



# Application Photocatalysis for Treatment of Industrial Waste Water—A Short Review

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Received: 2 May 2014; revised 15 June 2014; accepted 25 July 2014

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## Abstract

Occurrence of persistent organic compounds in industrial effluents and their efficient removal technique has emerged as a crucial problem to waste water treatment plants. This review aims to focus on the plight associated with the effluents from textile industry, agricultural and pharmaceutical effluents. The occurrence of dyes, pesticides and endocrine disrupting chemicals in aquatic ecosystems may cause chronic diseases, affect the human endocrine system and have appeared as crucial factor to consider for drinking and non-potable end uses of water. Extensive researches have been attempted to screen effective and safe method of contaminants removal by modifying conventional treatments as well as advanced processes by renowned authors. This paper aims to review different possible routes of effluent treatment emphasizing on complete mineralization of the targeted contaminants. With this purpose, a comprehensive review has been presented to deliver essential information about dealing with photocatalytic mineralization of pollutants.

## Keywords

Photocatalysis, Textile Effluent, Pesticide, Waste Treatment, Endocrine Disrupting Chemical

**Subject Areas:** Chemical Engineering & Technology, Environmental Sciences

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## 1. Introduction

Due to an increase in human and livestock population, industrial developments have raised the concern of safe drinking water and non-potable water supply whereas, environmental protection, waste management and pollution control are also emerging for crucial problems of urbanized civilization. According to WHO and UNICEF, polluted drinking water and lack of sanitation are responsible for death of approximately 4500 - 5000 children per day, and one billion people still lack access to safe drinking water [1]. The second most critical issue is the

disinfection of water for agricultural usage purpose. According to the Food and Agriculture Organization (FAO) of the United Nations, agricultural purposes consume 70% of fresh water used worldwide with increased over 95% of the available fresh water in developing countries [2]. Enormous ongoing researches explore innovative techniques and ideas to treat waste stream of various industrial sources. This review highlights the polluted streams of agricultural fields, textile industries, and pharmaceutical industries to critically assess all possible practices of waste water treatment for obtaining ecofriendly discharge. This review also portrays about the applicability and recent advancement of the photocatalytic process for treating industrial waste (dyes, pesticides and pharmaceutical waste). In recent years, semiconductor photocatalytic process has shown a great potential being cost effective, environment friendly and in the field of sustainable treatment technology with zero waste discharge. Photocatalysis involves removal of water contaminants that are chemically stable and resistant to biodegradation. The method offers advantage over usual wastewater treatment techniques such as activated carbon adsorption, chemical oxidation, biological treatment and membrane separation. Activated carbon adsorption involves phase transfer of pollutants without decomposition. This incomplete removal process further increases pollution load on environment. Chemical oxidation is also a cause for incomplete mineralization of organic substances with generation of undesirable toxic byproducts' complex reaction mechanism. Biological treatment faces crisis for sludge removal, for very slow reaction rate and control of proper process conditions (microbial growth condition). The setback of retentive components, severe membrane fouling and costly process setup possess a great impact on membrane process. In this context, photocatalytic processes offer a number of advantages for the removal of pollutants from water, complete mineralization, use of low cost catalyst system and comparatively trouble-free arrangement. First report on photocatalysis using TiO<sub>2</sub> for disinfection was reported in 1985 [3]. Authors reported the inactivation of Gram-positive bacteria *Lactobacillus acidophilus*, a Gram-negative bacterium *E. coli*, *Saccharomyces cerevisiae* and *Chlorella vulgaris* with irradiated TiO<sub>2</sub>/Pt powder. The principle of photocatalysis process relies on “*in-situ*” generation of hydroxyl radicals under ambient conditions which are capable of converting a wide spectrum of toxic organic compounds including non-biodegradables into relatively less toxic end products such as CO<sub>2</sub> and H<sub>2</sub>O [4]. Several authors have summarized the steps of photocatalysis reaction [5]. The semiconductor oxide (e.g. TiO<sub>2</sub>) under irradiation with light having energy higher than that of the band gap (hν), a pair of conduction band electron (e<sup>-</sup>) and valence band hole (h<sup>+</sup>) is generated (Equation (1)). After this primary event, the charge carriers either recombine with the bulk of the material or migrate to the particle surface. Some authors suggested that, two different mechanisms may take place simultaneously either they get transferred to the adsorbed pollutant causing immediate oxidation (Equation (2)), or they are first transferred to adsorbed water molecules generating hydroxyl radicals, OH<sup>•</sup>, upon which reaction with the pollutant produce the respective oxidation products (Equation (3)).



