface of the photocatalyst. Table 1 summarizes a variety of EDCs studied under various initial concentrations. Kusvuran et al. [102] examined the effect of initial concentration on the photocatalytic degradation of 2,4-dichlorophenol (DCP) using UV/TiO_2. Increase in the DCP concentration from 0.1 to 0.5 mM decreased the degradation rate constant, k_{obs}, from 0.0259 to $0.0061\,min^{-1}$. Tsai et al. [20] found that the degradation efficiency of bisphenol A (BPA) was strongly dependent on the initial substrate concentration. The degradation efficiency of BPA over TiO_2 suspension decreased gradually, ranging from 100% to 97% as the initial substrate concentration increased from 1 to $20\,mg{\cdot}L^{-1}$. Nevertheless, the BPA concentration increased from 20 to $50\,mg{\cdot}L^{-1}$; the degradation efficiency showed a significant decreasing trend, ranging from 97% to 67%. Jung et al. [90] investigated the effect of initial concentration in the range of 2.5 to $10\,mg{\cdot}L^{-1}$ on the photocatalytic degradation of pentachlorophenol (PCP) using TiO_2 thin films coated on stainless steel cloth. Maximum PCP degradation was observed at $2.5\,mg{\cdot}L^{-1}$. Chung and Chen [70] conducted the TiO_2 photocatalytic experiment at different di(2-ethylhexyl)phthalate (DEHP) concentrations ranged from 25 to $300\,\mu g{\cdot}L^{-1}$. Their results showed that the degradation efficiency decreased with the increased concentration of DEHP. This was attributed to the rise of internal optical density, which caused the solution became impermeable to UV light. Thiruvenkatachari et al.

Table 1: Effect of initial substrate concentration on the photocatalytic degradation of various EDCs.

Organic pollutant	Light source	Photocatalyst	Tested initial concentration ($mg{\cdot}L^{-1}$)	Optimum initial concentration ($mg{\cdot}L^{-1}$)	Reference
Di-*n*-butyl phthalate	UV	TiO_2/glass beads	2.5–12.5	2.5	Chiou et al. [105]
2,4-Dichlorophenol	UV	Ti-GAC	15.3–33.2	15.3	Gu et al. [106]
Bisphenol A	Solar	TiO_2/Ti	0.15–0.60	0.30	Daskalaki et al. [107]
	Solar	TiO_2-P25/Ti	0.15–0.60	0.15	Daskalaki et al. [107]
Bisphenol A	UV	Zr/TiO_2	15–60	15	Gao et al. [108]
n-Butyl benzyl phthalate	UV	TiO_2	0.5–2.5	0.5	Xu et al. [69]
2,4-Dichlorophenol	Visible	TiO_2/porphyrin	10–100	10	Chang et al. [109]
Bisphenol A	UV	TiO_2	5–20	5	Wang et al. [110]
Pentachlorophenol	UV	TiO_2/SS	2.5–10	2.5	Jung et al. [90]
Bisphenol A	UV	TiO_2/PF	10–50	10	Wang et al. [104]
Di(2-ethylhexyl)phthalate	UV	TiO_2	0.025–0.3	0.025	Chung and Chen [70]
Dimethyl phthalate	UV	TiO_2	5–80	5	Liao and Wang [101]

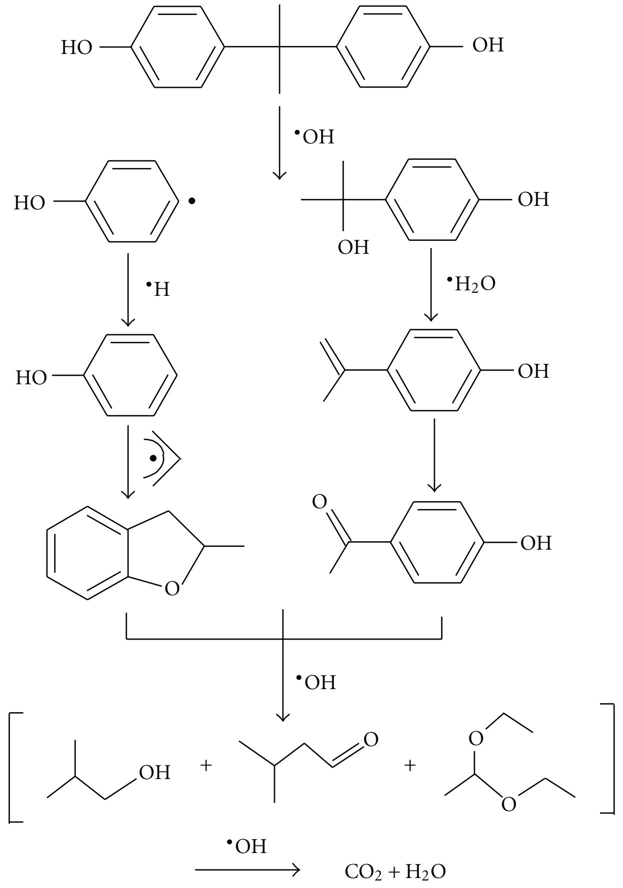


Figure 8: Photocatalytic degradation scheme for BPA [88].

