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*Review Article*

# Recent Progress in $TiO_2$-Mediated Solar Photocatalysis for Industrial Wastewater Treatment

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The current paper reviews the application of $TiO_2$-mediated solar photocatalysis for industrial wastewater treatment, starting with a brief introduction on the background of industrial wastewater and the development of wastewater treatment processes, especially advanced oxidation processes (AOPs). We, then, discuss the application of solar $TiO_2$ photocatalysis in treating different kinds of industrial wastewater, such as paper mill wastewater, textile wastewater, and olive mill wastewater. In the end, we compare solar $TiO_2$ photocatalysis with other AOPs in terms of effectiveness, energy, and chemical consumption. Personal perspectives are also given, which may provide new insights to the future development of $TiO_2$ photocatalysis for industrial wastewater.

## 1. Introduction

Industrial wastewater is of global concern due to its severe effects on the environment. Compared with municipal wastewater, industrial wastewater generally contains high concentration of toxic or nonbiodegradable pollutants, such as fats, oil, grease, heavy metals, phenols, and ammonia [1]. The water quality of wastewater can be indicated by some parameters such as suspended solids (SS), biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) [2]. These parameters are typically very high in industrial wastewater, which significantly reduce the performance of conventional wastewater treatment processes. Industrial wastewater also has much more complex composition than other wastewaters. Moreover, the water quality of industrial wastewater varies from one industry to another. Huge difference in water quality of wastewater between different factories may also happen in some cases. For example, the wastewater produced from iron and steel industry contains a large amount of ammonia, cyanide benzene, naphthalene, phenols, and cresols due to the reduction reactions in blast furnace and the production of coke [3]. In contrast, dispersed dyes are considered as dominant pollutants in textile wastewater and effluent from paper industry generally contains high concentration of SS and BOD [4]. Unlike other wastewaters, high concentration of radioactive materials is present in nuclear industry wastewater. Owing to the high concentration of toxic pollutants and diversity of water quality, the treatment of industry wastewater is always a big challenge. In recent years, various novel technologies such as membrane technology, electrochemical method, and membrane bioreactor (MBR) have been proposed for the treatment of industrial wastewater. Unfortunately, these treatment processes still face several problems, for example, complicated technical requirements, high operational cost, and long reaction time, which severely restrict their applications.

Electrochemical method is to apply a voltage between an anode and cathode to remove pollutants via direct oxidation or reduction on electrodes or indirect oxidation or reduction by the reactive oxygen species generated by electrochemical reactions [5, 6]. Electrochemical method can be categorized to electrodeposition, electrodisinfection, electrocoagulation, electroflotation, electroadsorption, electrooxidation, and electroreduction. Suspended pollutants, colloids, and many charged pollutants can be effectively

removed from wastewater by this method [7]. For instance, electroflotation is successfully used for the treatment of oil mill effluent [8], oily wastewater [9], coking wastewater, and mining wastewater. In addition, electrooxidation process has been extensively investigated since the late 1970s [7]. Although many research works have already been done on optimization of the operation parameters, improvement of the electrocatalytic activity, the degradation mechanisms, and kinetics of pollutants, it is clear that electrode materials have big impact on the degradation of pollutants, which has to be improved in term of stability and durability [10].

With the increasing requirement of water supply and the more stringent environmental regulations, great progresses have been seen globally in membrane technology in past two decades. Compared with other processes, membrane technologies have many advantages such as high removal rate on pollutants, well arranged process conductions, and no addition of chemicals [10]. These superiorities make it suitable for wastewater treatment. However, membrane fouling caused by pollutants in wastewater is a major obstacle, which restricts the large-scale application of membranes in industry. Thus, how to achieve an effective and low cost way to treat wastewater is a crucial point.

Biological wastewater treatment is widely used in municipal wastewater treatment due to its low operation cost compared to other treatment processes such as thermal oxidation and chemical oxidation [11]. MBR is an improved activated sludge system, which is a combination of suspended biomass with a membrane process that replaces gravity sedimentation to clarify the wastewater effluent [12]. MBR process has small footprint, flexible design, and automated operation properties. However, like other membrane technologies, membrane fouling by mixed liquor remains and activated sludge is considered as a major obstacle for its applications. In addition, membranes with high chemical resistance are required due to the chemical cleaning process. Currently, MBR technology is mostly applied in small or moderate scale. Moreover, only biodegradable pollutants can be removed by biological treatment processes. There are still large amounts of toxic nonbiodegradable materials present in industrial wastewater.

Advanced oxidation processes (AOPs), which rely on the generation of highly reactive and oxidizing hydroxyl radicals (•OH), are considered as highly competitive water treatment technologies. As an important technology of AOPs, photocatalytic oxidation (PCO) has attracted increasing attention in recent years because of its excellent performance on pollutants removal, low cost, and photochemical stability and without addition of toxic chemicals [13, 14]. $TiO_2$ is the most widely used catalyst in heterogeneous photocatalysis, because of its photostability, nontoxicity, low cost, and stability in water under most environmental conditions [15]. Large amount of reactive oxygen species such as hydroxyl radicals (•OH) and superoxide radical anion ($\bullet O_2$) are produced on the surface of $TiO_2$ under light irradiation, and these reactive radicals are regarded as the major responsible species for the degradation of organic pollutants in wastewater [16–19]. Preis and coworkers [13] studied the degradation of phenolic compounds in wastewater from oil shale under UV-light irradiation. The results revealed that the wastewater quality characteristics have obvious influence on the photodegradation rate of the pollutants. PCO can also serve as a pretreatment, which can significantly enhance the biodegradability of industrial wastewater to meet requirements of the subsequent biotreatment process. Sioi et al. [19] investigated the decolorization of a typical pharmaceutical wastewater using $TiO_2$ P25 as a heterogeneous photocatalyst, revealing that photocatalytic oxidation is a powerful alternative technology for the degradation of hematoxylin. Their results also showed that the performance of P25 nanoparticles didn't decrease after reuse and, thus, was suitable for practical wastewater treatment. To further improve the efficiency of wastewater treatment, some other techniques can be combined with PCO process. For example, Kim and Park [20] developed a novel hybrid process combining PCO with biofilm. Their results revealed that the pretreatment using biofilm could largely enhance the efficiency of PCO. Moreover, the integrated technology showed better performance as compared to Fenton oxidation in terms of color and COD removal. PCO process has many advantages, but it also faces some drawbacks. One is the relatively high operating cost because of the use of UV lights. Nevertheless, the UV lights in such systems could be replaced by natural solar radiation, which is free in most areas and feasible especially for industrial wastewater treatment [21]. The PCO process can also be combined with constructed wetlands [22]. The combined system was tested under natural irradiation, showing that organic pollutants, nutrients, and pathogenic bacteria can be effectively removed. More importantly, $TiO_2$-mediated solar photocatalytic oxidation is low cost and environmental friendly and thus may be a promising solution for wastewater treatment.

