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Operational parameters effects on photocatalytic reactors of wastewater pollutant: A review

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ABSTRACT

This study presents the operational parameters effects on photocatalytic degradation of liquid pollutants using titanium dioxide. Organic pollutants photodegradation is the most widely studied method, where photocatalysis is observed in many forms. Due to the cost efficiency of titanium dioxide as a photocatalyst, it has a greater role in this process as compared to other semiconductors. The operating parameters effects on photocatalytic degradation in wastewater pollutant using titanium dioxide based photocatalyst are presented in this paper. The findings are used to identify and explain the individual influence of different parameters, such as the photocatalyst composition, catalyst loading, initial pH, pollutant concentration, light intensity and temperature, on wastewater pollutants photocatalytic degradation. The successful application of laboratory scale techniques and the choice of treatment are generally dependent on the wastewater composition, however, much research is needed from the aspects of modelling and engineering design for a large scale operation. Besides that, a general overview of a prevailing trend in the use of titanium dioxide photocatalyst is presented with the emphasis placed on its achievements and problems.

Keywords: Photocatalyst; Pollutant; Semiconductor; Titanium dioxide; Wastewater

1. Introduction

Wastewater is generally discharged from industrial and domestic sources into waterways, often without treatment. This could be detrimental to human health and environment due to the presence of harmful pollutants. One major group of pollutants includes heavy metals and anionic species [1–3]. Several physical wastewater treatment techniques, such as ultrafiltration, activated carbon adsorption, reverse osmosis, ion exchange on synthetic adsorbent resins, etc. have been widely used for pollutant removal [4,5]. However, these techniques incur more operational effort, taking into account the need for replacement of filters, regeneration of the adsorbent materials, post-treatment of the solid wastes, etc. Alternatively, these drawbacks can be sidelined by adopting other techniques, such as ozonation [6], enzymatic decomposition or microbiological [7], bio-degradation [8], as well as, advanced oxidation processes, such as H_2O_2/UV processes [9], and Fenton catalytic reactions [10].

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Recent studies have proposed the use of photocatalysis in wastewater treatment applications because of its ability to completely mineralize targeted pollutants [11–19]. In this regard, several requirements need to be taken note for effective execution, such as the operation must be conducted at room temperature or pressure, the mineralization of targeted pollutants should be complete without causing secondary pollution, as well as, the operational cost and efficiency should be optimized. To achieve such requirements, the individual influence of different parameters, such as the photocatalyst composition, catalyst loading, initial pH, pollutant concentration, light intensity and temperature, on the photocatalytic degradation efficiency should be studied thoroughly [1–3,19–21]. Therefore, it is the intent of this paper to provide a comprehensive review of the factors affecting the photocatalytic pollutant degradation efficiency. A brief introduction of photocatalysis will first be presented, followed by the elementary explanation of semiconductor based photocatalysis, the study of titanium dioxide photocatalyst, and lastly, the factors affecting the photocatalytic degradation efficiency.

2. Photocatalysis

Photocatalytic process accelerated by the existence of a catalyst is denominated as a photo-induced process. The process is activated by sufficient energy through the absorption of photons [22]. The absorption of photons induces a charge separation upon excitation, which promotes the propagation of an electron from the valence band (VB) to the conduction band (CB) of a semiconductor, therefore, producing a hole in the VB, as demonstrated in Fig. 1. The conclusive aim of the process is to produce a reduced product from the reaction between oxidant and activated electrons, as well as, to produce an oxidized product from the reaction between a reductant and generated holes. The photo-generated electrons would react with electron acceptors, such as molecular oxygen to be superoxide radical anion. Photo-generated holes can oxidize organic molecules to form cationic radicals, or react with hydroxyl anion or water to form hydroxyl radicals [5],which is a very powerful oxidizing agent, that can oxidize most pollutants to become mineral end products. The complete mechanisms of photocatalysis, as well as the detailed comparisons between the oxidation strength of hydroxyl radicals and superoxide radicals have been presented in [23,24].

