

REVIEW PAPER

Photocatalytic treatment of detergent-contaminated wastewater: A short review on current progress

Collin Glen Joseph^{*,**,**,†}, Yun Hin Taufiq-Yap^{****,*}, Nur Ammarah Affandi^{*,***},
Janice Lay Hui Nga^{****}, and Veena Vijayan^{*,***}

^{*}Sonophotochemistry Research Group, Faculty of Science and Natural Resources,
Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia

^{**}Water Research Unit, Faculty of Science and Natural Resources, Universiti Malaysia Sabah,
88400 Kota Kinabalu, Sabah, Malaysia

^{***}Industrial Chemistry Programme, Faculty of Science and Natural Resources,
Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah

^{****}Planning and Development Economics Programme, Faculty of Business, Economics and Accountancy,
Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia

^{*****}Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, Serdang, Malaysia
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Abstract—Detergents are emerging contaminants in water that require immediate attention due to their widespread use industrially and domestically. However, review articles on detergent treatment methods are not readily available in the literature as this topic is often overlooked. Various oxidation techniques have been applied to eliminate surfactants from the effluents completely. The photocatalytic treatment method is one of the most promising environmental-friendly oxidation technologies to degrade organic pollutants. Photocatalysis using TiO_2 as a catalyst shows outstanding properties, including excellent thermal and chemical stability, nontoxicity, and high photocatalytic degradation ability towards most of the organic compounds present in the wastewater. This paper reviews the research on photocatalytic degradation of detergent contaminated wastewater and the parameters that affect the semiconductor's photocatalytic activity. Lastly, critical remarks are also presented on the photodegradation treatment of laundry detergent wastewater, the economic feasibility of photodegradation treatment on an industrial scale, and suggestions for future work.

Keywords: Photocatalysis, Advanced Oxidation Process (AOP), Detergent, TiO_2 , Surfactants, Laundry Wastewater

INTRODUCTION

Water resources worldwide are continuously being contaminated with toxic organic contaminants such as surfactants, dyes, pharmaceuticals, pesticides, and heavy metals from industries, municipalities, and/or agricultural activities [1]. Water is essential for everyday basic needs as well as in industrial and manufacturing operations. As the world's population grows, potable water, also known as drinking water, is sure to become scarce. According to the World Health Organization [2], 4.2 billion people still lack proper sanitation due to poor water conditions in developing countries. The increasing demand for freshwater resources has made it clear that the world must urgently consider alternatives such as recycling and reusing the wastewater. In this paper, the characterization of laundry and detergent contaminated wastewater, following the application of photodegradation process technology for decontaminating the wastewater, and also the economic viability of the photocatalytic degradation technology in terms of capital and operation costs, are briefly discussed.

On average, industrial laundries use 15 litres of water to process 1 kilogram of load and roughly produce 400 m³ of wastewater per day per washing machine [3-5]. Wastewater generated from laundry cycles contributes to environmental pollution, as it may contain organic and inorganic contaminants, along with detergent and oil from different types of treated textile. Laundry wastewater consists of various cleaning chemical agents and soil or dirt, which can originate from many sources such as food, drink, oil, dyes, paints, and dusts. A major part of cleaning agent in laundry wastewater or detergent contaminated wastewater is surfactants. Anionic varieties of surfactants are the most used surfactants in cleaning agents and household detergents [6,7]. Anionic surfactants in detergents, as emerging contaminants (ECs) are non-biodegradable or partially degradable organics and are recalcitrant. The most commonly used anionic surfactant in household detergents is Linear Alkylbenzene Sulfonate (LAS), which consists of different homologous compounds containing aromatic rings and the sulfonate ion is attached to the long linear alkyl chain [8,9]. The products which are used as cleansers serves as a major topic to discuss, because their impact on the environment is highly visible. One of the most important after-effects of detergents on the natural ecosystem include extreme growth of algae, known as eutrophication, which in turn results in the inhibition of oxygen and light penetration into the

[†]To whom correspondence should be addressed.

E-mail: collin@ums.edu.my

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water. It has an impact on the characteristics of freshwater quality, which will adversely affect the animals and plants in soil and other aquatic organisms [10-12].

Conventional treatment processes are usually non-destructive, so they typically produce a large amount of sludge and need to be treated again. As removal rates are low, these removal operations require large storage tanks [13]. Operating from one organic removal compartment tank to another one can reduce the efficiency of the process significantly. Thus, to achieve complete mineralization of surfactants in wastewater, more effective oxidation methods need to be explored. There is a worldwide progressive interest in developing new techniques for the complete conversion of organic pollutants into harmless and inert by-products [14]. Advanced oxidation processes (AOPs) are considered to be more productive than any other conventional water treatment technology, especially in terms of its applicability for a wide range of pollutants, are fast and also have the ability to mineralize the organic pollutants into harmless products [15,16]. The term "advanced oxidation processes" for wastewater treatment process was first coined by Glaze et al. [17]. Photocatalysis, plasma oxidation, and ozonation are the most often used techniques in AOPs [18]. The basic principle of AOP is the generation of hydroxyl free radical ($\text{HO}\cdot$), a strong oxidant for destroying organic compounds as it is a non-selective chemical oxidant, resulting in an eventual mineralization of most of the organic contaminants present in water [19-21]. The photocatalytic degradation has a substantial interest in terms of environmental sustainability as it makes use of solar light based energy for the reaction [22]. Heterogeneous photocatalysis has attained great importance because it serves as a productive method for the decontamination of water from numerous organic contaminants, and also is cost effective in terms of application [23-25]. Photocatalytic degradation process has created a unique path in terms of inventing renewable energy resources and also for purging the environment.

CHARACTERIZATION AND IMPACTS OF DETERGENT CONTAMINATED WASTEWATER

The environmental problems caused by the production and consumption of detergents, one among the industrial pollutants, need prompt awareness [5,26]. The substance which is meant for cleansing in industrial and domestic purpose is commonly known as detergent. The main detergent components are surfactants, builders, enzymes, fillers, stabilizers, foaming agents, perfume agents, optical brighteners, dyes, and bactericide agents [11,26,27]. Several surfactants have been used in the formulation of detergents based on their nature of anionic, cationic, non-ionic, and/or amphoteric electrolytic dissociation which are presented in Fig. 1. Anionic surfactants serve as the most common one and are present in 60% of global production; non-ionic surfactants are calculated as 30%, while amphoteric and cationic surfactants are only 10% [9,12].