## 2. Process and Mechanism of Solar Photocatalysis

In last decades, many efforts have been devoted to the degradation of organic pollutants in wastewater using solar photocatalysis [27, 32]. Compared to the counterparts using UV light, solar driven PCO of organic pollutants using solar irradiation can be much more economical [33]. As a typical semiconductor-based heterogeneous photocatalyst, $TiO_2$ was successfully employed for the degradation of various families of organic pollutants in wastewater under solar light irradiation. Stylidi and coworkers [34] successfully used $TiO_2$ suspension to degrade azo dyes under solar light; while Herrmann and coworkers applied this technology for the detoxification of wastewater which contains multiple pollutants [32].

In a typical solar photocatalysis process (Figure 1), the electrons ($e^-$) on the photocatalyst surface can be excited from valence band to conduction band by photons with energy larger than its band gap under solar light irradiation, which forms $e^-$ and holes ($h^+$) on conduction and valence bands, respectively. The photogenerated electrons and holes then migrate to the surface of the photocatalyst, where they participate in redox reactions with adsorbed species and,

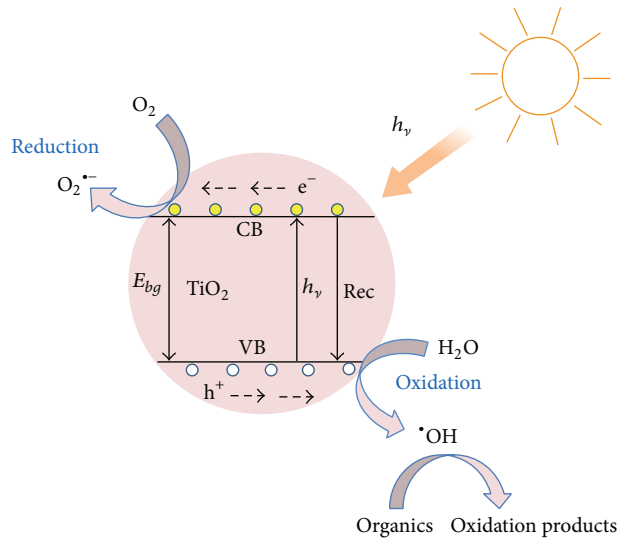



Figure 1: General mechanism of $TiO_2$ in solar photocatalysis process.

thus, form superoxide radical anion ($\bullet O_2^-$) and hydroxyl radical (•OH), respectively, as follows [13, 16–18, 48, 49]:

$$\begin{aligned} TiO_2 &\xrightarrow{\text{solar}} e^- + h^+ \\ h^+ + H_2O &\longrightarrow \bullet OH + H^+ \\ h^+ + OH^- &\longrightarrow \bullet OH \\ e^- + O_2 &\longrightarrow \bullet O_2^- \end{aligned} \quad (1)$$

The photogenerated reactive oxygen species are very strong oxidizers and play the dominant roles in the degradation of organic pollutants in wastewater. The organics in wastewater can be completely degraded to $CO_2$ and $H_2O$ and, thus, there is no secondary pollution. However, many $e^-$ and $h^+$ recombine releasing energy as heat before they participate in the redox reactions, which dramatically inhibit the practical photocatalytic activity of photocatalysts [50]. Moreover, owing to the larger band gap, $TiO_2$ can be excited only by UV lights, which account for less than 5% energy of the solar spectrum [15, 48, 51]. Thus, it is necessary to develop $TiO_2$ based materials which can utilize more solar energy. To solve this problem, some noble metals and their derivatives such as Ag, [52], Pt [53], AgBr [54], and CdS [55], have been tried to incorporate with $TiO_2$ forming hybrid photocatalysts [54], which would extend the photocatalytic activity of the photocatalysts into visible light range. The mechanism can be explained by two aspects. (1) The recombination rate of $e^-$ and $h^+$ is inhibited because of the presence of incorporated materials, which promotes interfacial electron transfer and consequently facilitates the separation of $e^-$ and $h^+$ [51]. (2) $TiO_2$ band gap is narrowed, which makes the excitation of $TiO_2$ easier. It will facilitate the electrons transfer from valence band to conduction band, and, thus, more oxidative species might be produced [56]. Özkan et al. reported that 1 wt.% Ag could effectively enhance the PCO efficiency [57]. Zang and Farnood found that AgBr can promote the PCO process for the degradation of methyl orange under solar light irradiation [54]. In addition, some researchers have already proven that the band gap of modified $TiO_2$ is lower than pure $TiO_2$ [58, 59]. Grzechulska and Morawski [58] investigated the modified commercial $TiO_2$ with metal hydroxides, and their study revealed that the band gap of modified material is 1.6 eV, which is lower than pure $TiO_2$. Moreover, $TiO_2$ can also be integrated with some other semiconductors with a narrow band gap, for example, CdS, to form composite photocatalysts [60].