Mechanism 1 represents direct oxidation or direct photocatalysis, while mechanism 2 shows indirect oxidation or indirect photocatalysis. In opinion of authors, mechanism 1 is associated with the systems which adsorb pollutants strongly at the photocatalyst surface with firm electronic contact, while mechanism 2 is dominant in systems with weak pollutant adsorption. According to principle, mechanism 2 can be as fast as mechanism 1, or it will be slower, but it is highly improbable to be faster. The electron-hole pair also initiates oxidation and reduction processes of adsorbed substrates. In aqueous solutions, the holes are scavenged by surface hydroxyl groups to generate strong oxidizing hydroxyl radicals (OH<sup>•</sup>), which can promote the oxidation and eventual mineralization of organic compounds [7]. All studies related to photocatalysis show that the presence of molecular oxygen and water is essential during the photo-mineralization process. The trapping of charge carriers by O<sub>2</sub> and H<sub>2</sub>O serves to suppress the electron-hole combination, thereby increasing the competitiveness of the light-induced redox processes. Basic principles of photocatalysis as well as the details of rate of degradation and effect of other factors controlling the photo-oxidation have been described in several research papers and review articles [2] [6] [7]. This versatile approach for removal of a broad range of chemical pollutants in waste streams has recently become an area of wide research particularly over the past decade. This paper summarizes recent researches dealing with application of semiconductor photocatalysis for the treatment of water contaminated

with dyes, pesticides and pharmaceutical components.