[103] investigated the effect of initial concentration on the photocatalytic degradation of bisphenol A (BPA) in the presence of TiO_2. After 10 h of UV irradiation, degradation efficiencies of 78%, 55%, and 30% were obtained for initial BPA concentration of 10, 50 and, 100 $mg{\cdot}L^{-1}$, respectively.

The effect of initial concentration on the bisphenol (BPA) degradation has also been investigated by employing immobilized TiO_2 as catalyst [104]. Under the conditions tested, the highest BPA degradation rate was achieved when the BPA initial concentration was 10 $mg{\cdot}L^{-1}$. The BPA degradation rate after 10 h of reaction time decreased when the initial BPA concentration increased from 10 to 50 $mg{\cdot}L^{-1}$. At higher initial concentration, the accumulation of BPA molecules in the inner layer spacing on the TiO_2 surface resulted in the adsorption competition for active sites between BPA molecules, which thereby decreased the amount of reactive $^{\bullet}OH$ radicals attacking BPA molecules. This led to a decrease in BPA degradation.

Using TiO_2/glass beads, Chiou et al. [105] studied the effect of initial concentration on the photocatalytic degradation of di-*n*-butyl phthalate (DBP) under UV light irradiation ($\lambda = 365$ nm). The degradation efficiency was found to decrease as the initial DBP concentration increased. The degradation process followed a pseudo-first-order reaction. The observed rate constant was shown to vary from 0.0188 to 0.0130 min^{-1} as the DBP concentration increased from 2.5 to 12.5 $mg{\cdot}L^{-1}$. Muneer et al. [53] studied the effect of substrate concentration (0.1–1.0 mM) on the photocatalytic degradation of 1,2-diethyl phthalate (DEP) using Degussa P25 and Hombikat UV 100. The photonic efficiencies for both employed photocatalysts increased as the initial concentration of DEP increased up to 0.25 mM and then decreased. In the presence of Zr/TiO_2, Gao et al. [108] considered the influence of initial concentration on the photocatalytic degradation of bisphenol A (BPA) over the concentration ranged from 15 to 60 $mg{\cdot}L^{-1}$. The degradation rates were high at lower concentration range and then decreased with increasing the BPA's initial concentration. The degradation was observed to fit well with the pseudo-first-order kinetic model. Tatti et al. [111] studied the effect of initial concentration on the photocatalytic mineralization of 2,4-dichlorophenol and pentachlorophenol over immobilized TiO_2. In their study, both chlorinated

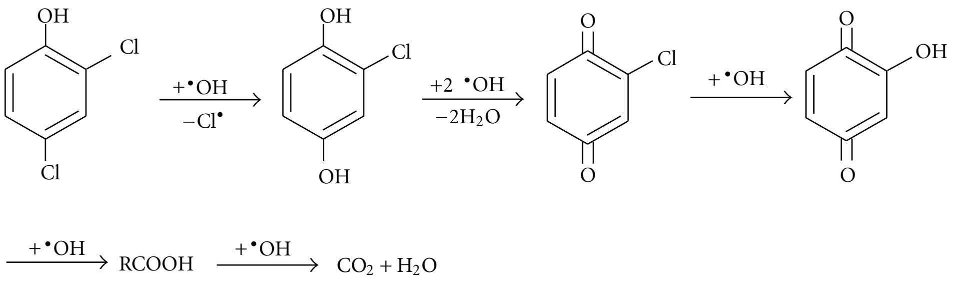


FIGURE 9: Photocatalytic degradation scheme for DCP [89].

phenol concentrations were varied in the range of 9.9×10^{-4} to 3.8×10^{-5} M. The degradation rates of the chlorinated phenols were observed to decrease linearly with the increase in the initial concentration. Using TiO_2 supported on GAC, Gu et al. [106] reported that the degradation efficiency of 2,4-dichlorophenol (DCP) decreased from 100% to 70.2% with initial concentration increasing from 15.3 to 33.2 $\mathrm{mg{\cdot}L^{-1}}$. This was ascribed to that increase of the DCP concentration can decrease the path length of photons entering the reaction solution, resulting in weak photons absorption on the surface of supported TiO_2. Thus, the DCP degradation decreased. As shown in many literature reports, the initial substrate concentration dependence of the degradation rate of organic pollutant can be realized by the fact that the photocatalytic reaction occurs on TiO_2 particles as well as in solution. On the surface of TiO_2 particles, the reaction occurs between the $^{\bullet}OH$ radicals generated at the active OH^- sites and organic molecules from the solution. When the initial substrate concentration is high, the number of these available active sites is reduced by organic molecules because of their competitive adsorption onto TiO_2 surface. Since the intensity of light and the irradiation time are constant, the $^{\bullet}OH$ radicals formed on the surface of TiO_2 remained practically the same. Thus, the active $^{\bullet}OH$ radicals attacking the organic pollutants decreased due to the lower ratio of the $^{\bullet}OH$/organic pollutant. In addition, a significant amount of light may also be absorbed by the organic molecules rather than the TiO_2 at a higher initial substrate concentration. This condition can be ascribed to the increase in the initial concentration, led to less photons reached to the TiO_2 surface, and resulted in a slower production of $^{\bullet}OH$ radicals. Consequently, the degradation rate is decreased, since fewer $^{\bullet}OH$ radicals are available to degrade more organic molecules. Furthermore, the formation of intermediates during the photocatalytic reaction of target pollutant also affected the reaction rate. The generated intermediates may compete with the organic molecules for the limited adsorption and active sites on TiO_2 surface. According to several authors [112–116], this competition could be more marked in the presence of a high concentration level of reaction intermediates produced by the degradation of higher initial substrate concentration.