## 3. Application in Industrial Wastewater

*3.1. Application in Paper Mill Wastewater.* The paper mill is the fifth largest industry in North American economy [61]. Over 50% wastes in Canada's water can be attributed to the pulp and paper industry [62]. Large amounts of water are required by paper industry, which also produced equally large amounts of wastewater [63, 64]. Previous study indicated that 2000–6000 gallons water were consumed to produce one ton of paper [61]. The wastewater produced by this industry is commonly treated by biological process [65]. However, the effluent from paper industry contains highly toxic and refractory compounds, which restricts the application of biological method. In pulp and paper industry, water is required in each stage, and wastewater is also generated in each stage. The produced pollutants at different steps of a paper mill plant are shown in Figure 2 [23, 66]. Among these processes, the cellulose pulp bleaching stage produced the largest amount of high-strength wastewater, which contains several chlorinated compounds and some toxic organics [63]. Previous reports [67] showed that wastewater with BOD/COD ratio smaller than 0.3 is not suitable for biological treatment. Thompson and coworkers [68] reported that the biodegradability index of wastewater from pulp bleaching process is around 0.02–0.07, which indicated a further treatment process should be taken after biological process for the complete removal of pollutants. For example, Bajpai et al. [69] studied the degradation of pollutants from pulp and paper mill by anaerobic technology, and they found that the treated wastewater still contains high residual COD due to the incomplete degradation. In addition, the typical characteristics of paper mill wastewater at different processes are shown in Table 1 [23]. It shows that the pollutants vary dramatically from one plant to another plant.

Another important work was conducted by Ghaly and coworkers [24]. The paper mill wastewater was treated by a synthesized nanosized $TiO_2$ under solar light, and they found that the biodegradability index of the paper mill wastewater increased from 0.16 to 0.35. It indicates that solar photocatalytic oxidation of the paper mill wastewater can be used as an efficient pretreatment method before biological treatment process.

Many factors can influence the performance of solar $TiO_2$ photocatalysis on the treatment of paper mill wastewater [24]. The first one is the size of $TiO_2$. New physical and chemical properties will emerge when the size of $TiO_2$ is reduced

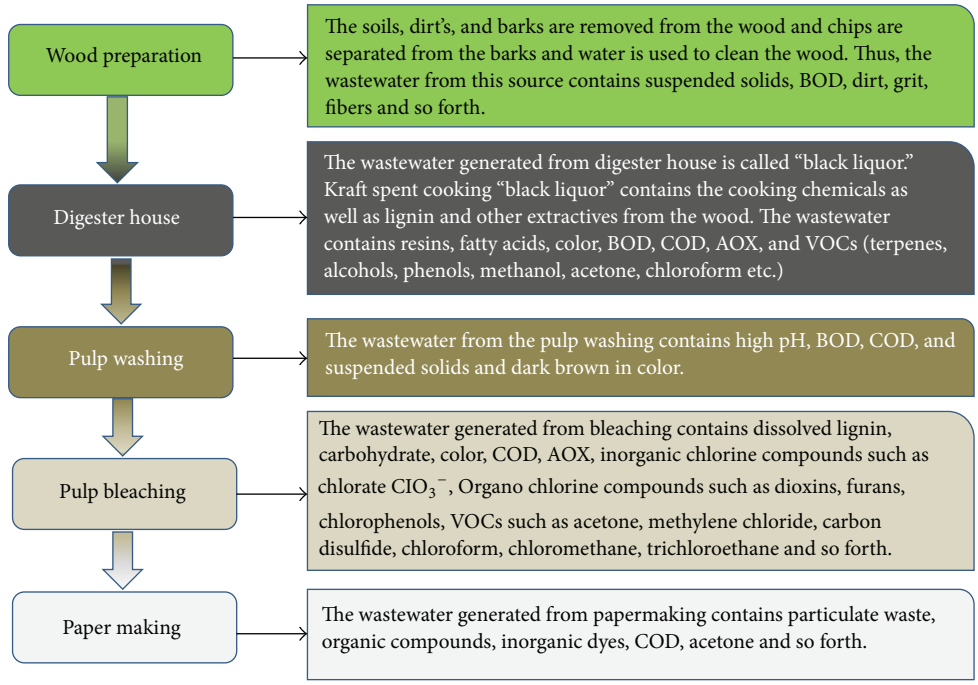



Figure 2: Pollutants produced in different stages of paper industry. (Figure 2 is reproduced from reference [23]. Copyright 2004, with permission from Elsevier).

Table 1: Typical characteristics of wastewater at different pulp and paper processes. (Table 1 is reproduced from [23]. Copyright 2004, with permission from Elsevier).