## 2. Photocatalysis in Dye Removal

In textile industries, dyeing process generates voluminous quantities of polluted effluents that are discharged on the surface of water bodies and ground water aquifers emerge as responsible for environmental degradation. The effluents consist of high concentrations of dye stuff, biochemical oxygen demand, total dissolved solids, sodium, chloride, sulphate, hardness, heavy metals and carcinogenic dye ingredients [8]. The nature of pollution that accompanies the dyeing industry is primarily due to the non-biodegradable nature of the dyes [9] along with the strong presence of appreciable amounts of toxic trace metals, acids, alkalis and carcinogenic aromatic amines in the effluents [10]. Villegas-Navarro *et al.*, (2001) [11] reported that textile effluents are foxy in terms of LC<sub>50</sub> and exhibit very high toxicity with acute toxicity unit (ATU) levels between 22 and 960. Wynne *et al.*, (2001) [12] noted that textile effluents are highly colored and saline, contain non-biodegradable compounds, and are high in biochemical and chemical oxygen demand (BOD, COD). Reports articulate that the presence of “dye compounds” cause inhibition of microbial activity and some cases may cause failure of biological treatment system. The release of colored wastewaters in the ecosystem is a dramatic source of esthetic pollution, eutrophication, and perturbations in aquatic life. Since the conventional physical (adsorption), biological and chemical methods (chlorination and ozonation) severely lack efficient removal to accomplish the stringent international environmental standard. The technological developments of removal of organic pollutants have become indispensable to the related industries. Various chemical and physical processes like coagulation, electrocoagulation and adsorption on activated carbon are not destructive but only transfer dye from one phase to another [13], moreover, due to the huge occurrence of organics in modern textile dye molecules and stability of dyes, conventional biological treatment methods are ineffective for their decolorization and degradation and these have led to the exploration of other effectual methods like photocatalysis, which can be used to destroy dye compounds using semiconductor photocatalysts under light irradiation [14] and holds several advantages over conventional oxidation processes, such as 1) complete mineralization of the pollutants; 2) use of near-UV or solar light; 3) no addition of other chemicals; and 4) operation at near room temperature [15]. Among the new oxidation methods or “advanced oxidation processes” (AOP), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of many organic pollutants [16] as presented in **Table 1**. A very recent study has reported in details about effect of dyes’ nature, concentration level of the various dyes in waste streams, concentration effect and effect of other interfering material on the overall process efficiency of dye photodegradation process [17]. The studies have reported the photocatalytic degradation of poorly soluble indigo dye in aqueous heterogeneous suspension and in the solid state mixed with titanium. Many catalysts like TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub>, WO<sub>3</sub>, SrO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, CdS and ZnS had also been made attempted for photocatalytic degradation of a wide variety of environmental contaminants [18] Effect of catalyst on overall performance for dye removal is presented in details by Mehta *et al.* 2011 [19]. The TiO<sub>2</sub> photocatalyst and surface modified TiO<sub>2</sub> (Ag-TiO<sub>2</sub>) has attracted much interest in recent years for its highly active photocatalytic functions, like the ability to decompose of chemical compounds, dye components [20]-[23], as well as super hydrophilic and antibacterial properties [24] [25]. Although photocatalytic degradations of trace toxic organic compounds in water and air have been investigated intensively, there are still few problems for their practical applications [20]. In recent years, vast majority of investigations in the area of photocatalytic degradation of pollutants have employed suspension of the semiconducting particles [15] [21] [26] [27], however, from practical point of view it may not be possible for complete recovery of the photocatalyst used in the reactor. The use of catalyst as slurry, after photocatalytic degradation, leads to the problem of leaching and separation of photocatalyst from the degraded reaction mixture, which necessitates either long time settlement or centrifugation. The need of a difficult, tedious and costly step of filtration to eliminate catalyst particles and recycle the catalyst limits the commercial application of photocatalytic degradation method in practice. To eliminate the filtration step, the concept of immobilizing the photocatalyst on a solid support was developed [28]. Researchers had attempted to study the feasibility of coating the photocatalyst on inert surfaces like glass; polythene fibers and cement surface highlighting the fundamental parameters regarding the preparation of photocatalyst with high photocatalytic activity, the immobilization of powder photocatalyst and the improvement of photocatalyst performance [29]-[32]. Fixation of the catalyst on stationary supports circumvents the need to recover the catalyst from the reaction mixture without any leaching. Many supports were suggested, *i.e.* quartz, silica, different kinds of glass, ceramics [33], activated

**Table 1.** Some commonly used dyes destroyed in photocatalytic degradation.

Name of dyes	Catalyst used	Reference
Methylene blue	TiO <sub>2</sub>	[18]
	TiO <sub>2</sub>	[21]
	TiO <sub>2</sub>	[27]
	TiO <sub>2</sub>	[32]
	TiO <sub>2</sub> on HDPE	[40]
Methyl orange	TiO <sub>2</sub>	[149]
	TiO <sub>2</sub>	[21]
	TiO <sub>2</sub>	[27]
Indigo	Titania-pillared zirconium phosphate	[48]
	TiO <sub>2</sub>	[16]
Azo dye	TiO <sub>2</sub>	[27]
	Ag doped TiO <sub>2</sub> , TiO <sub>2</sub> -P25 (Degussa)	[13] [44]
Rhodamine B	TiO <sub>2</sub>	[23]
	ZnO	[150]
Methyl violet	TiO <sub>2</sub>	[21]
Sudan blue II B	TiO <sub>2</sub>	[21]
Malachite Green	TiO <sub>2</sub>	[20]
	TiO <sub>2</sub>	[150]
Azodye acid red 18	TiO <sub>2</sub>	[22]
Congo red	Anatase nano fiber	[43]