5.3. *Effect of Catalyst Loading.*

It is well documented that the rate and efficiency of photocatalytic degradation would increase with catalyst loading. The increase in the efficiency seems to be due to the effective surface area of catalyst and the absorption of light. At lower catalyst loading, the absorption of light controlled the photocatalytic process due to the limited catalyst surface area. However, as the catalyst loading increased, an increase in the active surface area of TiO_2 is obtained. The enlarged amount of photons absorbed and the amount of organic pollutants adsorbed on the TiO_2 surface improved the photocatalytic degradation. When the TiO_2 loading is overloaded nevertheless, owing to an increase in the particles aggregation, the surface that absorbed the photons is not increasing in a geometrical ratio [104]. In addition, the number of active sites on the TiO_2 surface also decreased because of the decrease in light penetration due to light-scattering effect with an increase of the turbidity of the suspension and leading to the shrinking of the effective photoactivated volume of suspension. The integration of these two reasons resulted in a reduced performance of photocatalytic activity rather than the linearly increased with the overloaded catalyst. Hence, many researchers have verified that there was an optimum amount of catalyst loading in the photocatalysis studies [74, 92, 117–119]. Table 2 lists the effect of catalyst loading on the photocatalytic degradation of various EDCs in numerous studies. Kuo and Lin [120] studied the effect of catalyst concentration (0.5–3.0 $\mathrm{g{\cdot}L^{-1}}$) on the photocatalytic degradation of bisphenol A (BPA) irradiated using UV lamp. Their results showed that the photocatalytic degradation rate of BPA increased linearly with TiO_2 concentration up to 2 $\mathrm{g{\cdot}L^{-1}}$ and then decreased due to the reduction of UV light penetration. Chan et al. [96] observed that the degradation efficiency of di(2-ethylhexyl)phthalate (DEHP) increased gradually from 8.64% to 69.87% as the concentration of TiO_2 increased from 0 to 150 $\mathrm{mg{\cdot}L^{-1}}$. However, further increase in the catalyst concentration from 150 to 400 $\mathrm{mg{\cdot}L^{-1}}$resulted in a decrease in the degradation efficiency from 69.87% to 55.87%. Xu et al. [69] examined the effect of TiO_2 dosage (0–5 $\mathrm{g{\cdot}L^{-1}}$) on the photocatalytic degradation of *n*-butyl benzyl phthalate (BBP) over TiO_2 suspension. After 2 h of UV irradiation, the highest degradation efficiency of BBP was achieved at the concentration of 2 $\mathrm{g{\cdot}L^{-1}}$.

Chung and Chen [70] carried out a series of experiments to assess the optimum TiO_2 catalyst loading by varying the amount of catalyst from 0 to 500 $\mu\mathrm{g{\cdot}L^{-1}}$ in the di(2-ethylhexyl)phthalate (DEHP) solution. As the amount of TiO_2 increased, the total surface area for the photocatalytic reaction was also reported to be increased. Therefore, the DEHP degradation was improved. Further increase in the

Table 2: Effect of catalyst loading on the photocatalytic degradation of various EDCs.

Organic pollutant	Light source	Photocatalyst	Tested catalyst concentration ($g\cdot L^{-1}$)	Optimum catalyst concentration ($g\cdot L^{-1}$)	Reference
Di(2-ethylhexyl)phthalate	UV	TiO_2	0–0.0005	0.0001	Chung and Chen [70]
Bisphenol A	Solar	TiO_2	0–20.0	10.0	Kaneco et al. [97]
Bisphenol A	UV	TiO_2	0–3.0	0.5	Tsai et al. [20]
2,4-Dichlorophenol	UV	Ti-GAC	5.0–9.0	9.0	Gu et al. [106]
1,2-Diethyl phthalate	UV	TiO_2	0–5.0	1.0	Muneer et al. [53]
Pentachlorophenol	UV	TiO_2/SS	0–20.4	10.1	Jung et al. [90]
n-Butyl benzyl phthalate	UV	TiO_2	0–5.0	2.0	Xu et al. [69]
Bisphenol A	UV	Ti-MCM-41	0–0.2	0.1	Tao et al. [88]
2,4-Dichlorophenol	UV	TiO_2	0–2.0	0.5	Bayarri et al. [121]
Dibutyl phthalate	UV	TiO_2	0.001–0.005	0.005	Bajt et al. [122]
Diethyl phthalate	UV	TiO_2	0.04–0.4	0.2	Huang and Chen [94]