COMPOSITION OF LAUNDRY DETERGENT SURFACTANTS

The word "surfactant" can be used as an abbreviation for the surface-active agent. Surfactants are generally used for lowering the

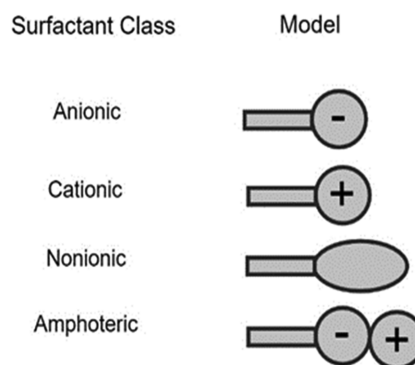


Fig. 1. Categorization of surfactant.

interfacial tension between a solid and a liquid or between two liquids. It is a long-chain hydrocarbon molecule that possesses hydrophilic and hydrophobic ends [3,30]. The hydrophilic part is often referred to as the polar head group, and the hydrophobic part is the tail. To meet the demands for biodegradability, the hydrophobic part normally used is linear having 10 to 20 carbon atoms [31]. This part could be aromatic, aliphatic or a combination of both. The primary classification of surfactants is based on the charge of the hydrophilic clusters and is categorized as cationic, anionic, non-ionic and zwitterionic (amphoteric). These surfactants will form micelles. When the critical micelle concentration is achieved, the hydrophobic part of the surfactants will trap the grease into these micelles; meanwhile, the hydrophilic part will help them to solubilize into the water, resulting in the extraction of dirt [32-34].

Anionic surfactants, which are used in most detergent formulations, are used in greater volume than any other surfactant class [9,12,28,29]. The most important anionic surfactants used in laundry detergents are soaps, alkyl benzene sulfonates (mainly LAS), alkyl sulfates (AS), alkyl ether sulfates (AES), and secondary alkane sulfonates (SAS) [35-37]. Non-ionic surfactants have been identified as surfactants with a low irritating effect, widely used in topical products [38]. The higher use of non-ionic surfactants in detergent formulations has partly been associated with washing at lower temperature [36,37]. The most important non-ionic surfactants are alcohol ethoxylates (AE), alkylphenol ethoxylates (APE), fatty acid alkanolamides (FAA), alkylamine oxides (AO), and alkylpolyglycosides (APG) [35-37]. Cationic surfactants in detergent formulations are usually used as a fabric softener in the washing processes [37,39]. The major use of cationic surfactants depends on their tendency to absorb at surfaces like minerals, plastics, metals, and cell membranes since most of the surfaces are negatively charged. The most important ones are the quaternary nitrogen compounds [37]. Lastly, zwitterionic or amphoteric surfactants as a group of surfactants are characterized by having excellent dermatological properties and exhibiting low eye irritation [40]. They are frequently used in cosmetic products and shampoos. Amphoteric surfactants possess both anionic and cationic groups in the same molecule, even in an aqueous solution. Despite excellent detergent properties, these surfactants are only rarely employed in laundry detergents, primarily because of cost reasons [37]. The most important type of amphoteric is alkyl betaine, alkylamidopropyl betaine, betaines

derived from imidazolines, and alkylamphoacetates [35-37].

BUILDERS

Builders, also called as chelating or sequestering agents, are the second most crucial detergent ingredient because they can improve the cleaning action of the surfactant [41]. Most of the water sources contain some dissolved minerals, which have metal cations, particularly calcium and magnesium ions. The metal cations can react with surfactants to form soap scum, lowering the effective cleaning action and precipitating into both fabric and washing machine components [42]. Hence, builders are designed to soften water by binding the hard water minerals by sequestration, precipitation, and/or ion exchange [41].

ENZYMES

Detergent enzymes are biological enzymes used in detergents to catalyze the reaction between stains and the water solution, thus improving and aiding the removal of dirt and stain [43]. Enzymes aid in breaking down complex soils, especially proteins, such as blood, to remove from the fabrics more easily. The five classes of enzymes found in laundry detergent include proteases, amylases, lipases, cellulases, and mannanases [43,44].

OTHER INGREDIENTS

Many other ingredients are added depending on the purpose for which the detergent is used. Some additives are added to modify the foaming properties of the detergent by either stabilizing or counteracting the foaming properties [45,46]. Corrosion inhibitors aid in counteracting damage to washing equipment [47]. Dye transfer inhibitors prevent the transfer of colored dyes from one fabric to another one [48]. Anti-redeposition agents such as carboxymethyl cellulose are used to prevent the recombination of fine soil particles to the product after its cleaning [49]. Other than that, some ingredients will affect the aesthetic properties of the fabric to be cleaned, or the detergent itself, before or during use. These ingredients include optical brighteners, perfumes, fabric softeners, and also colorants.

ENVIRONMENTAL IMPACTS OF DETERGENT

To study the adverse effects of detergents on the environment is of great importance in terms of the disposal of wastewater coming after industrial and household purposes to the nearby water bodies, which is used as a primary disposal method. One of the main effects is the partial mineralization of surfactants and will result in the formation of extreme foam in rivers and streams. Thus the excessive foaming on the water surface will reduce the rate of oxygen penetration from the atmosphere into water, which in turn reduces the availability of dissolved oxygen for aquatic organisms [10,50]. Phosphate is used as a builder in detergent and adding excessive dose of phosphate will cause eutrophication, which is the excessive growth of algae in water. The main impact of eutrophication is that, when the algae decays, the amount of organic sub-

stances will be increased, thereby decreasing the dissolved oxygen levels of water [26,51]. Moreover, detergent components will alter the physical and chemical parameters including pH, temperature, salinity, and turbidity of natural water.

The presence of detergent in water can directly influence aquatic animals. The accumulation of detergent in water may disrupt the sight of the fish and can cause problems to their gills even if for a short time [50]. Rejeki and Rahmat [50] reported that the toxicity level (LC_{50} , 96 h) is 1.8 mg/L of detergent on fish larvae, *sea bass* (*Lates calcarifer* Bloch). The exposure of larval fish to a concentration lower than the lethal dose by 30 days resulted in the congestion and vacuolar degeneration of their liver, whereas the mortality rate was increased at higher concentration [50]. Besides, according to Rajan [10], it has been proven that the increase in the concentration of detergent imparts difficulty in the breathing and there is a sign of distress in the fish species of *Anabas testudineus*. Additionally, a concentration above 200 ppm is deadly for the fish.

Detergents are undeniably harmful to plant life, especially for aquatic plants. The eutrophication process is the major impact of excess amount of phosphate in the detergent contaminated water bodies [11]. This process is a massive threat to marine life, such as seaweed and corals by decreasing the population of sea plants and will affect the sea species and creatures that depend on them for food, home, and protection. Pandey and Gopal [11] investigated the effect of sodium dodecyl benzene sulfonate (SDBS) on two aquatic plants (*Azolla pinnata* and *Hydrilla verticillata*) in five different concentrations. It was found that the growth of *A. pinnata* increased at 1-10 ppm concentration of SDBS and the highest growth was observed at 10 ppm. The growth was reduced at 15-20 ppm concentration and color of the plant changed to brown at this concentration. The chlorophyll content decreased with all the concentrations [11].

The detergent contaminated water can also enter into the soil and give rise to unfavorable effects on the soil flora in the area. Sawadogo et al. [52] reported the effect of LAS detergent on soil irrigation with grey water on soil properties and two plant species (okra [*Abelmoschus esculentus*] and lettuce [*Lactuca sativa*]). By increasing the quantity of detergents, the amounts of EC, pH, and soluble salt in the water will increase, and consequently, it increases the parameters in the soil. Increase in the concentration of detergent will cause a decrease in dry biomass of the root and shoots. With a high level of detergent (678 mg/L), there is a statistically significant decrease in the irrigation, eventually causing the death of two plant species (lettuce and okra) [52].