carbon [34], zeolites [34] [35], glass fibres [36] [37], stainless steel [36]. By investigating the related expediency and inconveniences [38] it has been reported that commercial glass fibres covered with TiO<sub>2</sub> and suspended TiO<sub>2</sub> have comparable activities for the transformation of phenol. Commercial inorganic fibres coated with TiO<sub>2</sub> were reported to be less efficient than suspended TiO<sub>2</sub>, but much more efficient than TiO<sub>2</sub> deposited by sol-gel dip coating on red brick, cement or glass [37]. It was also reported that porous supports such as pumice stone can be impregnated with TiO<sub>2</sub> and used as immobilized photocatalyst for the transformation of nitrobenzenesulfonic acids, in thin-film fixed bed reactor to prevent damage in the support by stirring [39]. Efficient degradation of methylene blue dye was also achieved with multilayer coating of TiO<sub>2</sub> on HDPE [40]. Further efforts were made to improvise the photocatalytic technique by using a variety of reactor designs and arrangements. Several authors had reported the efficient applications of photocatalytic reactor assisted with UV irradiation to mineralize dyes [41]-[44]. Modifications of TiO<sub>2</sub> catalyst has become an inquisitive area of photocatalytic degradation research. Doping of TiO<sub>2</sub> with carbon was found to be interesting to enhance the performance of photocatalyst [45]. Similar attempts have also reported with erbium [46], tungsten [47] zirconium phosphate [48] and various ions [49]. All recent reviews and publications supports the potency of photocatalytic degradation technique with immense advantages over conventional of dye treatment methods but require more investigation on the extent of degradation and nature of the dye degraded products which in turn may raise further issues regarding practical applications. In context of dye removal, though there exists several technical advantages of photocatalysis process over other conventional techniques but, being an emerging technology detail of the economic aspects of dye degradation is scanty. Since this process can also use sunlight as energy resource other than synthetic energy

sources so, it is expected that the process will be cost effective in terms of energy requirement [5].

### 3. Application of Photocatalysis in Treating Pesticide Contaminated Waste Stream

Although the usage of these pesticides has been prohibited since 20 years, the original compounds as well as their degradation products have still been found in some foods and surface water [50]. Increasing pesticide applications and improper wastewater disposal methods are of particular concern for the freshwater (surface and groundwater), coastal and marine environments [51]. Low-level residues of pesticides in water generally do not acquire acute toxicity problems, but chronic effects are likely to be of concern [52]. This is because pesticides can harm with chronic effects such as cancer [53], Parkinson's disease [54], reproductive effects, fetal damage, delayed neurologic manifestations and possible immunologic disorders [55]. Pesticides represent a class of highly toxic anthropogenic compounds, which have led to search for a powerful method of degradation due to their persistence and bio-accumulative abilities [56]. These have motivated immense researches to develop efficient and rapid methods of degrading pesticides including microbial degradation, mechanochemical destruction, thermal degradation and photocatalytic degradation. In microbial degradation [57], only special kinds of microorganisms are used to degrade targeted pesticide. Though the action is very specific, but the cultivation and purification of the microorganism as well as the degradation are reported as time consuming and laborious. Some pesticides being bio-recalcitrant, non-biodegradable, the biological process does not define to be an ideal process and other more efficient technologies such as advanced oxidation technologies (AOTs) have been proposed for treatment of pesticides-polluted water [58]-[60] which allow pesticides to be removed by mineralization. The photo-mineralization of organic compounds by semiconductor photocatalysts such as TiO<sub>2</sub> or ZnO has become an area of intensive research, as ideally the end products of these processes are carbon dioxide, water and inorganic mineral salts [61], which have minimum environmental impact as presented in **Table 2**. In area of basic and applied researches reviewed, photocatalytic process with anatase TiO<sub>2</sub> is competent, since it operates in ambient temperature and pressure with low energy photons ( $\lambda < 388$  nm), requires no chemical reagents except oxygen in the ambient air [61]. Titanium dioxide appears as the most widely accepted photocatalyst for pesticide destruction in water as it is considered as very efficient catalyst that, unlike other semiconductors, being non toxic, stable to photo-corrosion, low cost and workable in sunlight considered as energy source [61]. Ahmed *et al.*, 2011 [4] presented a complete review on process parameters of heterogeneous photocatalysis that affects the performance of photocatalytic degradation. They studied some important aspects like composition of catalyst, light intensity and wave length, nature of pollutants, catalyst loading, pH of medium, mode of catalyst