amount of catalyst showed a negative effect. Under the conditions investigated, the maximum degradation was noticed at $100\,\mu g\cdot L^{-1}$ of TiO_2. The decrease in degradation above $100\,\mu g\cdot L^{-1}$ was ascribed to the saturation of the catalyst surface area and scattering of light. Kaneco et al. [123] indicated that the degradation of di-*n*-butyl phthalate (DBP) (0–30 mg) increased with catalyst amount up to 5 mg. Then, the degradation efficiency decreased slightly and became nearly constant when the TiO_2 was higher than 10 mg. An increase in the amount of catalyst provided greater number of active sites available for DBP adsorption, however, the simultaneous increase in the light scattering and agglomeration of free catalyst particles hindered the degradation of DBP. Consistent trend of results has also been observed on the solar photocatalytic degradation of bisphenol A (BPA) using TiO_2 as a catalyst [97]. The degradation efficiency was found to increase with increasing catalyst content up to a level of 500 mg, and, thereafter, the efficiency was nearly constant. The photocatalytic degradation of $2.5\,mg\cdot L^{-1}$ pentachlorophenol (PCP) for different concentrations of TiO_2 thin film coated on the surface of stainless steel cloth has also been investigated [90]. The results showed that the PCP degradation followed the order of 2% ($w\cdot w^{-1}$) TiO_2 $\geq$ 1% TiO_2 $>$ 0.5% TiO_2 $>$ 0.1% TiO_2. Since the change of catalyst concentration from 1% to 2% $w\cdot w^{-1}$ did not have much effect on the PCP degradation efficiency, they suggested that 1% $w\cdot w^{-1}$ TiO_2 was the optimal catalyst concentration for the photocatalytic degradation of PCP. Using the TiO_2 loaded on MCM-41, Tao et al. [88] studied the effect of catalyst loading ranging from 0 to 0.2 g on the photocatalytic degradation of bisphenol A (BPA). Their findings demonstrated that the BPA degradation efficiency increased as the catalyst loading increased from 0 to 0.1 g. Nevertheless, further increase in catalyst loading showed an adverse effect due to interception of the light by the suspension and aggregation of catalyst particles. In the presence of TiO_2 supported on GAC, Gu et al. [106] investigated the effect of catalyst loading in the range of 5.0 to $9.0\,g\cdot L^{-1}$ on the photocatalytic degradation of 2,4-dichlorophenol (DCP). The increase of the catalyst dosage was observed to have a faster degradation of DCP, and the degradation efficiency was increased from 50% with $5.0\,g\cdot L^{-1}$ Ti-GAC to 100% with $9.0\,g\cdot L^{-1}$ Ti-GAC. The increase of Ti-GAC dosage was reported to enhance the interactions between catalytic components and UV, leading to an increase of $^{\bullet}OH$ radicals formation. This led to an increase in its degradation. Giménez et al. [124] tested the effect of catalyst concentration ($0–2\,g\cdot L^{-1}$) on the solar photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) in the CPC modules and the flat reactors. The observed optimum catalyst concentrations were $0.5\,g\cdot L^{-1}$ and $0.2\,g\cdot L^{-1}$ for the CPC modules and the flat reactor, respectively, on the degradation of 2,4-DCP. Further increase in the catalyst concentration in both reactors decreased the degradation rate. This suggests that the different designs of reactor (such as larger exposure area, more UV lamp, or faster agitation) might affect the optimal catalyst loading. In any given application, the optimum catalyst loading has to be determined in order to avoid an ineffective excess of catalyst and to ensure total absorption of efficient photons.

5.4. Effect of Solution pH. The pH of an aqueous solution significantly affects all metal oxide semiconductors including the surface charge on the semiconductor particles and the size of the aggregates formed [115, 125]. Due to amphoteric behaviour of TiO_2 particle suspended in aqueous solution, the effect of solution pH on degradation rate depends on the acid-base properties of the semiconductor surface and can be explained on the basis of zero-point charge. The principal amphoteric surface functionality is the "titanol" surface group, TiOH. Hydroxyl groups on the TiO_2 surface can undergo the following acid-base equilibrium [78, 126, 127]:

$$\begin{aligned} pK_{a1} &: \mathrm{TiOH} + \mathrm{H}^+ \longleftrightarrow \mathrm{TiOH_2}^+ \\ pK_{a2} &: \mathrm{TiOH} + \mathrm{OH}^- \longleftrightarrow \mathrm{TiO}^- + \mathrm{H_2O} \end{aligned} \tag{12}$$

where K_a is the acidity constant. The pK_a values for Degussa P-25 TiO_2 have been estimated as 4.5 for pK_{a1} and 8 for pK_{a2}, which resulted in a pH of zero-point charge ($pH_{zpc} = 0.5(pK_{a1} + pK_{a2})$) of 6.25 [128–130]. Accordingly, TiO_2 surface is protonated becoming positively charged as $TiOH_2{}^+$