In general, surfactants do not belong to the compounds which can directly harm humans and the organisms living in water. However, they can create insoluble toxic substances in the water, which will eventually become harmful to humans and aquatic organisms. By decreasing the water's surface tension, they induce foaming, which deteriorates oxygen diffusion in the water, decreasing the oxygen concentration in the water [10,50]. This situation will negatively impact water reservoirs' self-purification ability and biological life development [23]. The bubbles produced will inhibit oxygen and light penetration and increase some contaminants' solubility in the water system, causing eutrophication and endangering of planktonic species [53-55]. The polluted river water is

toxic for fishes and other water creatures [56]. Besides, water contaminated by a high concentration of surfactant can cause eye and skin irritation. Consuming such water will cause health problems, including diarrhoea and kidney damage [57]. The toxicity of surfactants increases in proportion to their hydrophobicity, expanding the alkyl group length [58].

APPLICATIONS OF PHOTODEGRADATION PROCESS TECHNOLOGY FOR WASTEWATER TREATMENT

The treatment methods commonly used for treating detergent contaminated water is shown in Fig. 2. Physical, chemical, and biological methods are the conventional wastewater treatments used for treating the wastewater. Most of the large sewage treatment plants make use of biological systems for removing organic pollutants, followed by physical treatment steps. In physical treatment methods, the advantages of the technique are its robustness, being chemical-free, and requiring less operational input, while it has some disadvantages like high retention time, high capital cost, and the production of unwanted secondary waste [59]. Treatment employing adsorption by various adsorbents, coagulation and flocculation methods, and ion-exchange methods are merely transferring the organic pollutants from one phase to another. These methods do not completely degrade the pollutant, resulting in the spent solid sorbent material having to be treated before disposal as it is saturated with the organic pollutants, which may again find its way back into the sub-surface water [25,60]. The advantages of chemical treatment methods are lower sludge generation and high pollutant removal efficiency rate. Some of its disadvantages include high operational and chemical cost with the production of secondary waste [61,62].

Easy application and low cost are the advantages of biological treatment method. In contrast, the generation of sludge during the treatment and high retention time are its significant disadvantages. The biological treatment method is only suitable for a low level of surfactant as the surfactant's high concentration may kill the bacteria used [63]. Also, under anaerobic conditions, some surfactants cannot be degraded by biological treatment, while others are only partially mineralized in aerobic systems [37].

There is a worldwide progressive interest in inventing novel technologies for the efficient transformation of organic pollutant into non-toxic and inactive by-products [14]. Advanced oxidation processes (AOPs) are preferable alternatives for conventional water treatment technologies, particularly in terms of the wide range of applicability, fast and complete mineralization of the organic pollutants into harmless products [15,16]. The basic principle of AOP is the generation of hydroxyl free radical (HO^\bullet), a strong oxidant for degrading organic compounds, as it is a non-selective chemical oxidant, causing complete elimination of most of the organic pollutants [19-21,64-69]. Hydroxyl radicals are reactive electrophiles that can react immediately and non-selectively with almost all organic compounds that are electron-rich [70-72]. Photocatalysis, plasma oxidation, and ozonation are the most commonly used techniques in AOPs [18,73]. Among AOPs, heterogeneous photocatalysis has been proven to be a productive tool for degrading both aquatic and atmospheric organic contaminants. Even though the process begins with a partial oxidation, photocatalysis results in the complete mineralization of organic compounds to CO_2 and H_2O . Heterogeneous photocatalysis involves a semiconductor photocatalyst, which accelerates the photoreaction [74,75]. The most commonly used photocatalysts are ZnO , TiO_2 , Fe_3O_4 and carbon-

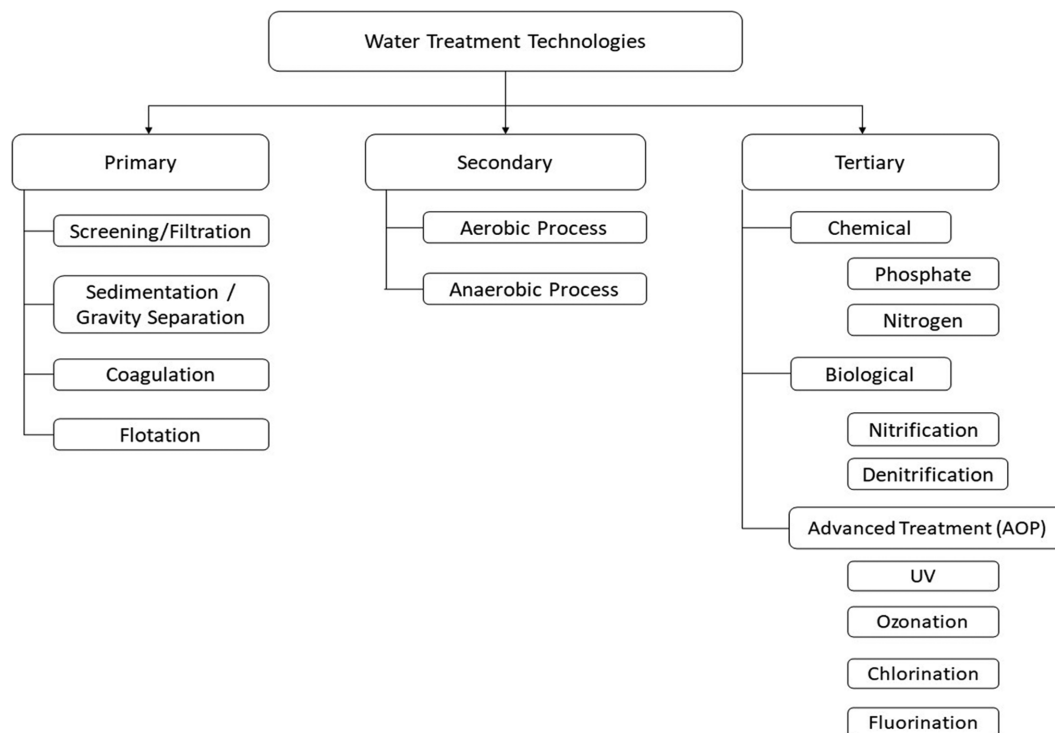


Fig. 2. Treatment methods for detergent wastewater.