| Process | Parameters | | | | | Reference |
|---|---|---|---|---|---|---|
| | PH | TS (ppm) | SS (ppm) | $BOD_5$ (ppm) | COD (ppm) | |
| Large mills (India) | 11.0 | 5250 | 1233 | 983 | 2530 | [35] |
| Small mills (India) | 12.3 | 15120 | 4890 | 2628 | 6145 | [35] |
| Digester house | 11.6 | 51589 | 23319 | 13088 | 38588 | [36] |
| Combined effluent | 7.6 | 3318 | 2023 | 103 | 675 | [36] |
| TMP whitewater | 4.7 | — | 91 | 1090 | 2440 | [37] |
| TMP whiterwater | 4.7 | — | 105 | 1125 | 2475 | [38] |
| Kraft mill | 8.2 | 8260 | 3620 | — | 4112 | [39] |
| Pulping | 10 | 1810 | 256 | 360 | — | [40] |
| Kraft mill (unbleached) | 8.2 | 1200 | 150 | 175 | — | [41] |
| Bleached pulp mill | 7.5 | — | 1133 | 1566 | 2572 | [42] |
| Bleaching | 2.5 | 2285 | 216 | 140 | — | [40] |
| Pulp and paper | 7.8 | 4200 | 1400 | 1050 | 4870 | [43] |
| News air and land paper deinking | 8.3 | 450 | 400 | 16 | 78 | [44] |
| Paper making | 7.8 | 1844 | 760 | 561 | 953 | [45] |
| Paper mill | 8.7 | 2415 | 935 | 425 | 845 | [46] |
| Paper machine | 4.5 | — | 503 | 170 | 723 | [42] |
| Paper machine | 8.3 | — | 1032 | 240 | — | [40] |

down to nanoscale. Due to this, the nanosized material may possess with better performance as compared to a conventional bulk material [70]. Chen and Mao [48] reported that morphology of nanomaterials can also affect their properties and performance in specific applications. Nowadays, researchers have put many efforts to develop new functional nanomaterials for the removal of pollutants [71–73]. Ghaly et al. [24] synthesized nanosized $TiO_2$ via a conventional sol-gel process using $TiCl_4$ as the precursor. The synthesized material exhibited good photocatalytic activity under sunlight irradiation because of its mixture phase of anatase and rutile [18]. As shown in Figure 3 [24], the PCO process was carried out in aqueous suspensions where $TiO_2$ was irradiated by concentrated sunlight. In a typical operation

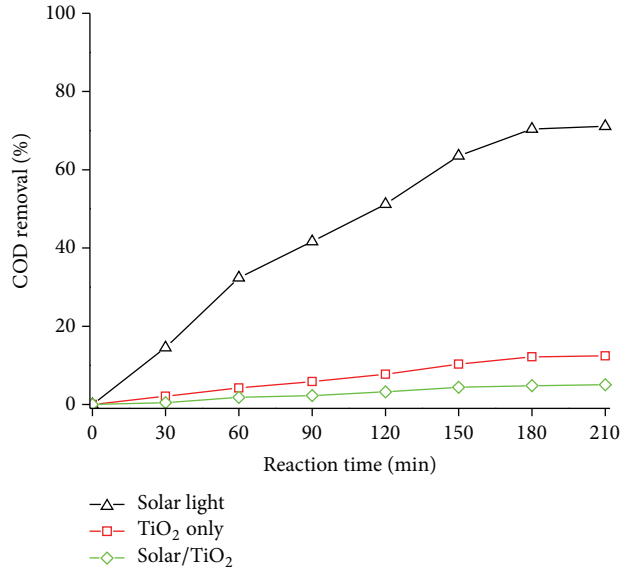



FIGURE 3: %COD removal during the treatment of the wastewater by different oxidation processes against reaction time, with solar light only, with $TiO_2$ only, and with solar/$TiO_2$ [$TiO_2$ = 0.75 g/L, pH = 6.5]. (Figure 3 is reproduced from reference [24]. Copyright 2011, with permission from Elsevier).

process, the wastewater from paper mill was fed into the solar reactor, where it was stirred with the synthesized $TiO_2$ in dark for 10 min. After the adsorption equilibrium between wastewater and $TiO_2$ was achieved, solar energy was applied for the photodegradation of the pollutants in wastewater. Subsequently, the wastewater and $TiO_2$ would circulate in the system and, thus, the treatment efficiency can be enhanced by this continuous process. The COD removal rates under different conditions were evaluated by the authors and shown in Figure 3 [24]. Over 70% COD was removed after the PCO process, indicating that solar photocatalysis is effective for the treatment of paper mill wastewater. It is worth noting that some intermediate compounds may be produced in the process which would retard the degradation of pollutants [24]. In addition, COD concentration decreased in the absence of solar light, which can be attributed to the adsorption effect of $TiO_2$ on the pollutants in wastewater.

Recent studies indicated that the dosage of photocatalysts is another important influencing factor [63]. It should be noticed that the increase of photocatalyst would increase the reaction sites on the material and, thus, enhance the PCO efficiency. However, some experiments [63] revealed that high $TiO_2$ concentration does not imply a high reaction performance. According to the previous reports [74], the optimal photocatalyst concentration for industrial wastewater treatment is several hundred mg/L in solar photoreactors. This phenomenon can be explained by the turbidity effect of $TiO_2$. Excess $TiO_2$ would affect the penetration of sunlight through the suspensions due to the light scattering effects [63, 75, 76]. Hence, the dosage of $TiO_2$ in the photoreactor should be optimized, which can also lower the cost on photocatalyst. As shown in Figure 4(a), the optimum $TiO_2$ concentration is 0.75 g/L in the system [24]. Liu and coworkers reported that the optimum dosage of catalyst was determined not only by the type and concentration of pollutants but also by the design of photoreactors [77]. Thus, the dosage of catalyst should be investigated for each individual system.

In addition, pH values of wastewater can also affect the PCO efficiency because the generation of hydroxyl radicals is related with pH conditions [76]. Several studies showed that the COD removal rates increased with the increase of pH values, as shown in Figure 4(b) [24, 78]. It can be attributed to the following reasons. Firstly, $H^+$ can interact with aromatic organic pollutants in paper mill wastewater and lower the electron densities at the polycyclic groups, leading to the decrease of hydroxyl radicals [78]. Secondly, the $TiO_2$ particles tend to agglomerate under acidic condition and, thus, lead to the decrease of reaction sites for the degradation of pollutants in paper mill wastewater [79]. Finally, the surface of $TiO_2$ would be negatively charged under high pH conditions due to the presence of $OH^-$, which acted as an efficient trap for the generation of $h^+$ and hydroxyl radicals. These oxidative species are responsible for the degradation of organic pollutants [79]. Thus, pH condition can be considered as a key factor for the production of hydroxyl radicals, which finally affect the efficiency of solar photocatalysis.