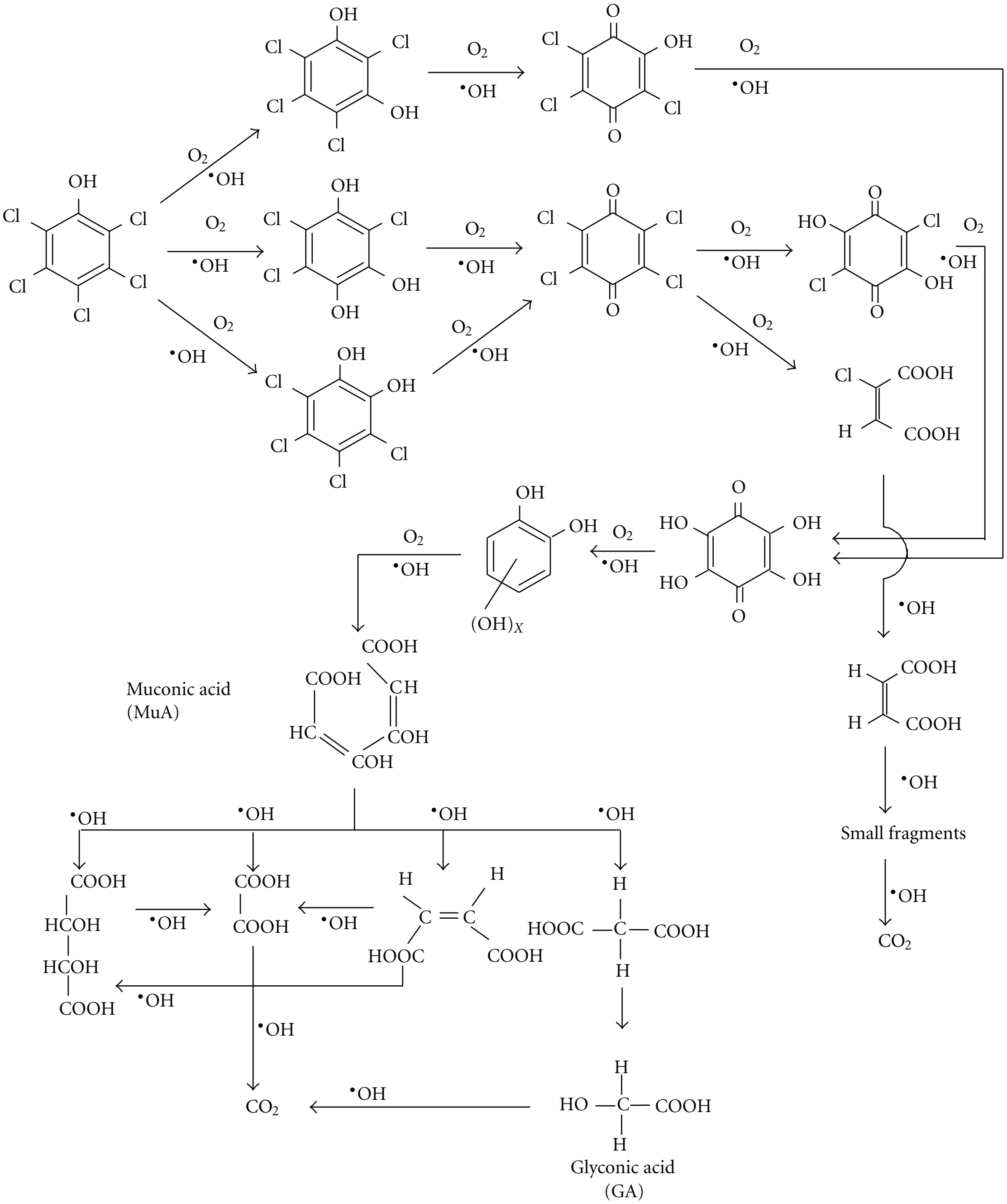


Figure 10: Photocatalytic degradation scheme for PCP [90].

below pH 6.25, and, above this pH, catalyst surface is predominantly negatively charged by adsorbed OH^- ions present as TiO^-. In addition, the pH of the solution can affect the formation of $^\bullet OH$ radicals by the reaction between OH^- ions and positive holes. The positive holes are favoured as major oxidation species at low pH, whereas $^\bullet OH$ radicals are favoured as principal oxidizing species responsible for the degradation process at neutral or high pH levels [92]. It was stated that, in alkaline medium, excess of OH^- ions on the TiO_2 surface as well as in the reaction solution facilitated the formation of $^\bullet OH$ radicals, and, thus, the efficiency of the process is logically enhanced. Wastewaters usually contain a mixture of large complex organic pollutants which may not be neutral. These organic pollutants present in wastewater differ greatly in several parameters, particularly in their speciation behaviour, solubility in water, and hydrophobicity. While some organic pollutants are uncharged at common pH conditions typical of natural water or wastewater, others exhibit a wide variation in speciation (or charge) and physicochemical properties. At pH below its pK_a value, an organic pollutant is primarily in its molecular form. Above this pK_a value, an organic pollutant tends to undergo deprotonation becoming negatively charge. These characteristics can significantly affect selective adsorption and photocatalytic degradation of charged pollutants by altering the surface charge of TiO_2 when a variation of solution pH takes place [131, 132]. Table 3 presents the solution pH influence on the photocatalytic degradation of various EDCs.