Table 1. Advantages and disadvantages of various AOPs [73]

AOP	Advantages	Disadvantages
TiO ₂ /UV	<ul style="list-style-type: none"> • Catalysts can be recycled • Performance is better in solar irradiation and at higher wavelengths 	<ul style="list-style-type: none"> • Not established up to an application level • Removal step of catalyst slurry is needed • Optimization of catalyst concentration needs in-depth study
Fenton's Reaction	<ul style="list-style-type: none"> • Ability to degrade soluble and insoluble dyes from industrial effluents 	<ul style="list-style-type: none"> • Formation of iron sludge by the flocculation of reagent and contaminants • Maintain low solution pH (<2.5) for the existence of iron • Operation costs will be high by maintaining a low pH solution
H ₂ O ₂ /O ₃	<ul style="list-style-type: none"> • Formation of highly reactive and non-selective hydroxyl free radicals that can break down the conjugated double bond • Ozone can be used in its gaseous state and no change in the volume of wastewater • Sludge generation is very low 	<ul style="list-style-type: none"> • Production of hydroxyl radicals is less compared to other AOP processes and the rate of degradation is slow • Ozone can create harmful by-products • Cost is high compared to other AOPs • Pre-treatment is required to generate H₂O₂
O ₃ /UV	<ul style="list-style-type: none"> • More efficient compared to O₃ or UV used alone • Used as a disinfectant • Better efficiency to generate hydroxyl radicals than H₂O₂/UV 	<ul style="list-style-type: none"> • Bromated by product formation • Turbidity may hinder UV light from entering in the solution • The absorbance of UV light may be interfered by the presence nitrate like compounds • Needs more energy and high cost of operation
H ₂ O ₂ /UV	<ul style="list-style-type: none"> • Established water treatment system 	<ul style="list-style-type: none"> • Turbidity will hinder the irradiation of UV light into the solution • Absorbance of light is obstructed by the presence of nitrate like compounds.

based nanomaterials, graphene and graphene oxide etc [76-79]. Advantages and disadvantages of using various AOPs for the treatment of wastewater is presented in Table 1.

GENERAL MECHANISM OF PHOTOCATALYTIC DEGRADATION

Schematic representation of different types of AOPs are given in Fig. 3. Photocatalytic oxidation is the one in which organic contaminants present in water can be degraded in the presence of semiconductor photocatalysts such as TiO₂ and ZnO and oxidizing agents such as oxygen or air, and also an energy source. The semiconductor TiO₂ has attained more importance as a photocatalyst for inducing a series of reductive and oxidative reactions on its surface [80,81]. For a photocatalyst to be perceived as useful, it should be photoactive, biologically and chemically inert, reactive on visible or near UV light, photostable, non-toxic, and cost effective. TiO₂ has an oxidation potential of 3.2 eV, efficient in decaying a wide range of organic pollutants, non-toxic, inexpensive, possess chemical and thermal stability [81,82]. The semiconductor is insoluble as the pH varies, like acids and alkalis, and it is also resistant to photo-corrosion, unlike CdS that degrades to form toxic products after repetitive use [20,83].

Photocatalysis generally implies the generation, separation, recombination, and surface capture step of photo-generated electrons and hole pairs [84]. The photodegradation of organic pollutants in the presence of semiconductor TiO₂ starts with the absorption of light radiation equal to or higher than that of the band gap energy, i.e., 3.0 eV for rutile and 3.2 eV for anatase [85]. Anatase polymorph

displays more photocatalytic activity than the rutile because of its conduction band position; thus, anatase exhibits more potent reducing power compared with that of the rutile type of TiO₂ [85]. Only photons with energies equal to or greater than the band gap energy (ΔE) can excite the valence band (VB) electrons, thereby promoting the possible reactions. The absorption of photons with lower energy than ΔE or longer wavelengths usually results in energy dissipation in the form of heat [74]. The absorption of light radiation subsequently generates holes and electron pairs in the valence band and conduction band of the semiconductor. The energized holes and electrons will react with the electron donor or acceptor species adsorbed on the semiconductor surface or close to the double layer surrounding the particle. The electron-hole pairs will recombine again and dissipate heat if no electron scavengers are present in the system. If oxygen is present in the system, the electron will be scavenged, can form superoxide radicals ($O_2^{\cdot-}$) and hydroxyl radicals ($\cdot OH$ with $E^\circ=2.80$ eV), which helps in suppressing the electron-hole recombination [86-88]. As the lifetime of hydroxyl radicals is very short, they have a tendency to react instantly after their formation [89,90]. Therefore, the adsorbed oxygen species such as hydroxyl radicals ($OH\cdot$) is immediately followed by the formation of hydroperoxyl radicals ($HO_2^{\cdot-}$), and superoxide radicals ($O_2^{\cdot-}$), in successive oxidative and reductive reactions. These reactive radicals can together react with organic pollutants and completely mineralize them into carbon dioxide, water, and mineral acids [80].

In summary, the mechanism of semiconductor photocatalysis starts with the absorption of a photon by the semiconductor. When the photons of light with energy equal to or more than band gap



Fig. 3. Types of advanced oxidation processes.

energy irradiate on the semiconductor surface, electrons in the valance band get excited into the conduction band. Thus, holes are produced in the valance band and it can oxidize donor molecules. The donor molecule may be water or any other organic pollutant. The hole-oxidation of water generates more potent and stable oxidizing agent, such as hydroxyl radicals which are responsible for further degradation of the pollutants. At the same time, the electrons in the conduction band can facilitate the redox reactions and they react with the dissolved oxygen species present in the system to form superoxide ions.

POTENTIAL NANOMATERIALS USED FOR SEMICONDUCTOR WASTEWATER TREATMENT

1. TiO₂

Anatase crystalline form of TiO₂ has a gained widespread atten-

tion as a photocatalyst having high quantum yield, which makes it an efficient photocatalyst [79,92]. Anatase, rutile, and brookite are the three types of polymorphs of TiO₂ crystals [93]. Anatase shows the highest photocatalytic activity than other polymorphs, with the most extended lifetime and the fastest migration of photo-generated electrons [94]. TiO₂ has a bandgap energy of 3.2 eV, which is acquired by a photoexcitation wavelength below 385 nm and it is at the near-UV light irradiation. Among the commonly used Photocatalysts, TiO₂ is known to be the more appropriate one for the decontamination of water from bacteria and other organic pollutants [95,96]. The general mechanism of photocatalytic process on TiO₂ as shown in Table 2.

Additionally, TiO₂ particles can take part both in oxidation and reduction reactions to remove organic and inorganic impurities [100-102]. When a semiconductor is modified by doping with nitrogen ions or metal oxides, the photocatalytic behavior of TiO₂

Table 2. General mechanism of photocatalytic process on TiO₂ [91]

No.	Process	Reaction Steps
1	Electron-hole pair formation	$\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2^- + \text{OH}\cdot (\text{or } \text{TiO}_2^+)$
2	(Semiconductor valence band hole and conduction band electron)	$\text{TiO}_2^- + \text{O}_2 + \text{H}^+ \rightarrow \text{TiO}_2 + \text{HO}_2$
3		$\text{TiO}_2^- + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{TiO}_2 + \text{H}_2\text{O} + \text{OH}\cdot$
4	Electron removal from the conduction band	$\text{TiO}_2^- + 2 \text{H}^+ \rightarrow \text{TiO}_2 + \text{H}_2$
5	Hole trapping	$h^+ + \text{H}_2\text{O} \rightarrow \text{OH}\cdot + \text{H}^+$
6		$h^+ + \text{HO}^- \rightarrow \text{OH}\cdot$
7	Oxidation of organic pollutant molecules	$\text{OH}\cdot + \text{O}_2 + \text{Cx Oy H} (2x - 2y + 2) \rightarrow x \text{CO}_2 + (x - y + 1) \text{H}_2\text{O}$
8	Non-productive radical reactions	$\text{TiO}_2^- + \text{OH}\cdot + \text{H}^+ \rightarrow \text{TiO}_2 + \text{H}_2\text{O} \text{ (recombination)}$
9		$2 \text{OH}\cdot \rightarrow \text{H}_2\text{O}_2$
10		$2 \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
11		$2 \text{OH}\cdot + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^+ + \text{H}_2\text{O}$
12		$2 \text{OH}\cdot + \text{HCO}_3^- \rightarrow \text{CO}_3\cdot + \text{H}_2\text{O}$

can be extended to visible light [97]. Numerous material modifications are implemented to widen the photoactivity of TiO₂ catalyst for solar spectrum by compositing the photocatalysts with carbon nanotubes (CNTs), noble metals or metal ion incorporation, and non-metal doping.