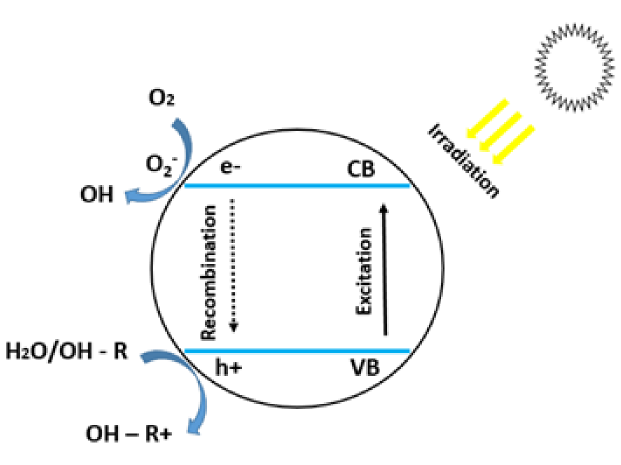

Fig. 1. Photoinduced formation mechanism of an electron-hole pair in a semiconductor.

2.1. Semiconductor based photocatalysis

Semiconductors (Fe_2O_3, TiO_2, ZnO and CdS) can be utilized as a sensitizer for light-induced process owing to their electronic structure which is characterized by a filled VB, and an empty CB [25–27]. Under irradiation, the electrons are promoted from the VB to the CB, which leaves positively-charged holes in the VB. The holes may react either with hydroxide ions or electron donors, such as superoxide or hydroxyl radicals in the solution to produce powerful oxidizing agents [4].

As seen from Fig. 1, in semiconductors, the VB and CB are separated by a band or energy gap. Excitation of electron-hole pairs, involving the transfer of electrons from the VB to the CB, will only occur when a semiconductor molecule adsorbs photons with the same or greater energy than its band gap. Subsequently, charge carriers would be generated. On the other hand, recombination of electron-hole pairs might occur and this might consequently cause a considerable drop in the photocatalytic activity [28]. Therefore, to minimize the occurrence of recombination of electron-hole pairs, as well as to improve the photocatalytic activity, the addition of secondary semiconductors can be one of the alternatives [29–31].

2.2. Titanium dioxide photocatalyst

Titanium dioxide (TiO_2) is the most widely used semiconductor among the mentioned semiconductors in photo-induced operation owing to its several advantages [32–39]. Firstly, it is chemically stable, biologically benign and non-toxic, thus, giving rise to its safe application in photocatalysis. In addition, it does not undergo photo-corrosion degradation due to the direct reaction between the charge-pair on the surface of titanium dioxide with the solid lattice ions under irradiation. Titanium dioxide also exhibits a strong resistance against alkalis and acids [40]. Furthermore, titanium dioxide is an industrially mass produced material that can be synthesized easily in a laboratory and hence, contributing to its accessibility and affordability. Besides, it can be manufactured and produced in various forms, such as colloid dispersion in a liquid phase, white TiO_2 powder or sometimes as thin films coated onto substrate. This in turn promotes and widens its industrial applications, such as the manufacture of brightening cosmetics, fabrication of paints and coatings, enhancement of the brittleness of polymer-based items, etc. Generally, titanium dioxide exists in various polymorphs and the three most common polymorphs are rutile, anatase and brookite [41]. In the crystal family categorization, rutile and anatase are tetragonal, while brookite is orthorhombic. As compared to rutile and anatase, brookite is relatively rare in nature. In common, they do exhibit photocatalytic activity [42].

In scientific definition, titanium dioxide photocatalysis is a photo-induced charge separation phenomenon that occurs in the titanium dioxide semiconductor, producing a number of reducing and oxidizing species that lead to organic mineralization and microbial inactivation without causing secondary pollution [40,43–45]. To initiate photocatalytic reactions, light with a suitable wavelength at a sufficient intensity is needed to attain energy that equals or exceeds the titanium dioxide band gap. Referring to the two crystalline structures of titanium dioxide, anatase has a band gap of ~3.2 eV, while rutile has a band gap of ~3.0 eV. As demonstrated in Fig. 2 [46], the VB redox potential of both anatase and rutile are more positive than that of the hydroxyl species, thus, leading to the oxidation of adsorbed water and hydroxyl groups to highly reactive hydroxyl radicals upon irradiation. However, rutile appears to be less negative in the CB redox potential with respect to those of oxide species and anatase, hence, inhibiting the reduction of molecular oxygen. On the contrary, molecular oxygen can be reduced to superoxide radicals by illuminated anatase due to the more negative CB redox potential of anatase. In this regard, anatase can thus be claimed to be relatively more photocatalytically active than rutile [47].