Liao and Wang [101] studied the effect of pH in the range of 3 to 11 on the photocatalytic degradation of dimethyl phthalate (DMP) over TiO_2 under UV light irradiation. The efficiency of DMP degradation in acidic solution at pH 5 was found to be higher than the alkaline solution. The enhanced degradation efficiency in acidic medium was due to more H^+ ions in the solution; more conduction band electron could migrate to the surface of the catalyst and reacted with O_2 to generate more $^{\bullet}OH$ radicals. Lin et al. [141] reported on the influence of pH on the photocatalytic degradation of pentachlorophenol (PCP) using metal-modified TiO_2 over the pH range of 3 to 11. Their results showed that the degradation of PCP enhanced in an acidic medium, and the maximum degradation rate was achieved in the solution at pH 3. At pH 3, the degradation rate of 1.0 wt% metal-modified TiO_2 was shown in the order of $Au/TiO_2 > Ag/TiO_2 > Pt/TiO_2 > Cu/TiO_2$. In acidic solution, the positive surface charge of TiO_2 strongly attracted the negatively charged PCP since its pK_a value was 4.74, resulting in an increase of PCP degradation. The variation of bisphenol A (BPA) degradation efficiency under different pH values has been investigated [98]. Under the conditions tested, the photocatalytic degradation of BPA using immobilized TiO_2 was done more rapidly in acidic solution than in alkaline solution. After 6 hr of irradiation, the degradation rate constants were reported to be $0.54\,h^{-1}$, $0.16\,h^{-1}$, and $0.01\,h^{-1}$ at pH 3, 7, and 10, respectively. Kuo and Lin [120] studied the influence of solution pH on the photocatalytic degradation of bisphenol A (BPA). Their results showed that the BPA degradation rate followed the order of pH 4 > pH 7 > pH 10 in the UV/TiO_2 system. Since the pK_a value of BPA is 9.6–10.2, the coulombic repulsion between negatively charged TiO_2 surfaces and BPA molecules resulted in weak adsorption of BPA onto the surface of TiO_2 at high pH. The photocatalytic degradation of BPA over UV/TiO_2 was reported to obey the pseudo-first-order kinetics. Using the nitrogen-doped TiO_2, Subagio et al. [137] studied the effect of pH on the photocatalytic degradation of bisphenol A (BPA) irradiated under blue LED lights ($\lambda = 465\,nm$). The results in their work showed that the BPA degradation rate increased from $0.507\ h^{-1}$ to $1.342\,h^{-1}$ with increasing the pH value from 3 to 10. It is important to note that the photocatalytic degradation of some organic pollutants is more efficient in alkaline solution [137] and others at about neutral pH [69]. It has earlier been reported that in alkaline solution, there is a higher concentration of OH^- ions, which can lead to the photogeneration of much of the reactive $^{\bullet}OH$ radicals and, thus, increasing the rate of BPA degradation. In the presence of porphyrin/TiO_2 and visible light irradiation, Chang et al. [109] also noticed that the degradation of 2,4-dichlorophenol (2,4-DCP) was most favoured at a higher pH (10.0) but went on at a slower and inefficient rate at pH 4.0. The pH variations influence (3.4–11.2) on the photocatalytic degradation of diethyl phthalate (DEP) has also been studied using PW_{12}/TiO_2 composite [64]. Under the stimulated sunlight irradiation, the degradation efficiency was shown to be greater at higher pH due to more efficient generation of $^{\bullet}OH$ radicals on the catalyst surface with an increase of OH^- ion concentration. Daskalaki et al. [107] tested the effect of initial solution pH on the photocatalytic degradation of bisphenol A (BPA) using both TIP film (TiO_2 prepared by sol-gel method) and P-25 film immobilized on Ti support. After 180 min of solar irradiation, the BPA degradation efficiencies were 42%, 86%, 90%, and 62% for TIP film and 70%, 84%, 95%, and 90% for P-25 film at initial pH values of 3, 6, 8, and 10, respectively. The increased photocatalytic performance recorded at pH 8 was due to the fact that favourable formation of $^{\bullet}OH$ radicals at alkaline conditions. At pH above 8, BPA was reported in the forms of BPA^- and BPA^{2-}, and, thus, repulsion will eventually occur with negatively charged TiO_2. On the contrary, Xu et al. [69] observed that the degradation efficiency of *n*-butyl benzyl phthalate (BBP) using TiO_2 under neutral pH was beneficial and had higher degradation efficiency than that in the alkaline medium. At pH 7.0, the surface of TiO_2 at isoelectric point can adsorb the largest amount of BBP molecules. At higher pH (10.0), negative charges predominated on the surface of TiO_2 particles, which restrained the BBP degradation. Hanna et al. [135] studied the effect of pH on the photocatalytic degradation of pentachlorophenol (PCP) in water and in $2\,mmol\cdot l^{-1}$cyclodextrin solution. The degradation rates were found to be higher at pH 7 than that obtained at pH 11. Wang and Lim [133] investigated the effect of initial pH on the photocatalytic degradation of bisphenol A (BPA) catalyzed by C-N doped TiO_2. The order of degradation rates was shown to be pH 7 > pH 9 ≈ pH 5 > pH 3 > pH 11. The enhanced degradation efficiency at pH 7 was due to the $^{\bullet}OH$ radicals easier to generate by oxidizing more OH^- ions available on TiO_2 surface. At higher pH, BPA was deprotonated into bisphenolate anions (pK_a of BPA = 9.6–10.2). Thus, degradation of BPA was inhibited as BPA possessed similar charge to TiO_2, which resulted in mutual repulsion. In summary, different organic pollutants have different activities in photocatalytic reaction. Some are degraded effectively at lower pH, while others degraded effectively at higher pH. All these may be attributed to the type of catalyst used and the nature of the organic pollutant to be degraded. Therefore, appropriate pH control strategies should be implemented for an efficient photocatalytic water treatment process.

5.5. Effect of Reaction Temperature. A number of studies have been indicated on the dependence of the photocatalytic reaction rate of degradation of organic pollutants on the reaction temperature. Such dependency could be realized when operating the photocatalytic process under natural sunlight, where the reaction temperature of stream may increase as the solar irradiation contains a considerable infrared (IR) factor [75]. Generally, as the photocatalytic process proceeds on the surface of the TiO_2, higher reaction temperatures would promote collision frequency between the organic pollutants and the catalyst, leading to higher reaction rates.