**Table 2.** Some commonly used pesticides mineralized in photocatalytic degradation.

Name of pesticides	Catalyst used	Reference
S-triazines herbicides	TiO <sub>2</sub>	[151]
carboxin, oxycarboxin fungicides	TiO <sub>2</sub>	[7]
carbamate insecticides (carbaryl)	TiO <sub>2</sub>	[152]
	TiO <sub>2</sub>	[153]
Scala®	Solar photo-fenton	[68]
phosphamidon	TiO <sub>2</sub> and ZnO	[154]
Bromophos methyl	Aqueous TiO <sub>2</sub> suspension	[62]
chlorophenol pesticides	Aqueous TiO <sub>2</sub> suspension	[61]
chlortoluron	Coated TiO <sub>2</sub>	[63]
cyproconazole	Coated TiO <sub>2</sub>	[63]
fenitrothion	TiO <sub>2</sub>	[7]
DDT	Aqueous TiO <sub>2</sub> dispersion	[155]

application (suspended vs. immobilized system), influence of catalyst doping on the overall degradation process. Another review of Devipriya and Yesodharan, (2005) [7] reports the detail mechanism of photodegradation process and several case studies on different group of insecticides like, OP insecticides, organochlorine insecticides, carbamate insecticides, numerous herbicides (bentazone, carbetamide, monuron, S-triazines) and several fungicides (Pyrimethanil, chlorothalonil, diclofuanid, carboxin, oxycarboxin) using TiO<sub>2</sub> and ZnO. The photocatalytic degradation of S-triazines herbicides (atrazine, simazine, trietazine, prometon and prometryn) was first studied by Pelizzetti *et al.*, (1990) [62]. Several other publications about the solar TiO<sub>2</sub> photocatalyzed oxidation of S-triazines also revealed the full disappearance of the herbicide with incomplete mineralization and several degraded products. Anilide and amide herbicides also exhibited similar behavior under catalytic degradation. Enormous studies were also made on organophosphorous insecticides and organochlorine insecticides and chlorophenol pesticides [61]. Though photocatalytic degradation is a promising route of targeted pesticide mineralization, but may be affected by interfering compounds of real waste stream. Reports state that for a particular pesticide the degradation kinetic may differ from laboratory formulation in actual agricultural waste. Studies have also conducted commercial pesticide solutions of chlortoluron and cyproconazole highlighting the effects of interfering compounds and additives; exemplify the significantly lower degradation rate compared to simulated solution [63] [64]. Photocatalytic study also focuses on development of various reactor systems for mineralization of pesticides, like fixed bed fluidized bed, immobilized membrane fixed on reactor wall, reactive wall reactor, immobilized film coating a bundle of optical fibers. Some novel type of reactors like “rotating disk photocatalytic reactor” to mineralize lindane and chlorophenols in continuous flow mode [65] and photocatalyst coated “rotating drum reactor” to degrade phenol has been reported [66]. A study, featuring details of various reactor configurations by coupling photocatalysis with membrane process has been reported to mineralize a simulated solution of 4-nitrophenol with conclusively establishing the advantages of hybrid system over conventional reactor systems [67]. Coupling of photocatalysis with biological treatment [68] and wetland reactors [69] also proved effective to treat the real industrial waste water streams. Zinc oxide also exhibits interesting results which may be due to the wide band gap, large excitation binding energy, and piezoelectric properties. UV light with wavelength shorter than 380 nm was reported to excite the electrons in valence band to conduction band [70] for ZnO. They have reported the effective use of ZnO as photosensitizer in presence of an oxidant to treat several commonly used pesticides in pilot plant scale in presence of sunlight [4]. Several publications are available which substantiate the efficiency of TiO<sub>2</sub> as a photocatalyst for detoxification of pesticide contaminated water [63] [71] [72]. Recently, TiO<sub>2</sub> film has been developed and applied to degrade polychlorinated debenzo-*p*-dioxine under UV irradiation [73]. Moreover, low-density polyethylene-TiO<sub>2</sub> nanocomposite film has usually been selected to degrade polyethylene [74]. Yu *et al.* (2007) [75] have reported the photocatalytic degradation of organochlorine pesticides on a nano-TiO<sub>2</sub> coated film. Quite a few authors have reviews on the photo catalytic transformation of pesticides highlighting the complete degradation path way [62] [76]. However, several major drawbacks are also associated like, lack of an efficient visible light harvesting catalyst [77], the design of photoreactor [78], the recovery and reuse of titanium dioxide [77], the generation of toxic intermediates [62] [79] as well as concern in regard to catalyst deactivation [80]. Since, in photocatalytic detoxification technique, complete mineralization is hard to attain so, it obviates further toxicological analysis of end products. Since the heterogeneous photocatalytic treatment involve complex reaction mechanisms so, information regarding the chemistry of various classes of pollutants under reaction condition appears mandatory to know, as well as identification of harmful intermediates, which can be toxic, and in some cases, more persistent than the original substrate. Further, byproduct evaluation is brought into view, considering as a crucial factor in photocatalytic degradation of pesticides to assess overall process efficiency and feasibility. Among several rapid and established methods for direct acute toxicity assessment (DTA) [81], Microtox™ was reported as especially rapid and reliable [82]. Taking into account the amount of reported work and the potential practical applications dealing with photocatalysis of pesticide residues, economic aspects are continuously analyzed by several research groups [83]-[85] regarding the composition of the solution, the absorption of light and the reactor design.