*3.2. Application in Textile Wastewater.* Owing to the large amount of discharge and the degradation-resistant composition, textile wastewater is considered as a major resource of pollutants from industry [80]. There are several processes for textile industry, such as sizing of fibers, scouring, desizing, bleaching, rinsing, mercerizing, dyeing, and finishing [81]. A brief textile process was shown in Figure 5, revealing that large quantities of organics are involved in this technology. Although various textile products can be obtained nowadays, many contaminants are released into environment through indiscriminate discharge of wastewater, which causes severe pollution. Previous reports indicated that textile wastewater contains dyes, detergents, grease, oil, heavy metal, inorganic salts, and fibers [2]. Among them, dye residue is considered as a dominant pollutant which is mainly produced in the step of finishing [25]. An obvious characteristic of textile wastewater is the strong color due to the presence of various dyes. According to the Easton's reports [82], over 30% of the used dyestuffs remain in the reactor after the dyeing process, which results in that a huge amount of azo dyes enter into wastewater. Azo dyes have been considered as a mutagen and carcinogen by the US National Institute for Occupational Safety and Health [83, 84]. It is important to notice that this kind of dyes is difficult to be decolorized [47, 85].

Although most of the textile wastewater is treated before discharge, the conventional treatment process such as aerobic biological process and physical-chemical treatment cannot meet the requirement of elevated discharge standards [2]. A typical characteristic of wastewater from a textile dyeing process is summarized in Table 2 [86]. We can find that the wastewater contains high strength COD, which may destroy

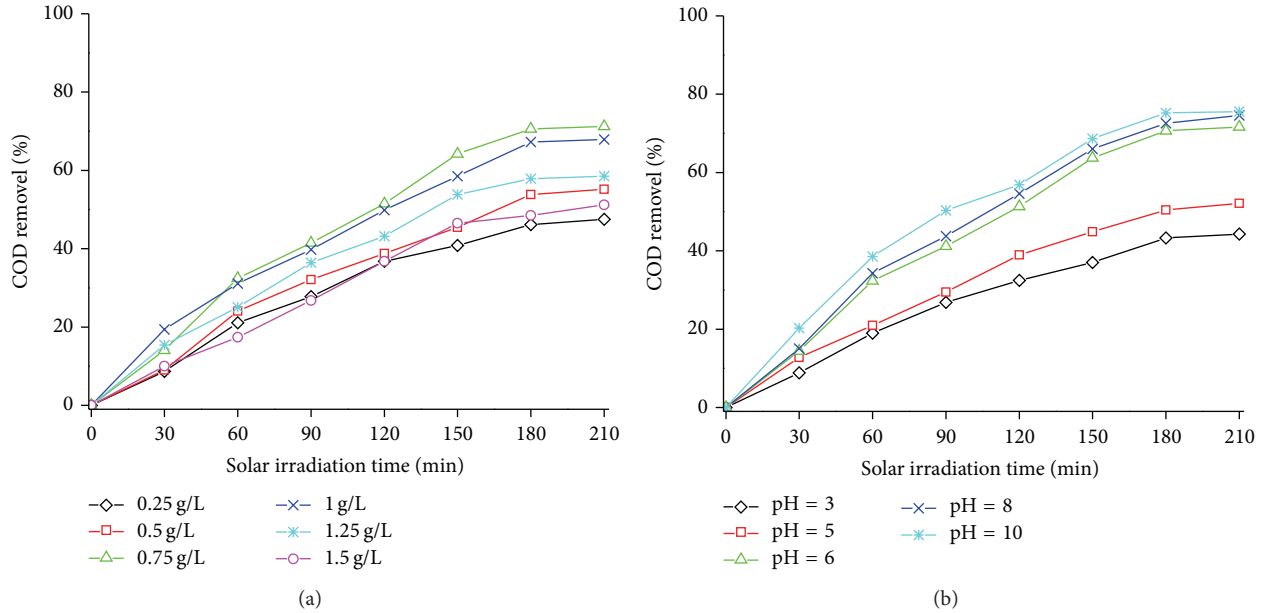



Figure 4: (a) %COD removal during the treatment of the wastewater by solar photocatalytic oxidation against solar irradiation time at different loading of $TiO_2$ [pH = 6.5], (b) %COD removal during the treatment of the wastewater by solar photocatalytic oxidation against solar irradiation time at different pH values [$TiO_2$ = 0.75 g/L]. (Figure 4 is reproduced from reference [24]. Copyright 2011, with permission from Elsevier).

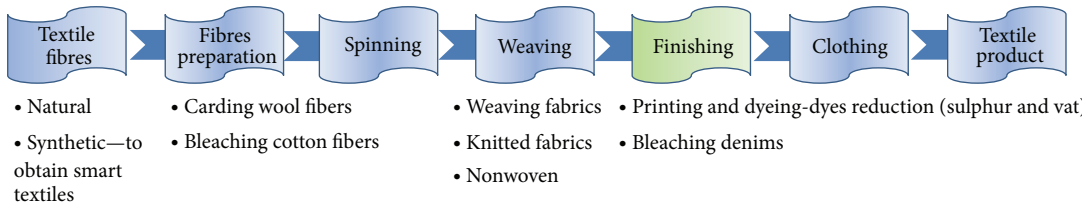



Figure 5: A typical textile process [25].