Table 3: Effect of solution pH on the photocatalytic degradation of various EDCs.

Organic pollutant	Light source	Photocatalyst	Range of solution pH	Optimum solution pH	Reference
Dimethyl phthalate	UV	TiO_2	3.0–11.0	5.0	Liao and Wang [101]
Bisphenol A	Visible	C-N/TiO_2	3.0–11.0	7.0	Wang and Lim [133]
2,4-Dichlorophenol	UV	TiO_2	3.5–10.6	10.6	Trillas et al. [134]
Bisphenol A	UV	TiO_2	4.0–10.0	4.0	Kuo and Lin [120]
Diethyl phthalate	Solar	PW_{12}/TiO_2	3.4–11.2	11.2	Xu et al. [64]
Pentachlorophenol	UV	TiO_2	7.0–11.0	7.0	Hanna et al. [135]
2,4-Dichlorophenol	UV	Porphyrin/TiO_2	4.0–10.0	10.0	Chang et al. [109]
n-Butyl benzyl phthalate	UV	TiO_2	3.0–11.0	7.0	Xu et al. [69]
Bisphenol A	Solar	N/TiO_2/AC	3.0–11.0	3.0	Yap et al. [136]
Bisphenol A	Visible	N/TiO_2	3.0–10.0	10.0	Subagio et al. [137]
1,2-Diethyl phthalate	UV	TiO_2	3.0–9.0	6.0	Muneer et al. [53]
Bisphenol A	Solar	TiO_2/Ti	3.0–10.0	8.0	Daskalaki et al. [107]
Bisphenol A	Visible	TiO_2	4.0 – 10.0	4.0	Kuo et al. [138]
2,4-dichlorophenol	UV	Fe^{o}/TiO_2/ACF	2.0–10.0	6.0	Liu et al. [139]
Bisphenol A	UV	Zr/TiO_2	2.0–11.0	9.0	Gao et al. [108]
Di(2-ethylhexyl)phthalate	UV	TiO_2	2.0–12.0	12.0	Chan et al. [140]

Nevertheless, several researchers have reported that, while an increase in photocatalytic reaction temperature may enhance the reaction rate of organic pollutants, reaction temperature would also lower the adsorption of organic pollutants and could reduce the oxygen concentration in the solution [142, 143]. This is consistent with Arrhenius equation, where the rate constant k is linearly proportional to the exponential $(-1/T)$:

$$k = A\exp\left(-\frac{E_a}{RT}\right), \tag{13}$$

where A, E_a, T, and R are the frequency factors, activation energy, temperature (K), and universal gas constant, respectively. In addition, as the irradiation energy simply serves to overcome the energy barrier for the process that it is often found the apparent activation energy is very small (a few $\mathrm{Kj\cdot mol^{-1}}$) [144]. Hence, the photocatalytic process does not appear to be particularly temperature sensitive. Chung and Chen [70] found that, the efficiency of photocatalytic degradation of di(2-ethylhexyl)phthalate (DEHP) increased gradually as the temperature increased from 20 to 40°C but was insignificant. The effect of temperature on the solar photocatalytic degradation of bisphenol A (BPA) using TiO_2 has been investigated in the range of 10 to 70°C [97]. Although the degradation efficiency of BPA increased steadily as the temperature increased, the appreciable change was not observed within their temperature range studied. Similar trend of results has also been observed for the photocatalytic degradation of dibutyl phthalate (DBP) using TiO_2 suspension [123]. The increase of degradation efficiency was reported to be insignificant in the temperature range of 10 to 40°C. In the photocatalytic degradation of bisphenol A (BPA) using immobilized TiO_2, the effect of temperature was studied in the range of 21.2 to 30.5°C [104]. Their finding revealed that the temperature has a limited influence on BPA degradation rate. The observed activation energy was relatively low and estimated to be $0.814\ \mathrm{Kj\cdot mol^{-1}}$; thus, no heating requirement was reported on the BPA photocatalytic system. Tsai et al. [20] examined the effect of temperature ranging from 10 to 70°C on the degradation efficiency of bisphenol A (BPA) under UV irradiation. Their results showed that the temperature played a less important role on the TiO_2 photocatalytic reaction system although the appreciable change in the enhancement of degradation efficiency was observed in the range of 10 to 25°C. In sum, the optimum temperature is generally in the medium temperature range ($20^\circ\mathrm{C} \leq \theta \leq 80^\circ\mathrm{C}$). This absence of heating is attractive for photocatalytic reactions carried out in aqueous media and in particular for photocatalytic water purification [145].