#### 4. Photocatalysis in Treating EDCs in Pharmaceutical Waste Water

EDCs are a special group of chemicals having steroid-like structures, that can disturb normal endocrine functions directly or indirectly through interaction with receptor-mediated processes such as steroid hormone receptors even at very low concentration ( $\mu\text{g L}^{-1}$  and  $\text{ng L}^{-1}$  range) [86] [87]. Studies had revealed that their propensi-

ty is to mimic endogenous hormones and to inhibit normal hormone activities and metabolism [88]. Reports substantiate, they can also influence thyroid hormone secretion patterns, [86] [88], abnormal sexual development in animals [88] [89] and a decrease in the average numbers of human spermatozoa [87] [90]. Studies have reported the development of “product resistant microbes” in aquatic environment [91] [92]; retardation of nitrite oxidation [93]; methanogenesis [93] [94] and increased toxicity of chemical metabolites [95]. As cited in experimental review literatures, EDCs in wastewater and the environment comprising antibiotics (e.g., sulfamethoxazole, erythromycin, and roxithromycin); analgesic drugs such as codeine and anti-epileptic drugs inclusive of carbamazepine; and non-prescription drugs such as acetaminophen and ibuprofen [91] [96]-[98]. Other class of important EDCs from industries include “bisphenol A”, which leaches from food cans, polycarbonate water jugs, and dental composites; “dioxin”, which is a near-ubiquitous byproduct of combustion from incinerators, paper bleaching and foundries; “nonylphenols”, which are added to polyvinylchloride (PVC) plastic and are also a byproduct of industrial detergents and pesticide decomposition; “polychlorinated biphenyls” (PCB) associated with adhesives and electrical transformers; and “vinclozolin”, a common fungicide [99]. EDCs also include natural and synthetic hormones such as human and animal steroids (estradiol, estrone, and estriol) and contraceptives (e.g., ethynylestradiol). Although the adverse effects of EDCs on people and aquatic ecosystems are not clearly understood but, it is becoming increasingly important to adapt the existing wastewater treatment processes to improvise their potential in removing micro-pollutants like EDCs. To ensure compliance with future discharge requirements, upgrading the existing wastewater-treatment facilities and implementation of new technologies is envisaged as the next step in improvement of wastewater treatment. A number of advanced treatment techniques are available and these include membrane filtration technologies [100] [101], advanced oxidation processes (AOPs) [102], ultraviolet (UV) irradiation, and hybrid systems [103]. Membrane technology has become a technically and economically feasible alternative for water and wastewater treatment, especially because of compact reactor volumes and is not limited by the settling characteristics of sludge [104]-[106]. In membrane filtration process, the release of pollutants retained by the membrane, however, does not eliminate the risk to the environment [100] [101] [107]. Many reported that the heterogeneous photocatalysis in the presence of semiconductor metal oxides act as a fast-growing field of basic and applied research and a promising tool for water treatment with effective degradation of major pharmaceuticals and EDCs without formation of harmful intermediates [105] [108] [109] as presented in **Table 3**. The photocatalyst TiO<sub>2</sub> based treatment system could also be integrated as a pre- or post-biological wastewater treatment to enhance the biotransformation process for pharmaceutical compounds [110] [111] with advantages of low chemical input, high energy efficiency and the capacity to use renewable and pollution-free solar energy [112]. Immense studies have been conducted on the photocatalytic degradation of antibiotics by several authors [114] [115], which is having undesirable effects on living organisms. They cause an increasing resistance of bacteria to drugs, spreading of antibiotic resistance genes in the environment and having genotoxic effects on microorganisms [91] [115] [116]. Numerous researchers had focused on photocatalytic degradation of very common drug components focusing on their concentration in aqueous stream, effect of drug component nature, their concentration effect different approaches of increasing the process efficiency, photo reaction design and economic aspects [117]. Some articles have reported the ability of heterogeneous photocatalysis to improve tetracycline biodegradability [118] [119] and on the identification of tetracycline by-products formed during the photocatalytic treatment [114]. It has been shown from various studies the availability of photo degradation of norfloxacin in presence of algae and Fe (III) in presence of mercury lamp [120]. The authors have mentioned a novel approach of using algae for degradation of antibiotics and also the combined effect of photodegradation and algal concentration on the degradation behavior of the antibiotics. Their studies claim the credit of being an informative study for understanding the photochemical degradation of antibiotics in aqueous environment. A review highlighting the presence of organic contaminants specially the pharmaceutical and personal care products have been reported by Ratola *et al.*, (2012) [121]. This review also focuses on the recent trends of water treatment process, fate and elimination of five different classes of chemicals namely, pharmaceutical and personal care products, illicit drugs, prohibited doping substances, persistent organic pollutants and perfluorinated compounds. Photocatalytic degradation of diclofenac by TiO<sub>2</sub> photocatalysis and bioassay of toxicity has been reported by Rizzo *et al.*, (2009b) [122]. In their study the degradation kinetics and mineralization of diclofenac (DCF) by TiO<sub>2</sub> photocatalysis were investigated in terms of UV absorbance and COD measurements in a batch reactor system. A set of bioassays was performed to evaluate the potential detoxification of DCF on *Daphnia magna*, *Pseudokirchneriella subcapitata* and *Artemia salina* was observed that fresh water unicellular algae (*P. subcapitata*) is highly sensitive to the degraded