Widely known for its photocatalytic activity, titanium dioxide has been utilized as a photocatalyst primarily in the decomposition of organic pollutants contained in either aqueous or gaseous waste channels. In this regard, under irradiation, the oxidation of hydroxyl species and the reduction of oxide species will be taking place concurrently at the VB and the CB, respectively. Two oxidation reactions can occur at the VB. Firstly, the direct oxidation of the adsorbed organic species by the positively charged holes is initated to form cationic radicals. Secondly, water and/or hydroxyl groups are oxidized and transformed into highly reactive hydroxyl radicals that will subsequently induce the oxidation of the organic pollutants [48–51]. On the other hand, two reduction reactions cantake place at the CB as well. Firstly, the reduction of adsorbed molecular oxygen by the conducting electrons is prompted, producing superoxide radicals, which will give rise to the subsequent formation of additional hydroxyl radicals via a number of reactions. Secondly, metal ions are reduced by reacting with photo-excited electrons. It is noteworthy that the reduction of metal ions may be restricted by the oxidation of water [52]. The photocatalytic decomposition of pollutants involving redox reactions is presented as follows [25,46,52]:

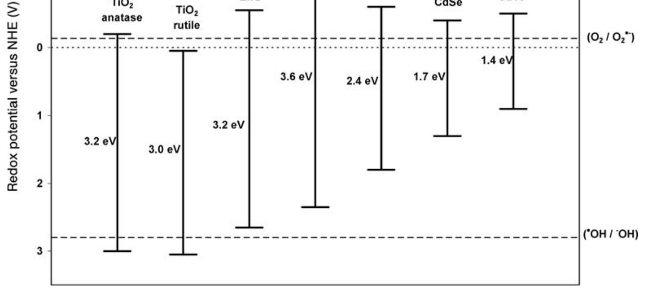

Fig. 2. Band gaps of various commonly-used semiconductors, placed alongside the standard redo potentials (versus normal hydrogen electrode (NHE)) of the and redox couple [46].

Charge-carrier generation of titanium dioxide photocatalyst

$$TiO_2 \xrightarrow{h\nu \geq E_{bg}} TiO_2\left(e^- + h^+\right) \tag{1}$$

Direct oxidation of adsorbed organic pollutants

$$RH + h^+ \rightarrow RH^+ \leftrightarrow R^\bullet + H^+ \tag{2}$$

Oxidation of water and/or hydroxyl group, followed by adsorbed organic pollutants

$$H_2O + h^+ \rightarrow H_2O^+ \leftrightarrow OH^\bullet + H^+ \tag{3}$$

$$OH^- + h^+ \rightarrow OH^\bullet \tag{4}$$

$$OH^\bullet + RH \rightarrow R^\bullet + H_2O \rightarrow CO_2 + H_2O \tag{5}$$

Reduction of adsorbed molecular oxygen, followed by formation of hydroxyl radical

$$O_2 + e^- \rightarrow O_2^{\bullet-} \tag{6}$$

$$O_2^{\bullet-} + H^+ \leftrightarrow HO_2^\bullet \tag{7}$$

$$2HO_2^\bullet \leftrightarrow H_2O_2 + O_2 \tag{8}$$

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \tag{9}$$

Reduction of metal cation

$$M^{n+} + e^- \rightarrow M^{(n-1)+} \tag{10}$$

where e^- and h^+ represent the photo-induced electron and hole, respectively, RH is the adsorbed organic pollutant, H_2O is water, $OH^\bullet$ is hydroxyl radical, OH^- is hydroxyl anion, O_2 is molecular oxygen $O_2^{\bullet-}$, is superoxide radical, H_2O_2 is hydrogen peroxide, and M^{n+} is metal cation with positivity.

3. Operating parameters on photocatalytic degradation

The efficiency and oxidation rate of a photocatalytic system after the integration of a semiconductor catalyst with a photoreactor are highly dependent on several operating parameters to qualify as the kinetics of photo-mineralization. This paper presents the significance of some operation parameters in relation to photocatalysis. These parameters include the type and composition of photocatalyst, catalyst loading, initial pH of the solution, concentration of pollutant, light intensity and wavelength, as well as operating temperature. The relationship between each parameter and the photocatalytic degradation efficiency or rate will be discussed individually.

3.1. Photocatalyst composition and type

Photocatalytic activity of a semiconductor is dependent on its structural and surface properties such as particle size, surface area, porosity, crystal composition, surface hydroxyl density and band gap. Particle size is directly related to the efficiency of a catalyst through the definition of particles specific surface area and this is of primary importance in heterogeneous catalysis.