According to Yu et al. [98], CNTs coupling with TiO₂ has observed potential prolongation of electron-hole pairs by the capture of electron within their structure. Ni et al. [99] reported that by depositing noble metals such as Pt, Ag, Cu, Ni, Pd and Rh on the TiO₂ surface improves the charge separation and electron transfer. The noble metal coupling is favorable in prolonging the surface charge separation but cost-effectiveness in terms of industrial application is usually replaced by more economical transition and/or non-metal doping [81]. Fujishima et al. [100] found that the use of non-metal dopants such as C, N, F and S on the TiO₂ surface can intensify the photoactivity of TiO₂, which results in an improved feasibility for industrial application.

2. ZnO

Zinc oxide is a wide band gap semiconductor with bandgap energy of 3.37 eV and a large exciton binding energy of 60 meV [101]. These two properties are well known for applicability in various environmental, optical and electronic sectors [78,102]. ZnO nanoparticles exhibit supreme photocatalytic efficiency against organic contaminants because of their non-toxic nature, wide band gap, and good quantum efficiency [103]. Furthermore, the past decade has witnessed an increasing interest in the photocatalytic applications of ZnO, as it is reported that ZnO has more unique photocatalytic properties than that of the commonly discussed TiO₂ [102]. The movement of electrons in ZnO is higher compared with that of TiO₂ based nanomaterials, approximately by two orders of magnitude. Therefore the photo-generated charge carriers can easily proceed towards the surface of ZnO based nanomaterials [104]. The perfect photocatalytic efficiency of ZnO is also due to the formation of defect sites which can prevent the electron-hole recombination by the absorption of photons. According to Xu et al. [105], ZnO is formulated in different morphologies, including cauliflower-like, truncated hexagonal, nanotubes, and hourglass-like morphologies. ZnO is also proven to be an efficient photocat-

alyst for the removal of toxic metal ions as well as harmful micro-organisms such as *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) from water [103]. Synthesis of new Schiff's based Zn-complexes for photocatalytic degradation of methyl arenes as well as xylenes in the presence of visible light was also reported. The mineralization of methyl orange and methyl violet dyes under photocatalysis as well as the photocatalytic degradation of methyl arenes was tested with the prepared Zn (II) complexes. All the Zn (II) complexes performed as good photocatalysts because of their magnificent photostability. The hydroxyl radicals which are formed in situ had a significant impact on the photocatalytic degradation of dyes and methyl arenes and were well established through the scavenger and terephthalic acid probe methods [106]. In another study, it was reported that a ZnO - [Zn (CPAMN)] complex-composite catalyst can be made as a piezo-photocatalyst in the treatment of industrial wastewater and recalcitrant dye pollutants. It was found that the ZnO - [Zn (CPAMN)] complex-composite material had better piezo-photocatalytic activity compared with simple or complex ZnO. For the study, sonication and visible light photolysis were used simultaneously in the presence of complex-composite catalyst, and about 98% of dye solutions including methyl red (MR) and rhodamine B (RhB) were mineralized at 60 and 80 min, respectively, by piezo-photocatalysis. By the comparison of precursor materials including [Zn (CPAMN)] and ZnO, it was observed that the photocatalytic activity of the ZnO - [Zn (CPAMN)] complex-composite was enhanced. It was well explained the heterojunction superiority by the less recombination rate of active species and the availability of large surface area, which resulted in an enhanced photocatalytic activity [107].

3. Ferritic Nanomaterials

Fe₃O₄ is considered to be the most important as a photocatalyst among the nanoparticles of the ferrite family because of its unique structure with iron cations in two valence states, Fe²⁺ and Fe³⁺, on tetrahedral and octahedral sites, respectively, having an inverse cubic spinel structure. According to Rahman et al. [108], Fe₃O₄ has exceptional superparamagnetic behavior, which can be used in easy magnetic separation of the semiconductor from the solution. The catalyst is highly reusable because of its long-term

stability, and its recovery by magnetic force is also very easy [77]. The nanoparticles have definite size, high surface to volume ratio, which makes it an efficient photocatalyst for the elimination of toxic metal ions from water [109,110].

PHOTOCATALYTIC DEGRADATION TREATMENT OF LAUNDRY WASTEWATER AND THE OPERATIONAL PARAMETERS

Good quality ground water resources are scarce nowadays due to the large consumption of water for industrial and domestic purposes. Considerable amount of wastewater is produced in laundry applications and it is commonly contaminated by residual surfactants. Therefore, improving the quality of laundry-treated water has become necessary due to stringent environmental regulations. There is a strict limit for anionic detergent which has been fixed by the regulatory authorities for environmental and public health, as 0.5 mg/L standard for drinking water, which is made up to 1.0 mg/L for other purposes [111].

Lizama et al. [112] studied the photocatalytic degradation of two industrial-grade surfactants, sodium lauryl sulfate (SLS) and sodium dodecylbenzene sulfonate, using immobilized TiO_2 on glass. The results indicated that the best condition for the treatment of surfactant solution having two commercial detergents is achieved with an 80% removal efficiency within 60 min of irradiation. According to Venhuis and Mehrvar [113], the degradation of linear alkylbenzene sulfonate using Degussa P25 TiO_2 combined with UV light (365 nm), UV light (254 nm) alone, or hydrogen peroxide combined with UV light (254 nm), has great potential to reduce the contamination generated by surfactants. From the results obtained, hydrogen peroxide combined with UV light at 254 nm is considered to be the most effective method based upon the estimated initial rates for the destruction of the compound.

Jariyanorasade and Junyapoon [114] compared the photocatalytic degradation of linear alkylbenzene sulfonate (LAS) in synthetic solution as well as in industrial laundry wastewater by UV/ TiO_2 process. From the experimental results it is given that the tetragonal anatase phase (82.58%) is the dominating crystalline structure of TiO_2 . Also, the optimum conditions estimated for the photocatalytic degradation of LAS are, at 20 mg/L of initial LAS concentration, 5.5 pH, 100 mg/L of TiO_2 dosage within an irradiation

time of 60 minutes. Under these optimum conditions, 83.20% removal efficiency of LAS in synthetic solution is achieved [114].