**Table 3.** Some EDCs mineralized in photocatalytic degradation.

Name of EDCs	Catalyst used	Reference
	TiO <sub>2</sub>	[118]
Tetracycline	TiO <sub>2</sub>	[119]
	TiO <sub>2</sub>	[156]
	TiO <sub>2</sub>	[114]
Tylosin	TiO <sub>2</sub>	[157]
Oxolinic acid	TiO <sub>2</sub> suspension	[113]
Levonorgestrel	TiO <sub>2</sub>	[124]
Estrogenic steroid hormones	TiO <sub>2</sub>	[137]
	TiO <sub>2</sub>	[138]
Bisphenol A	TiO <sub>2</sub>	[139]
	Bi <sub>2</sub> WO <sub>6</sub>	[140]
	Bi <sub>2</sub> WO <sub>6</sub>	[141]
Diclofenac	TiO <sub>2</sub>	[122]
Carbamazepine	TiO <sub>2</sub>	[123]
	MBR-TiO <sub>2</sub>	[110]
Atrazine	TiO <sub>2</sub>	[158]
17- $\alpha$ -ethynylestradiol	TiO <sub>2</sub>	[124]

product and not ecofriendly effluent. The toxicity was also reported to increase with increasing catalyst loading and DCF concentration. Photocatalytic treatment was found to be effective in treating highly concentrated carbamazepine from synthetic hospital waste water [123]. Authors used a titanium dioxide (TiO<sub>2</sub>) nanofiber based wastewater treatment process as a pre-treatment system to treat and enhance the biodegradability of carbamazepine (CBZ), in synthetic hospital wastewater and concluded that the TiO<sub>2</sub> pre-treatment system was capable of removing about 78% of CBZ from the influent wastewater within a 4 h reaction time. Steroid hormones, an important class of EDCs having strong potential to disrupt endocrine and other vital systems in aquatic organisms also reported to response strongly to photocatalytic degradation [124]. The heterogeneous photocatalysis process using TiO<sub>2</sub> was applied successfully for the removal of estrogens by several authors [125]-[136]. A recent review emphasizes on removal processes of estrogenic hormone (estrone [E1], 17 $\beta$ -estradiol [E2], estriol [E3], synthetic 17 $\alpha$ -ethynylestradiol [EE2]) has covered a broad range of possible elimination routes like, adsorption, membrane filtration, biological processes (bacteria, microalgae, enzyme), advanced oxidation processes (photolysis, heterogeneous photocatalysis) [137] and finally confers the concept of AOPs being more advantageous for their high removal efficiency compare to other processes and are thought to be one of the most promising treatments to deal with the problem of estrogens removal from contaminated water. Though TiO<sub>2</sub> has been widely used in degradation of organic chemicals in water and could completely mineralize bisphenol A to CO<sub>2</sub> under UV irradiation [138] [139] recent publication by Wang *et al.* (2012) [140] reports the efficiency of Bi<sub>2</sub>WO<sub>6</sub> in photodegradation of “bisphenol A” in aqueous medium. Their studies provide useful information about an alternative potential photocatalyst in treating organic pollutants in water in real application [141]. From existing literatures, though it is clear that photocatalytic degradation can efficiently be used in treating EDCs contaminated waste water from pharmaceutical industries but, most of them are related to the study of the effectiveness and the photocatalytic mechanism of targeted components. It is now appears to be crucial to maintain the quality of the final processed discharge ecofriendly for which ongoing researches should be oriented for more detail investigation on the degraded product identification and toxicity analysis.