Table 2: Typical characteristics of wastewater from a textile dyeing process. (Table 2 is reproduced from [47]. Copyright 1986, with permission from Elsevier).

| Aspect/component | Value |
|---|---|
| pH | 2–10 |
| Temperature, °C | 30–80 |
| COD, mg/L | 50–5000 |
| BOD, mg/L | 200–300 |
| TSS, mg/L | 50–500 |
| Organic nitrogen, mg/L | 18–39 |
| Total phosphorus, mg/L | 0.3–15 |
| Total chromium, mg/L | 0.2–0.5 |
| Color, mg/L | >300 |

the microorganisms in a biological wastewater treatment system.

Vilar and coworkers studied the treatment of textile wastewater by solar-driven advanced oxidation processes [26]. In this research, commercial $TiO_2$ P25 was used as the photocatlayst. Figure 6 shows the decolorization and mineralization of the textile wastewater by $TiO_2$ solar photocatalysis [26]. We can find that almost 70% of colour in the wastewater was removed when the catalyst concentration was 200 mg/L. The dosage of catalyst was considered as an optimum concentration for the photoreactor used in the study [87]. However, the mineralization of organics in this treatment process is relatively low, which can be attributed to the high concentration of chloride. Owing to the presence of chloride, the produced hydroxyl radicals would be scavenged and some less reactive inorganic radicals such as Cl•, $Cl_2^{-}$• and $SO_4^{-}$• would also be generated [26, 88]. In addition, previous reports indicated that some organic dyes are capable of photosensitizing $TiO_2$ due to the absorption of visible light [51]. The major initial steps of the photosensitization reactions are shown in the following equations [89]:

$$\text{dye} + h\nu \longrightarrow \text{dye}^*$$

$$\text{dye}^* + TiO_2 \longrightarrow \text{dye}^{\bullet+} + TiO_2\,(e)$$

$$TiO_2\,(e) + O_2 \longrightarrow TiO_2 + O_2^{\bullet-}$$

$$O_2^{\bullet-} + TiO_2\,(e) + 2H^+ \longrightarrow H_2O_2 + TiO_2$$

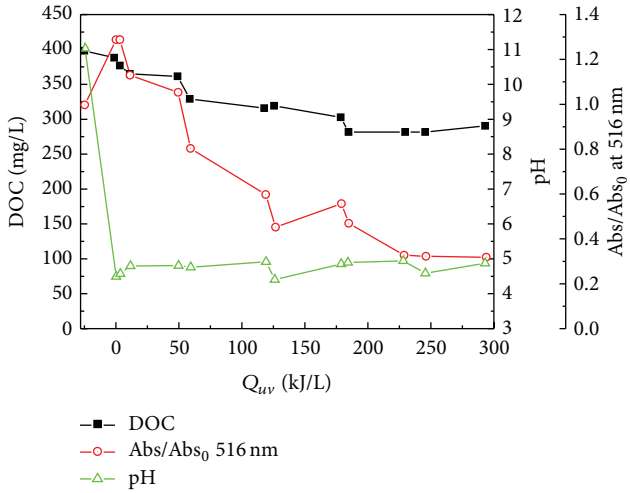



Figure 6: Decolourisation and mineralization of the textile wastewater by $TiO_2$ solar photocatalysis: DOC degradation curve, $Abs/Abs_0$ AT 516 nm and pH evolution. (Figure 6 is reproduced from reference [26]. Copyright 2011, with permission from Elsevier).

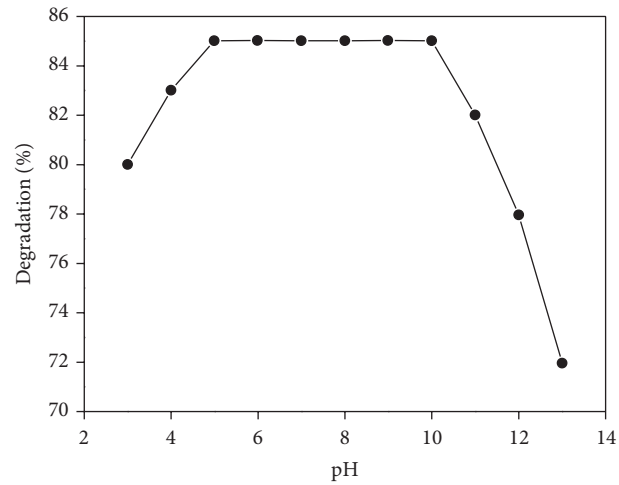



Figure 7: Influence of pH on the degradation of the dye. (Figure 7 is reproduced from reference [27]. Copyright 2002, with permission from Elsevier).

$$2O_2^{\bullet-} + 2H^+ \longrightarrow O_2 + H_2O_2$$
$$H_2O_2 + TiO_2\,(e) \longrightarrow {}^{\bullet}OH + OH^- + TiO_2$$
$$\text{dye}^{\bullet+} + \left(O_2^{\bullet-} \text{ or } {}^{\bullet}OH\right) \text{ the degradaed products} \quad (2)$$

It is clearly shown that the photosensitized degradation of dyes under visible light irradiation is another pathway beside the PCO process. Moreover, some transition or posttransition metal ions such as $Cu^{2+}$, $Zn^{2+}$, and $Fe^{3+}$ also have significant effect on the degradation of dyes in textile wastewater via a similar photosensitization [89]. Thus, the decolorization of textile wastewater is relatively easier as compared to the mineralization process.