EFFECT OF LIGHT INTENSITY AND IRRADIATION WAVELENGTH

The intensity of light can determine the extent to which light is absorbed by the semiconductor catalyst at a specified wavelength. The rate of initiation for the formation of electron-hole pairs in the photochemical reaction is fully dependent upon the intensity of light provided [74]. Then, light intensity diffusion inside the reactor will determine the complete removal of pollutants and the degradation efficiency [115]. As a result, the dependent behavior of pollutant degradation rate on the intensity of light has been explained in several researches with various organic contaminants. The rate of reaction is independent at very high light intensity. It can be explained that the formation of electron-hole pairs are the predominant reactions at low intensity, and the recombination of electron-hole pair is negligible. The effect of light intensity and irradiation wavelength on various surfactants is given in Table 3. Kaneco et al. [116] analyzed the outcome of light intensity by solar photocatalysis for the removal of bisphenol A in water using TiO_2 as the catalyst on both sunny and cloudy days. The removal rate rapidly increases with an increase in the intensity of light up to 0.35 mW/cm^2 , and the efficiency is enhanced successively.

The photochemical effects induced by light sources at different emitting wavelength ranges will profoundly modify the photocatalytic reaction rate, depending upon the different morphologies of photocatalysts used in the crystalline phase, such as anatase and rutile. The bandgap energy of crystalline phase of rutile TiO_2 with 3.02 eV is small compared to that of the anatase TiO_2 with 3.2 eV [80]. This dictates that rutile TiO_2 can be activated with a light wavelength of up to 400 nm, depending on the bandgap threshold for the type of rutile TiO_2 used. The corresponding electromagnetic spectrum can be classified as UV-A, UV-B and UV-C, according to the wavelength emitted under UV irradiation. The UV-A light consisting of wavelength ranges from 315 to 400 nm (3.10-3.94 eV), whereas UV-B has wavelength ranges from 280 to 315 nm (3.94-4.43 eV), and the germicidal UV-C ranges from 100 to 280 nm (4.43-12.4 eV) [117]. The natural UV radiation that irradiates the surface of the earth consists of both UV-A and UV-B spec-

Table 3. Effect of light intensity and irradiation wavelength

Target compound	Irradiation sources	Results/Remarks	Ref.
Non-ionic surfactant (Triton X-100)	40 W UVA lamp ($\lambda_{\text{max}}=365$ nm)	The photocatalytic degradation of detergent contaminated water follows first-order kinetics.	[119]
Anionic surfactant (NaDBS)	300 W UVA lamp ($\lambda_{\text{max}}=365$ nm)	The removal efficiency of NaDBS is enhanced to 89% after 100 min by combination of photocatalysis and membrane filtration technique.	[120]
Anionic surfactant (LAS)	130 W UVC lamp ($\lambda_{\text{max}}=254$ nm)	The rate of removal under UV/ H_2O_2 at 10, 20, and 30 min are reported to be 86.2, 90, and 96.5%, respectively.	[121]
Car Shampoo, Cleentex	150 W medium-pressure lamp and 8 W medium-pressure lamp	By the irradiation time of 5 hours, 19% COD reduction is attained in the presence of 8 W lamp and it is 47% in the case of 150 W lamp	[23]

trums. Puma and Yue [118] examined the effect of light wavelength on the photocatalytic degradation of 2-chlorophenol using UV-A alone with simultaneous UV-A, B, and C radiation. There is a substantial improvement in the rate of degradation and mineralization of 2-CP with UV-ABC radiation compared to UV-A radiation. The initial rate of 2-CP degradation is 1.8 times faster under UV-ABC radiation than that of the UV-A radiation, and efficiency of the degradation of 2-CP is 98% at an irradiation time of 20 minutes. The improvement in the rate of degradation with UV-ABC is attributed to the photon flux with UV-ABC, which is reported to be 1.56 times more than that of UV-A radiation.

EFFECT OF SOLUTION pH

pH is one among the fundamental operating parameters in heterogeneous photocatalysis, as it will influence the surface charge of the semiconductor photocatalyst, which are normally existing in their positive, neutral, and negative forms in an aqueous solution. An organic compound will exist as a neutral species at a pH below its pKa value, and above this value it will be negatively charged. This variation can also significantly influence their photocatalytic degradation behavior. The pH of an aquatic environment plays a vital role in the photocatalytic degradation of organic contaminants since it determines the surface charge of the photocatalyst and size of the aggregate which it can form [74]. Due to the nature of the catalyst used, any adjustment in the operating pH is known to affect the isoelectric point or the surface charge of the photocatalyst used. Generally, the effect of pH on the photocatalytic degradation of organic compounds in the presence of semiconductor

oxide catalyst can be studied by making use of the point of zero charge (PZC) of the same catalyst [81]. According to the type of the catalysts used for the study, the PZC can be varied from a pH range of 4.5 to 7, and it is known to be a state at which the surface charge of the photocatalyst appears to be zero or in the neutral form. In the case of TiO_2 , at PZC, there is no electrostatic force is operating and at this point, the interactivity between semiconductor photocatalyst and the pollutants present in water will be very low. But, when the pH of the solution is lower than the PZC value (TiO_2), the surface of the catalyst becomes positively charged and an electrostatic force of attraction will be moderately operating in the direction of negatively charged particles present in the system. Such polar attractions between the catalyst and charged anionic organic compounds will result in an improved adsorption of organic compounds into the surface of TiO_2 , which is photon activated, and eventually the photocatalytic reactions can be completed [81]. When the pH is higher than the PZC value (TiO_2), the surface of the catalyst is negatively charged and it will be repulsed against the anionic particles present in water. Table 4 provides the photocatalytic behaviour of various surfactants at different pH ranges.

Eng et al. [122] investigated the effect of initial pH on the photocatalytic degradation of non-ionic surfactant, Brij 35, in aqueous TiO_2 suspensions. The author reported that the photocatalytic degradation rate of Brij 35 at neutral pH is more compared with that at pH 4.2 or 9.2. The point of zero charge (pzc) of Degussa P25 is 6.9 [123]. Therefore, the electrostatic force of attraction between the compound and the surface of the photocatalyst is not too strong and the degradation of the pollutant at pH 7.0 becomes

Table 4. Effect of solution pH

Target compound	pH studied	Results/Remarks	Ref.
Nonionic surfactant (Brij 35)	pH 4.2, 7, and 9.2	The photocatalytic degradation rate of Brij 35 is more at neutral pH (pH 7) compared to pH 4.2 and 9.2.	[122]
Non-ionic surfactant (Triton X-100)	In the range between 2-10	The rate of mineralization is enhanced by increase in the pH. From the results, it is observed that the intermediates formed during the primary degradation process may be carried out by the hydroxide ions.	[119]
Anionic surfactant (NaDBS)	In the range between 2-10	In the case of NaDBS surfactant for both types of photocatalysts (TiO_2/N and $\text{TiO}_2\text{-P25}$), the most efficient reaction was the one carried out at initial pH=4.8. The anionic surfactant was almost completely decomposed (99%) when using TiO_2/N after 180 min of UV irradiation, while $\text{TiO}_2\text{-P25}$ mineralized 90% of the same compound.	[124]
Cationic surfactant (BtCl)	In the range between 2-10	In the case of cationic surfactant (BtCl), the highest photocatalytic activity of both photocatalysts reached at pH=10.0, and P25 was more active than TiO_2/N . Surface of TiO_2/N is higher positive charge than surface of $\text{TiO}_2\text{-P25}$ and it is more repulsive to cationic surfactant molecules; it is the reason for slightly higher efficiency of commercial P25 photo-oxidation	[124]
Anionic surfactant (DBS)	In the range between 2-10	An enhanced photodegradation is observed up to 5. When the pH is further increased, the degradation is decreased and it may due the dissociation of formed H_2O_2 into water and oxygen, and thus there will be a reduction in the number of OH radicals.	[125]

more productive compared with other pH values. Also, the concentration of OH^- ions present in the system will be low in the acidic medium and the production of hydroxyl radicals tends to be minimum, and there is a subsequent reduction in the photocatalytic degradation rate of Brij 35.