5.6. Effect of Dissolved Oxygen. Oxygen dissolved in solution is typically employed as an effective electron scavenger in most heterogeneous photocatalyzed reactions. The O_2 can be reduced to the $O_2^{\bullet -}$ anions, which prevents the photogenerated conduction band electron from recombination or being further reacted to form H_2O_2 and $^{\bullet}OH$ radicals. Due to its electrophilic property, dissolved O_2 plays an indispensable role in the TiO_2 photocatalytic reaction [67]. Basically, the O_2 does not affect the adsorption on the TiO_2 catalyst surface since reduction reaction occurs at a different location from where oxidation takes place. The concentration of oxygen also influences the reaction rate, but it seems that the difference between using air ($p_{O_2} = 0.21$ bar) or pure O_2 ($p_{O_2} = 1$ bar) is not very drastic. It has been stated that the rate of reaction was independent of O_2 concentrations below air saturation levels, suggesting also that the mass transfer of O_2 to the close vicinity of the catalyst surface could be rate-controlling step [143]. According to Henry's law, it is assumed that the concentration of O_2 adsorbed on TiO_2 from the liquid phase is proportional to the gas phase p_{O_2}. In this equilibrium law, it is also necessary to account for the decrease in O_2 solubility with increasing the reaction temperature. Apart from its electron scavenging role, the dissolved O_2 is also suggested to induce the cleavage mechanism for aromatic rings in organic pollutants that are present in the water matrices [67].

Zang et al. [89] studied the effect of dissolved O_2 on the photocatalytic degradation of 2,4-dichlorophenol (DCP) catalyzed by TiO_2 suspensions. Their results showed that the DCP degradation under air saturation was better than that in the absence of air. Precisely, after the photocatalytic system was saturated with air, a thirtyfold increase in DCP mineralization rate was observed. Such an increase in mineralization rate was explained by the formation of additional $^{\bullet}OH$ radicals via reactions of O_2 with e^- and H^+. Yuan et al. [146] compared the efficiency of TiO_2/UV system on the photocatalytic degradation of dimethyl phthalate (DMP) using different gases. The experiment results performed in aqueous DMP with an N_2 gas flow showed that the degradation efficiency was very limited, while addition of O_2 as an electron acceptor with a concentration about $35\,\mathrm{mg{\cdot}L^{-1}}$ substantially increased the DMP degradation. Gu et al. [106] investigated the effect of O_2 flow rate in the range of 4 to $8\,\mathrm{L{\cdot}min^{-1}}$ on the photocatalytic degradation of 2,4-dichlorophenol (DCP) using TiO_2 supported on GAC. Their findings revealed that the photocatalytic activity of Ti-GAC increased rapidly and obtained a maximum degradation efficiency of 82.5% at $6\,\mathrm{L{\cdot}min^{-1}}$ as the O_2 flow rate increased from 4 to $6\,\mathrm{L{\cdot}min^{-1}}$. Further increase in the O_2 flow rate from 6 to $8\,\mathrm{L{\cdot}min^{-1}}$ decreased the photocatalytic activity slightly to 79%. The increased photocatalytic degradation efficiency was attributed to the coeffect of enhanced mass transfer and $^{\bullet}OH$ radicals generation. The decrease in photocatalytic degradation efficiency at $8\,\mathrm{L{\cdot}min^{-1}}$ sascribed to high bubbling rate can provide a bubble cloud to impede the interactions between UV and catalytic activity center. Chin et al. [147] reported on the effect of aeration rate (0.2–$4.0\,\mathrm{L{\cdot}min^{-1}}$) to provide good mixing and a desirable level of dissolved O_2 on the photocatalytic degradation of bisphenol A (BPA). Under the conditions tested, an optimum of $0.5\,\mathrm{L{\cdot}min^{-1}}$ was observed on the BPA degradation using TiO_2 as catalyst. The effect of different gases on photocatalytic degradation of bisphenol A (BPA) in the presence of TiO_2 and β-cyclodextrin has also been examined by purging air and N_2 gas [110]. Compared to the case where there was no additional of electron acceptor (by purging N_2 in BPA solution), the efficiency of BPA degradation increased significantly with the addition of air during the 60-min reaction time. This was related to electron-hole pairs which can easily recombine in the absence of O_2.

6. Conclusions and Future Prospects

The paper revealed the fact that the increasing consumption of EDCs worldwide has raised significant public concern due to their effects that exerted hormonal imbalance activity even in trace concentrations in water bodies. Sources of EDCs, phthalates, bisphenol A, and chlorophenols in particular, and their effects on the environment, have been discussed. The photocatalysis using TiO_2, based catalysts has been shown to be efficient for the degradation and mineralization of various EDCs in wastewater in the presence of UV, visible, or solar light and oxygen. By the detailed illumination for the degradation pathways and intermediate products of these EDCs, this paper can provide theoretic evidences for seeking new and high efficiency of photocatalytic reactions for EDCs. The findings also suggested that various operational parameters such as light intensity and wavelength, initial substrate concentration, catalyst loading, solution pH, reaction temperature, and the presence of oxygen can influence considerably the photocatalytic degradation rate and efficiency of EDCs. Optimization of the operational parameters is of paramount importance from the design and the operational points of view when selecting a sustainable and competent technique for the wastewater treatment processes. The application of this technique under multicomponents of EDCs using the optimization of process parameters needs further attention as the pollutants in the real-world wastewater are in the form of mixture. Additionally, most of the photocatalysis studies concentrated only on the degradation rate, and efficiency of target EDCs disregarding the toxicity and estrogenic potency of the degradation intermediates. This aspect should not be overlooked while reporting any future work. A demonstrated ability to use TiO_2-based catalysts at a pilot scale for photocatalytic degradation of EDCs would certainly benefit the environment. Although this paper is nonexhaustive in the scope of photocatalytic degradation of EDCs, it does, however, address the fundamental principles and application in this area.

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