Some other reports [27, 28, 81, 90] also proved that $TiO_2$ is a powerful photocatalyst for the degradation of pollutants in textile wastewater. Neppolian et al. [27] found that dye molecules could be completely degraded to $CO_2$, $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, and $H_2O$ by solar photocatalysis, and addition of other auxiliary chemicals such as $H_2O_2$ and $Na_2CO_3$ could greatly promote and inhibit the photodegradation efficiency, respectively. pH also plays an important role in the treatment of textile wastewater because it affects both the generation of hydroxyl radicals in PCO process and the structure of dye pollutants. Figure 7 reveals that a neutral pH condition would facilitate the degradation of dyes in solar photocatalysis process. High concentration of proton would retard the photodegradation of dyes under acidic conditions; while basic conditions also have suppressive effect on the solar photocatalysis process because the dyes become chemically stable at high pH ranges [27].

Although $TiO_2$ based materials have many advantages for environmental application, the separation of them from the suspension of textile wastewater is still a big issue which restricts the reuse of photocatalyst. Alinsafi et al. [91] reported that $TiO_2$ can be immobilised on various substrates such as glass slides and glass fibers. Although the performance of the supported photocatalysts was strongly dependent on the chemical structure of dyes and other additives, the immobilized photocatalysts presented excellent decolourization ability for the treatment of textile industry wastewater. Furthermore, Rao et al. [28] developed a novel pebble bed photocatalytic reactor for textile wastewater treatment under solar irradiation. $TiO_2$ was successfully coated onto the silica rich white pebbles, and a pebble bed photoreactor was further constructed, as shown in Figure 8. In this research, catalyst loading, pH, and initial concentrations of dyes were found as important influencing factors. In addition, the recirculation flow rate in the system was also investigated, presenting that the conversion of pollutants decreased with the increment of flow rate. This phenomenon can be explained by the nonideal flow behaviour of the photoreactor. The flow diversion should be controlled, which enhances the contact area between the textile wastewater and the coated photocatalysts [28].

*3.3. Application in Olive Mill Wastewater (OMW).* OMW is considered as one of the most important agricultural pollutants, which was largely produced by some countries such as Spain, Italy, and Greece [92]. The annual production of olive oil was estimated in $2.5 \times 10^6$ t, resulting in huge amount of OMW [93]. Production of 1000 kg of olives may generate 0.5–1.5 $m^3$ of OMW which is dependent on the oil extraction methods [94, 95]. OMW contains high strength of suspended solids and organic pollutants, such as polysaccharides, sugars, phenols, polyalcohols, proteins, organic acids, and oil [96, 97]. Due to the high concentration of organic pollutants, COD and COD values of OMW are high up to 220 g/L and 100 g/L, respectively [94]. In addition, the characteristics of OMW are variable with the change of climatic conditions, different type of olives, methods of extraction, and regions [94]. The extraction process of olive oil is shown in Figure 9.

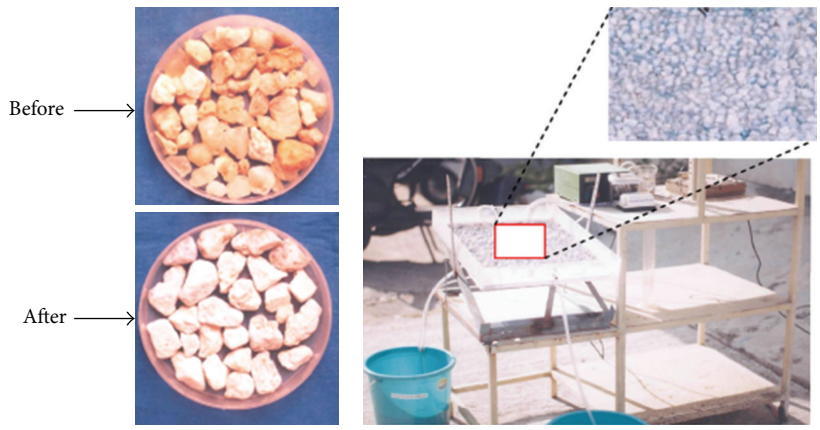



FIGURE 8: (a) Pebbles before and after $TiO_2$ coating, (b) solar photocatalytic pebble bed reactor, and the close-up of pebbles. (Figure 8 is reproduced from reference [28]. Copyright 2012, with permission from Elsevier).