Numerous titanium dioxide based photocatalysts have been examined for the degradation of various organic compounds in liquid solution. Degussa P-25, Hombikat UV100, PC10, PC50, PC500, Rhodia, and Travancore Titanium Products (TTP) have been widely used in laboratory applications [53–56]. P-25 consists of 25% rutile and 75% anatase with a primary particle size of 20 nm and a specific BET surface area of 50 m^2/g. Furthermore, Hombikat UV100 is composed of 100% pure and smaller anatase with a primary particle size of 5 nm and a specific BET surface area of 250 m^2/g, while PC500 is also made of 100% anatase with a primary particle size of 5–10 nm and a specific BET surface area of 287 m^2/g. It has been demonstrated that as compared to other photocatalysts, the degradation rate is much more rapid in the presence of P-25. The efficiency of photocatalysts is generally ranked in the order of P-25 > UV100 > PC500 > TTP for the degradation of various pollutants [53,54,57–61]. The relatively higher photocatalytic activity of P-25 can be explained by its mixed-composition of crystalline anatase and rutile. Rutile has a relatively less negative reductive power and thus it plays an important role in inhibiting the electron-hole recombination in anatase. There exist several transition points between these two phases, which promoting the rapid transfer of electrons, and consequently, the photocatalytic activity is enhanced [62].

Differences in the lattice mismatches, density of hydroxyl groups on the surface of the catalyst, impurities and BET surfaces could be the factors affecting the adsorption behaviour of a pollutant or intermediate molecule, as well as the lifetime and recombination rate of electron-hole pairs, which, subsequently leading to variations in photocatalytic activities [54,55,57–59,61,63,64].

3.2. Catalyst loading

Extensive studies have been conducted, signifying that the pollutant degradation rate depends substantially on the catalyst loading. An initial increase, followed by a decrease in the degradation rate can be observed in conjunction with an increase in the catalyst loading because of the light scattering and screening effects. A linear dependency holds true to a certain extent when the reaction rate starts to intensify until a limit is reached. Thereafter, it becomes independent of the titanium dioxide photocatalyst concentration. This limit depends on the geometry and working conditions of the photo-reactor. With an increase in the amount of titanium dioxide photocatalyst above the saturation limit, particles agglomeration and accumulation are prompted. These subsequently reduce the photocatalyst surface area available for light absorption and eventually aggravate the photocatalytic activity. Therefore, an optimal dose of photocatalyst is important to achieve tiptop photocatalytic degradation efficiency [65].

However, some researchers have claimed that the direct comparison of the photocatalytic degradation rate in variations of catalyst loading is inconclusive because of differences in photon wavelengths, light intensity, radiation fluxes and working geometry [66–71]. Despite, from the perspective of industrial applications, such as in wastewater treatment applications, where the presence of uncertainties is inevitable, the amount or concentration of titanium dioxide photocatalyst has seen a direct influence on the entire system efficiency [72–74].

3.3. The effect of pH

One of the effective operating parameters in heterogeneous photocatalytic processes as well as other photochemical processes is the pH as it affects the catalyst surface charge, the catalyst particle size and the conditions of the VB and CB. Organic pollutants have differences in terms of speciation behaviour, water solubility and hydrophobicity. At a common pH, some compounds are uncharged, such as waste or natural water. This is different from the other compounds with varied speciation and physico-chemical properties.

Owing to the nature of titanium dioxide photocatalyst used, variations in the operating pH lead to variations in the isoelectric point or surface charge of the photocatalyst used. The pH value at which the surface charge is completely neutralized is known as the point of zero charge, or PZC. Many researchers have been using the PZC of titanium dioxide to study the effect of pH on the photocatalytic oxidation performance [66–68,71–75]. Titanium dioxide photocatalyst has a PZC of between 4.5 and 7.0, depending on its type and composition. At the PZC, due to the absence of electrostatic force, the interaction between water contaminants and photocatalyst particles is minimal. At an operating pH less than the PZC, the photocatalyst surface is positively charged and it gently exerts an electrostatic attraction force towards the negatively charged compounds. For further photocatalytic reactions, such polar attractions between the charged anionic organic compounds and titanium dioxide can intensify the adsorption onto the photon activated titanium dioxide surface [76,77]. This is specifically discernible when the concentration level of anionic organic compounds is low. On the contrary, at a pH more than the PZC, the photocatalyst surface is negatively charged which, subsequently exorcising anionic compounds. Furthermore, the solution pH plays a significant role in the photocatalytic oxidation and adsorption of pollutants because of the different pH effects on the surface charge density of titanium dioxide photocatalyst. The surface ionization state of photocatalyst can be protonated under acidic conditions and deprotonated under alkaline conditions according to the following water equilibrium equations:

$$pH < pH_{PZC}, TiOH + H^+ \leftrightarrow TiOH_2^+ \tag{11}$$

$$pH > pH_{PZC}, TiOH + OH^- \leftrightarrow TiO^- + H_2O \tag{12}$$

Typically, the PZC of titanium dioxide is about 6.25 [78]. In acidic media (pH < 6.25), the surface of titanium dioxide photocatalysis is positively-charged, whereas it is negatively-charged in alkaline conditions (pH > 6.5). In addition, the pH of the solution has seen an effect on the hydroxyl radicals. There is a reaction between the induced holes and hydroxide ions on the surface of titanium dioxide. The low pH of positive holes is important during the oxidation phases besides the high pH and neutral levels or hydroxyl radicals [79,80]. It would be expected that due to the presence of more available hydroxyl ions, the generation of hydroxyl radicals is higher on the surface of titanium dioxide. At a high pH, the procedure degradation efficiency will be logically raised. Numerous investigations have been carried out to elucidate the effect of pH on the adsorption and photocatalytic degradation of organic compounds on titanium dioxide surface [54,55,57,58,61,64]. With the change in pH, the degree of electrostatic attraction or repulsion between organic molecule ionic forms and the surface of photocatalyst can be varied. Hence, the pH can be used as the controlling variables for the enhancement or inhibition of organic pollutants degradation depending on one's need. The pH effects on the photocatalytic degradation of some organic compounds are listed in Table 1.

From Table 1 it can be seen that different contaminants have different optimal pH levels to undergo optimal photocatalytic degradation. In addition, it is of great importance to determine the pK_a values of pollutants for a better prediction of the catalytic activity at a specific pH, because these affect the adsorption property of the catalyst as well as the stability of the pollutants molecules. Basically, the pK_a value measures the acidity of pollutants present in the solution. The strength of acidity is said to be inversely proportional to the pK_a value, such that the weaker the acidity of a pollutant, the larger its pK_a. Therefore,to attain tiptop photocatalytic reaction in wastewater treatment applications, it is imperative to perform suitable pH control strategies with the provision of the pK_a values [29,81–86].

3.4. Pollutant concentration and type

The study of the relationship between the substrate concentration and the photocatalytic degradation rate is of utmost importance for effective execution of wastewater treatment. Various pollutants investigated under varied initial concentrations are summarized in Table 2. With increasing substrate concentration, the probability of collision between pollutants and the surface of photocatalyst will be higher. Consequently, this increases the degradation rate due to very short lifetime of the hydroxyl radicals, which are responsible in oxidizing the organic pollutants [81,87,88]. However, when the substrate concentration increases to a certain extent, more intermediates will probably be generated and adsorbed on the photocatalyst surface since the photo-degradation process is a non-selective process and thus, the decomposition of the pollutants as well as the obtained intermediates will take place concurrently by the produced hydroxyls and superoxide radicals. As a result, active sites on the photocatalyst are partially compromised and hence, incurring a slower adsorption rate, which eventually leading to a drop in the overall degradation rate. In short, it can be deduced that at low substrate concentrations, the degradation rate is less dependent on the number of catalytically active sites. Instead, it is proportional to the substrate concentration in accordance with apparent first order kinetics. In addition, the molecular structure of the pollutants can be one of the factors affecting its degradation extent, which has been discussed in [89–91].

Langmuir–Hinshelwood (LH) kinetics is the most commonly used kinetic expression to explain the kinetics of the heterogeneous catalytic processes. The Langmuir–Hinshelwood expression that explains the kinetics of heterogeneous catalytic systems is given by:

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1 + KC} \tag{13}$$

where r represents the rate of reaction that changes with time. The term r in Eq. (13) was represented in terms of initial reaction rate, r_0, as a function of the initial dye concentration, C_0, or in terms of C_e, where, C_e is the equilibrium dye concentration in solution after the completion of dark