EFFECT OF INITIAL CONCENTRATION

It is reported clearly that, as the contaminant concentration in the system increases, a greater number of target molecules will get a chance to be adsorbed onto the surface of the semiconductor photocatalyst. Therefore, the elimination of increased concentration of contaminant molecules in the system demands more reactive species such as $\cdot\text{OH}$ and $\cdot\text{O}_2^-$. Anyway, the reactive species found on the surface of the catalyst will be the same for a specific operation conditions, such as intensity of light irradiation, catalyst dosage and irradiation time. Therefore, the OH radicals present in the system may not be sufficient for the complete removal of target compounds at higher concentration. Subsequently, as the initial concentration of the pollutant increases, the rate of degradation decreases [126]. Moreover, an increase in the substrate concentration will lead to the production of intermediates and they compete with the pollutant molecules to be adsorbed on the surface of the catalyst, which will affect the photocatalytic degradation of the pollutant. Also, the slow diffusion of the intermediates formed on the surface of the catalyst may deactivate the active sites of the photocatalyst and, as a result, the degradation rate is inhibited.

The number of active surface sites present in the catalyst is not a limiting factor at lower concentration, and the degradation rate is directly proportional to the initial concentration of the substrate and evidently follows first-order kinetics [127]. There are several reports emphasizing the importance of the TiO_2 photocatalytic reaction rate on the initial concentration of the target pollutant under treatment [74]. Although the working conditions are the same, a difference in the initial concentration of the contaminants present in water will exhibit an inconsistency in the time of irradiation needed to attain the complete mineralization of the pollutant. An excess concentration of the organic substrate will ultimately saturate the surface of the TiO_2 catalyst and inhibit the photonic efficiency and result in deactivation of the photocatalyst [128].

Hong et al. [129] studied the influence of initial concentration (50-400 ppm) on the photocatalytic degradation of phenol in the presence of TiO_2 . The degradation is more at low initial concentration and it is found to be 50 ppm. Parida and Parija [130] compared the impact of initial concentration of the substrate (2-25 g/L) on the photocatalytic degradation of phenol under sunlight, visible and UV light, respectively. By increasing the initial concentration of the substrate, the efficiency of degradation reduced from 100% to 60% in the presence of sunlight. Whereas the degradation was found to be decreased from 94% to 52% under UV light by increasing the initial concentration. In the presence of visible light, the efficiency was reduced from 95% to 50%. The effect of initial concentration on the photocatalytic degradation of various surfactants is given in Table 5.

EFFECT OF CATALYST DOSAGE

The concentration of TiO_2 catalyst dosage in the photocatalytic water treatment system affects the overall photocatalytic reaction rate, where the amount of TiO_2 is directly proportional to the overall photocatalytic reaction rate [80]. A linear dependency will be present to a certain extent, and when the reaction rate starts to aggravate it turns to be unimportant about the TiO_2 concentration [132]. When the amount of TiO_2 exceeds above a saturation point, it will result in a high turbid condition and the coefficient of light absorption decreases. Thereby inducing a screening effect in the solution by the excess of catalyst particles present in the system. Thus, the active surface sites of TiO_2 which is to be exposed to light illumination will be less and it eventually inhibits the photocatalytic efficiency. Table 6 provides the effect of catalyst dosage on the photocatalytic behaviour of detergent wastewater.

Several studies have indicated that the photocatalytic rate initially increases with catalyst loading and decreases after optimum value because of the scattering of light and the screening effects [80,81]. The tendency towards agglomeration is also more at high solid concentration, resulting in the reduction of active surface area available for light absorption and thereby inhibiting the photocatalytic degradation rate. Although the number of active sites in the solution is increasing with catalyst loading, a point will be reached where light penetration is compromised because of excessive particle concentration. This phenomenon results in an opti-

Table 5. Effect of initial concentration

Target compound	Initial concentration	Results/Remarks	Ref.
Anionic surfactant (LAS)	10, 50, and 100 mg/l concentrations were studied at a pH of 8, using 40 mg/L optimum concentration of H_2O_2	The degradation rate is decreased at higher initial concentration of the pollutant	[121]
Nonionic surfactant (Sanonic SS-90)	Ranging from 1 to 3 g/m ³	Degradation rate constant was almost independent of the initial concentration of Sanonic SS-90 for the range of 1-3 g/m ³	[132]
Nonionic surfactant (Brij 35)	Studied from 0.086 to 0.011 mM and the optimum dosage of TiO_2 is 0.1 g/L	The degradation follows first order kinetics at lower concentration and eventually it becomes zero-order at higher concentration	[122]

Table 6. Effect of catalyst dosage

Target compound	Catalyst dosage	Results/Remarks	Ref.
Non-ionic surfactant (Brij 35)	Tested between 0.008 and 3 g/L at a flow rate of 300 mL/min	The optimum catalyst loading is 0.1 g/L TiO ₂ at neutral pH.	[123]
Laundry wastewater	Ranging from 10 to 60 mg/50 mL	The photodegradation increases along with the increase of the photocatalyst dose. However, after 30 mg, further increase of the photocatalyst dose leads to the decline of photodegradation. Increase in the dosage of TiO ₂ will increase the turbidity of the solution and can reduce the penetration of light into the solution.	[137]
Anionic surfactant (DBS)	Ranging from 20 to 80 mg/100 mL	The photocatalytic degradation of surfactants in the laundry wastewater can be enhanced by increasing the TiO ₂ dosage. But the catalyst loading beyond 40 mg/100 mL does not improve further degradation of the surfactant.	[125]

imum catalyst loading for the photocatalytic reaction [133]. A further increase in catalyst loading beyond the optimum will result in non-uniform light intensity distribution so that the reaction rate will be decreased with an increase in catalyst dosage.

Parida et al. [134] studied the effect of varying concentration of ZnO (0.2 to 2.0 g/l) on the photocatalytic treatment of 4-nitrophenol by making use of solar irradiation. By the optimization of operation conditions, the degradation of 4-NP is evidently enhanced by increasing the catalyst dosage, and the optimum is at 0.6 g/l of the catalyst. It is clear that as the catalyst concentration increases it will facilitate more active sites for the adsorption of large number of target molecules. However, after an optimum catalyst loading, the opacity of the solution will decrease and it may hinder the photon flux from penetrating into the solution. Therefore, further enrichment in the catalyst loading beyond an optimum value will inhibit the rate of degradation. Selvam et al. [135] indicated that the degradation rate constant of 4-fluorophenol increases from 0.0152 to 0.0358 min⁻¹ as the concentration of TiO₂ increases from 50 to 150 mg in the presence of TiO₂ P25. Further increase in the catalyst concentration (150 to 250 mg) reduces the rate constant from 0.0358 to 0.0296 min⁻¹. This can be explained on the basis that catalyst particles freely present in the solution will form aggregates and there will be a screening effect as the transparency of the solution is affected by these aggregates.