## 5. Future Prospects of Membrane Separation and Photocatalysis in Waste Water Treatment

In sphere of advanced wastewater treatment technologies, integration of the membrane separation process with photocatalysis offers a novel research topic. Modification of the membrane with photocatalyst improves the operational performance in terms of good antifouling properties [142]-[145]. In waste water treatment, increase in the time between membranes cleaned or by reducing the cost for cleansing of lead to significant improvements of process. Integration membrane bioreactor (MBRs) with photocatalytic oxidation, offers great operational flexibility and superior performances in removing suspended solids and micropollutants [123] [141] [146]. The absence of suspended solids in the MBR effluent executes particular benefit for application of UV light, avoiding light shielding and scattering by suspended particles. Moreover, the use of MBR instead of conventional activated sludge systems offers further advantage of higher potential for biomass acclimation and augmentation, especially when operated at high sludge retention time [123]. Coupling of MBR with photocatalysis can also be a novel approach of treating wastewater from dye and agricultural land for mineralization of the respective pollutants and recycling of treated effluent for non potable end uses. Researches in this field are sparse and need thorough studies to make this approach profitable in practice. This review aims to make researchers more attentive in the novel approaches of waste water treatment to control pollution, protection of environmental and to obtain zero discharge effluent. Types of membrane those are normally modified with catalyst, modification techniques and about the catalyst life cycle are presented in details by several research groups [147] [148].

## 6. Conclusion

This review aims to focus on the recent application and advances for the heterogeneous photocatalytic system to reveal its efficacy of wastewater treatment specifically dye/textile effluent, pesticide contaminated water and pharmaceutical effluents. In most of the reviewed literature, TiO<sub>2</sub> has been suggested to be an efficient and profitable photocatalyst for mineralization of organic pollutants such as dyes, pesticides and EDCs in wastewater in the presence of UV, visible or solar light but some researchers have also aimed to explore novel low cost catalysts composition. Majority of studies are related to optimization of degradation process parameters, studies on kinetics and mechanistic path way of degradation which are crucial for efficient design and the application of the photocatalytic degradation process to ensure sustainable operation. In spite of extensive process investigations, understanding of photoreactor design and its modeling as well as the scale up policy seems inadequate which limits the industrial exploitation of the photocatalytic degradation technique. The application of this technique for real waste waters requires further investigation to achieve eco-friendly discharge. This review is not comprehensive but covers the recent application and developments of photocatalysis in treatment of industrial waste water and is hoped to be informative to relate researchers for betterment of the existing processes.

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