Table 1
Influence of pH on the photocatalytic degradation of various pollutants

Pollutant	Light source	Photocatalyst	pH range	Optimum pH	Reference
Propachlor	UV	TiO_2	3.0–11.0	3	[64]
Carbofuran	UV	TiO_2	4.0–9.0	7	[54]
Phorate	UV	TiO_2	4.0–8.0	8	[65]
Fast Green FCF	UV	TiO_2	3.0–11.0	4.4	[14]
Turbophos	UV	TiO_2	3.0–8.0	8	[65]
Carbendazim	UV	TiO_2	3.0–9.0	9	[66]
Erioglaucine	UV	TiO_2	2.4–12.2	2.4	[68]
Propham	UV	TiO_2	3.0– 11.0	5	[64]
Thiram	Solar	TiO_2	2.5–11.4	8	[67]
Patent Blue VF	UV	TiO_2	3.0–11.0	11	[14]
Isoproturon	Solar	TiO_2	3.0–10.0	7	[69]
Bromocresol purple	UV	TiO_2	4.5 and 8.0	4.5	[70]
Atrazine	Solar	TiO_2	2.0–9.99	4 –5	[71]
Dimethoate	UV	TiO_2	2.04–11.05	11.05	[72]

Table 2
Influence of initial pollutant concentration on the photocatalytic degradation of pollutants

Pollutant	Light source	Photocatalyst	Concentration range, mM	Optimum concentration, mM	Reference
Thiram	Solar	TiO_2	4.2×10^{-4}–6.6×10^{-4}	4.2×10^{-4}	[74]
Indole-3-acetic acid	UV	TiO_2	0.2–0.6	0.3	[43]
Daminozid	UV	TiO_2	0.50–1.5	0.75	[75]
Prophachlor	UV	TiO_2	0.2–1.35	1.35	[64]
Bentazon	UV	TiO_2	0.02–0.062	0.02	[76]
Isoproturon	Solar	TiO_2	0.25–.75	0.75	[77]
Triclopyr	UV	TiO_2	0.25–1.0	0.75	[75]
Propham	UV	TiO_2	0.25–1.3	0.75	[64]
Tebuthioron	UV	TiO_2	0.25–1.5	1	[64]
Phosphamidon	UV	TiO_2	0.1–0.6	0.45	[92]
Diphenamid	UV	TiO_2	0.1–0.6	0.6	[78]
Dimethoate	UV	TiO_2	0.0195–0.49	0.0195	[79]
Carbofuran	UV	TiO_2	0.023–0.113	0.09	[54]
Acephate	UV	TiO_2	0.7–1.0	1	[78]
Erioglaucine	UV	TiO_2	0.006–0.02	0.006	[80]

experiments. The initial rate of reaction as a function of C_0 and C_e is given by Eqs. (14) and (15), respectively:

$$r_0 = \frac{k_r K C_0}{1 + K C_0} \tag{14}$$

$$r_0 = \frac{k_r K C_e}{1 + K C_e} \tag{15}$$

The parameters k_r and K which are a function of C_0 or C_e can be predicted by linearizing Eqs. (14) or (15) as follows:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K C_0} \tag{16}$$

Most of researchers approximated Eq. (13) to first order kinetics for the condition $KC << 1$. Recently, some papers reported that the LH kinetics, as shown in Eq. (14), can be approximated to zero order kinetics for $KC_0 << 1$. However, if the LH expression is written in terms of initial reaction rate, for $KC_0 >> 1$, the LH kinetics will not be reduced to a zero order kinetics.

3.5. Light intensity and wavelength

Light is an imperative source that initiates heterogeneous photocatalytic processes and other photochemical processes. In a photochemical process, the formation of electron-hole pairs as well as the initiation rate of photocatalysis depends considerably on the intensity of light [93]. The light distribution in a reactor basically decides the pollutant conversion efficiency as well as the pollutant degradation rate. Hence, extensive studies have been conducted in investigating the effect of light intensity on the pollutant degradation rate. In most studies, the pollutant degradation rate depends linearly on the light intensity, while in some cases, it demonstrates a square root dependency on the light intensity [94]. Notably, at high intensity, the reaction rate is independent of the light intensity. This is likely to happen because at low intensity, the reactions involving electron-hole formation are much more significant than that involving electron-hole recombination.