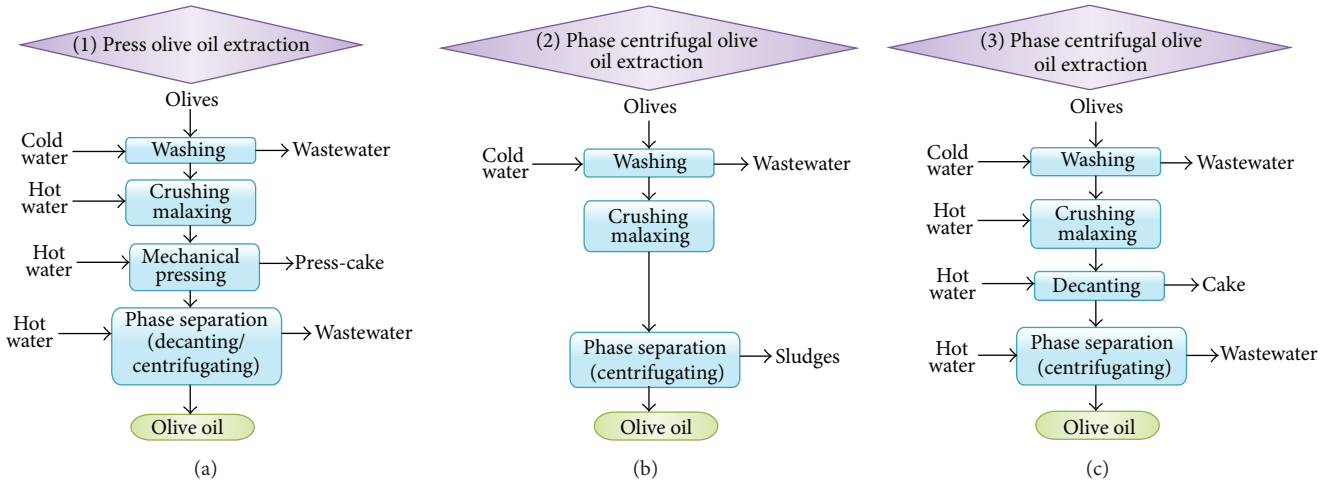
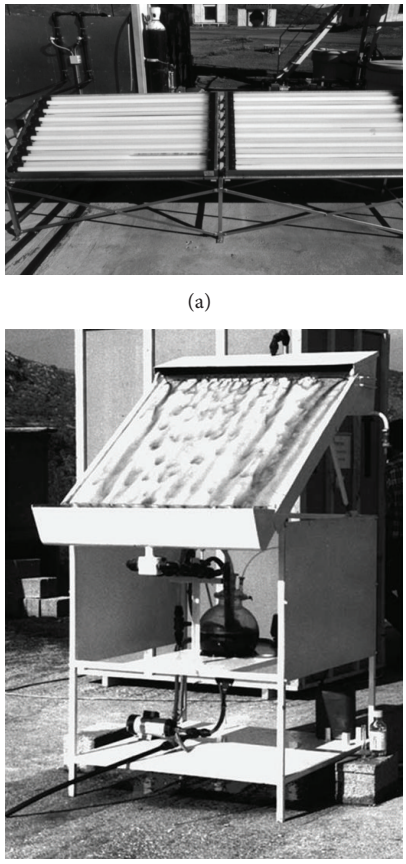



FIGURE 9: Olive oil extraction processes. (Figure 9 is reproduced from reference [29]. Copyright 2012, with permission from Elsevier).

Currently, the main olive process method used in many countries is the 3-phase system, which possesses some advantages such as high working capacity and automation of the industrial plants [29]. Although the olive oil, solids, and wastewater can be separated in this system, it requires a considerable volume of warm water for the dilution of olive paste. Thus, the production of OMW is still a big problem. It is estimated that 30 million $m^3$ OMW is discharged per year [29, 98]. OMW is characterized by a dark-colour due to the polymerization of phenolic compounds and lignin. Moreover, inorganic metals, high conductivity, and acidic condition of the wastewater can also affect the choice of the treatment methods [29].

Gernjak et al. compared two solar photocatalytic pilot-plant reactors (Figures 10(a) and 10(b)) for the degradation of OMW with different concentrations and from different sources [99]. For the compound parabolic collector (CPC), a complete module is formed by a series of collectors connected in a row. Wastewater flows simultaneously through all parallel tubes, and the number of collector components modules has no limit [30]. For the falling film reactor (FFR), the components contain flat plate, top distributor, bottom receiver, batch tank, and a centrifugal pump. Wastewater in a batch bank flows through the flat plate to bottom receiver, and this is a circulatory system [31]. As a cheaper alternative of CPC, the designed FFR shows comparable results to the CPC in terms of COD degradation rate based on the previous report [31]. Due to the open nonconcentrating geometry of the FFR, there is no reflectivity or transmissivity loss in the reactor. In addition, the shortage of the FFR is the short pathlength of the reactor, but it can be neglected because of the extremely high light absorption of the OMW [31]. Moreover, the temperature in the FFR is lower than that in the CPC due to the heat losses suffered from evaporation of water. This may retard the removal of volatile organic compounds. However, the low temperature would cause less foaming, and the decomposition of hydrogen peroxide can also be reduced [31].

In addition, some other researchers also studied the treatment of OMW using a $TiO_2$/UV system [100, 101].



(a)

(b)

Figure 10: (a) Two compound parabolic collectors (CPCs) of one prototype module, (b) falling film reactor (FFR). (Figure 10(a) is reproduced from reference [30]. Copyright 1999, with permission from Elsevier; Figure 10(b) is reproduced from reference [31]. Copyright 2004, with permission from Elsevier).

Although the UV light source is not economical as compared to the solar source, these studies can also provide some important references for the future work [102]. El Hajjouji et al. [100] investigated the removal rate of COD, colour scale, and phenols in OMW using a $TiO_2$/UV system. They found that colour and phenols were more difficult to be removed compared to COD, which can be attributed to the degradation of some nonconservative water pollutants in OMW. Chatzisymeon et al. [101] investigated the effect of operating conditions in a photocatalytic treatment process of OMW. Their results indicated that the removal of COD was determined by contact time. Thus, the hydraulic retention time of OMW in a photoreactor is a key factor. Moreover, the detoxification of OMW is strongly dependent on the residual organic matters, indicating that a complete degradation of COD is still required in future application.

## 4. Conclusions

Solar photocatalysis has been investigated as an effective wastewater treatment process during the past decades. Although fundamental and engineering researches have established the solar photocatalysis technology in wastewater treatment, the industrial application is still in an infantile stage and some challenges are still needed to be smoothed out, such as the solar utilization efficiency, the construction and operation of photoreactor, and the separation of photocatalysts. Photocatalytic membranes or microspheres might be able to solve the separation problem of photocatalysts [102–104]. Their photocatalytic activities for real wastewater need to be tested under solar irradiation in the future studies. Modification of the current photocatalysts such as doping is a good pathway to enhance the PCO efficiency under solar irradiation considering the low fabrication cost. More attention is also needed to be paid to the design of photoreactors to optimize the operational factors for the system's activity, and recycling should also be comprehensively considered for large-scale applications. We believe that solar $TiO_2$ photocatalysis method can provide a promising pathway for the deep degradation of the pollutants in industrial wastewaters.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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