In another study, fluorescent whitening agent used in laundry detergents was selected for identifying the catalytic property of newly synthesized photocatalysts using perovskite materials, for the degradation and mineralization of Congo Red dye (CR), which is commonly present in the textile industries as well as industrial wastewater. First, the degradation of CR, as monitored by the inhibition of UV absorbance of CR, was less than 1% if carried out in the dark for 20 min even if there was the presence of catalyst. Whereas, in the presence of visible light, the degradation of CR (25 mg) was still very low (3%) if no catalyst was present. In the presence of both catalyst and visible light, the mineralization progressed with a different rate based on the nature of catalyst used. The results reported that the mineralization of CR was remarkably affected by the catalyst dosage. Significant improvement for the decolorization as well as degradation of the dye solution was

experimented by the increased dosage of catalyst from 0.25 g/L to 1 g/L. It is well established that the increased amount of the catalyst will increase the number of active sites present in the system, thereby enhancing the dye degradation [136].

ECONOMIC FEASIBILITY OF PHOTODEGRADATION TECHNIQUE ON INDUSTRIAL SCALE

When scaling up a treatment method, one of the most significant hindrances is the economics and feasibility of the treatment process. There are several factors which are responsible for an effective photodegradation process. Some of these factors that influence the economics of degradation process include the time required for a complete surfactant degradation, electricity and energy consumption, operation and maintenance costs. In the case of a full-scale system, these costs strongly depend upon the nature and concentration of the pollutants, flow rate of the effluent and configuration of the reactor [138-140]. Mahmuni et al. [141] developed a method to estimate the costs of various AOPs used for the treatment of contaminants. Kinetic degradation data of various pollutants collected from literatures are used for the estimation of costs. The time taken by the pollutants to degrade by 90% of their original concentration is estimated based on the rate constants obtained from the kinetic data and is termed as the residence time of the reactor. The reactor capacity can be calculated by multiplying the residence time with the design flow rate. The total energy required for an AOP process is calculated, and it will help to estimate the cost of an AOP reactor. Scale-up approach has been already tested for several wastewater treatments. In particular, a good numerical analysis and kinetic modelling was proposed by Russo using microreactors [142]. Microreactors are extremely fast and secure in identifying the operational parameters, intermediates formed during the reaction, and other ecotoxicological evaluation. The devices are mainly programmed for the identification of pseudo-first order kinetics of the system. Even though the micro- and photo-microreactors cannot be used as a direct tool for the decontamination of wastewater, they performed as an outstanding working model for the identification of reaction kinetics of the contaminant degradation. Based on AOPs, one of the most import-

ant factors is to eliminate the barrier between the outputs of experimental data which is mostly generated based on lab scale and the design of a system at full scale. Another consistent work reported for comparing two scale-up approaches of meso and microreactor photocatalytic systems, which explains the important factors such as the treatment duration of the AOP, initial contaminant concentration, pathway of the UV light, reusability, economic feasibility in terms of energy consumption and quantum efficiency for meso- and microreactor photocatalytic devices, were presented to justify the viability of these systems [143]. The work was focused on the homemade meso- and micro photocatalytic systems which were designed to identify the impact of various reaction experiment systems on laboratory scale and scaling up of these systems based on a large-scale approach using meso as well as microfluidic systems. By enhancing the process of photocatalytic degradation within the microfluidic approach it can be a potential large scale wastewater treatment system. The process of organic decontamination photocatalytic systems in lab scale is important in demonstrating that the photoreactor design is practical and can be a scaled up environmental application. Thus, by combining the internal and external numbering up, it will be helpful to design a powerful chemical plant by the right design of microreactors for the decontamination of wastewater on an industrial scale.

Saritha et al. [139] investigated and compared the overall costs of various AOPs, including UV, UV/TiO₂, UV/H₂O₂, Fenton and H₂O₂ based AOPs, UV/Fenton in the degradation of 4-chloro-2-nitrophenol. The study declares that the AOPs carried out using H₂O₂ and Fenton are cost effective and UV is the most expensive. Esplugas et al. [140] studied and compared UV, O₃/UV, O₃/H₂O₂, O₃/UV/H₂O₂, O₃, and UV/H₂O₂ processes for degradation of phenol. Based on the total cost of all AOPs, O₃ based processes are the least expensive, while UV is again the most expensive among other AOPs. Photocatalysis and UV are considerably more expensive than the other AOPs because of the usage of high-power lamps in these experiments. Costs can be reduced significantly by using natural sunlight [140]. Furthermore, suspended TiO₂ particles are primarily used in the photocatalytic oxidation of contaminants [141, 144] and it requires recycling and recovery processes of these nanoparticles, making it as a disadvantage of using the suspended systems. Therefore, new methods for using immobilized TiO₂ to create systems with an immobilized active phase are needed [145, 146].

CONCLUSION

Heterogeneous photocatalysis is considered as one of the most promising wastewater treatment processes, as it can eliminate various harmful organic contaminants such as dyes, detergents, phenols, herbicides and pesticides from water. Based on the reported literature, heterogeneous photocatalysts can remove a wide range of organic contaminants from wastewater. The major characteristics of photocatalysis, which makes the technology more promising are, its simple technology, high performance, low cost, and also it is additive-free. However, unlike dyes, only a few studies have been conducted focusing on surfactants, which can be due to the detergent industries' privacy. Progress in physical and chemi-

cal modification of the catalyst used, pre-treatment, and reactor design will be helpful to improve the degradation efficiency of the technology.

The study suggests that various operating parameters, such as intensity of the light used, initial concentration of the pollutant, catalyst dosage, initial pH of the reaction system and the photodegradation process's reaction time, can considerably affect the photocatalytic degradation rate. Optimization of the reaction parameters is crucial for the efficient design of an operating system to ensure sustainability of the photocatalytic oxidation process. It is reported that metal and non-metal doping of TiO₂ can enhance the degradation rate. Although doped TiO₂ has shown significant improvement in the efficiency to treat wastewater in laboratory-scale systems, there is a need to develop pilot-scale treatment systems for applying this technique as a cost-effective wastewater treatment process and it requires in-depth research.

A number of aspects are present in the photocatalysis which are important for its commercial implementation. Among these, the dominant aspect is to eliminate the constraints related to the operational parameters. As the pH and chemical composition of the contaminated wastewater obtained from various regions are different, advanced studies should be made to invent photocatalytic materials, which can work in a wide range of operating conditions, such as temperature, pH and contaminant concentrations. Additional research is needed to modify TiO₂ and other semiconductors by doping to enhance continuous irradiation in the presence of visible light at a broader range of operating conditions. Water treatment processes in the presence of visible light can provide a great potential to restore conventional water and wastewater treatment methods, as it is a sustainable and environment-friendly technique. Doping and photosensitization can be used for enhancing the visible-light activity of semiconductors. It is well known that the combination of heterogeneous photocatalysis with other AOPs will impart a synergistic effect, which in turn improves the efficiency.

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