With increasing light intensity, the rate of electron-hole formation at the surface of titanium dioxide rises and consequently, enhancing its ability to oxidize organic pollutants. In a particular case, the first order rate constant of iodosulfuron degradation is found to be directly proportional to the photon flux when the flux is below 10^{16} photon 1/s·cm^2. At low flux, the oxidizable organic substrate concentration is higher than the formation rate of electron-hole pairs within the photocatalyst, and thus, exhibiting a linear relationship between the degradation rate and the photo flux. On the contrary, at elevated photon flux (above 10^{16} photon 1/s·cm^2), the rate constant varies with the square root of the flux, in which the degradation rate experiences an immense reduction due to the significant effect of electron-hole recombination [8].

A number of research has been carried out, claiming that the photocatalytic degration rate of titanium dioxide is not highly affected by the light intensity as a few photons of energy (as low as 1 μW cm^{-1}) are claimed to be sufficient to induce a surface reaction [95]. To obtain a high photocatalytic reaction rate in wastewater treatment applications, a relatively abundant light intensity is required to sufficiently provide the titanium dioxide surface active sites with adequate photons energy. However, in the application of titanium dioxide photocatalyst, the surface reaction is limited to photons with wavelengths shorter than 400 nm, such as, UV light. Under illumination of UV light (wavelength < 400 nm), the linear relationship between the degradation rate and the incident radiant flux is obeyed. It has also been demonstrated that the destruction of polychlorinated biphenyls and toxin is apparent in the presence of high intensity photons [96]. Furthermore, there are studies performed in investigating the dependency of reaction rate on the radiant intensity under various lighting conditions [97–99]. To calculate the light intensity of the source, the detailed formulations can be found in [100]. Based on the aforementioned literatures, it has been discovered that there is a good linear correlation between the light intensity and the first order rate constant. In some studies, the photocatalytic oxidation rate is also found to be dependent on the intensity of light. Therefore, preliminary studies of the microbial consortia presence and the photoreactor performance in wastewater applications are important as they can be used to predict the minimum irradiation required at constant irradiance [91].

3.6. Temperature effect

Since 1970s, many experimental studies have been performed in investigating the influence of the temperature on the pollutant degradation rate [101–106]. Besides, a number of researchers have also discussed the dependency of the photocatalytic reaction on the reaction temperature [103,104,107,108]. To activate the surface of titanium dioxide, the only presence of heat energy is insufficient when operating the process under illumination of natural sunlight. However, the perception of such dependency could be extrapolated. Studies have shown that an increase in temperature of the photocatalytic reaction (more than 80ºC) promotes recombination of charge carriers and thus, inhibiting the adsorption of organic compounds onto the surface of titanium dioxide [69].

In most cases, photocatalytic systems are operated at room temperature and heating is not required. The recommended range of operating temperature favouring the photo-decomposition process is generally between 20ºC and 80ºC [70,109,110]. At temperatures less than 0ºC, the desorption rate of the final product will be reduced and hence, inducing an increase in the apparent activation energy. On the contrary, at temperatures more than 80ºC, the adsorption of reactant will be the limiting factor, causing the apparent activation energy to become negative. In addition, an increase in the photo-decomposition rate has been observed with the reaction temperature augmented within the temperature range of between 20ºC and 60ºC [70,72,108,110–112].

4. Conclusion

The presented paper has discussed the effects of some operational parameters on the photocatalytic activity of titanium dioxide based photocatalysts. The study on the nature of the degraded samples is necessary because this will provide a strategy for the selection of a specific type of photocatalyst used in a degradation process. Under experimental conditions, the use of the Degussa P-25 has often led to a relatively higher pollutant degradation rate than the other titanium based photocatalysts such as PC500, UV100 and PC10 due to its mixed-composition. Furthermore, an optimal dose of the catalyst is important to achieve tiptop performance of a photocatalytic system. Besides, in wastewater applications, an appropriate pH should be selected for effective removal of various pollutants. Moreover, at a low substrate concentration, a proportional relationship between the rate of degradation and the substrate concentration is evident. Similarly, at a low intensity, the pollutant degradation rate varies linearly with the light intensity. In addition, an increase in the photo-decomposition rate has been observed with the reaction temperature augmented within the temperature range of between 20ºC and 60ºC.

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Author contributions

This study was initiated by Zhi Chao Ong, Peiman-Roushenas and Zubaidah Ismail. Zohre Majidnia, Bee Chin Ang, Mohammadjavad Asadsangabifard and Chiu Chuen Onn provided in-depth comments and advices. Zhi Chao Ong, Peiman Roushenas and Jun Hui Tam wrote the paper and contributed in revising the paper.

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