Review

Removing Humic Acid from Aqueous Solution Using Titanium Dioxide: A Review

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Abstract

Recently, the photocatalytic degradation technique with titanium dioxide (TiO_2) has been widely applied for the degradation of humic acid (HA) from aqueous solution due to its ability to achieve complete mineralization of organic contaminants. Because TiO_2 is the most commonly used semiconductor photocatalyst, efforts on the modification of TiO_2 in order to improve catalyst efficiency were presented in this review manuscript. The key photoreactor operation parameters such as TiO_2 loading, pH, temperature, oxygen concentration, concentration and nature of HA, light wavelength, light intensity, the presence of inorganic ions and mechanistic pathway for pollutant removal, and the formation of the intermediates and their effects on the mineralization and disinfection of the photo-process were also assessed. Although we can see an increase in the number of papers that have been published in this area, further progress is needed to improve the understanding of the dynamic interactions between TiO_2 photocatalytic oxidation process and HA, as well as to suggest possible future developments in this promising field.

Keywords: adsorption, aqueous solution, photocatalytic (PC), humic acid (HA), titanium dioxide (TiO_2)

Introduction

Natural organic matter (NOM) is defined as a complex matrix of organic materials present in all surface, ground, and soil waters [1]. The presence of NOM, mainly humic substances (HS) in surface waters, constitutes the main route for the absorbance of solar energy in aquatic systems through which a series of photophysical and photochemical processes occur. Humic acid (HA) accounts for a significant fraction of the HS.

The presence of HA in aqueous solutions is not directly toxic but could lead to organic disinfectant by-products (DBPs), which are undesired and hazardous products in water treatment after disinfection [2-3]. Furthermore, the high HA concentration in drinking water has the potential for some serious diseases, such as stomach cancer [4-5]. Thus, the presence of HA can be the cause of many problems, and their removal from water is a priority task [6] and has been attempted in different ways. Several processes have been attempted to remove HA from water such as coagulation [7-9], electrocoagulation (EC) [4, 10-15], electro-oxidation (EO) [16], ion exchange [17], membrane filtration [18-20], activated carbon adsorption and advanced oxidation processes [21-29].

Other approaches including ozonation (O_3, O_3/H_2O_2) [30-32] and gamma radiation/H2O2 [33-35], and/or UV-photolysis [36, 37] have also been widely attempted to eliminate HA from wastewater. However, the application of the proposed methods is associated with a number of disadvantages. Generally speaking, the removal of HA by conventional and advanced treatment processes is not always adequate with regards to removal efficiency, chemical, and energy consumption, and management of residuals.

Among these treatment processes, heterogeneous photocatalysis employing semiconductor catalysts has a widely demonstrated efficiency for removing or degrading HA. Compared with other photocatalysts, titanium dioxide (TiO_2) is much more promising and most commonly used [36-37] as it is stable, non-corrosive, environmentally friendly, abundant, and cost-effective [5]. Owing to its application for the complete mineralization of undesirable organic contaminants to CO_2, H_2O, and inorganic constituents [38-41], TiO_2-based photocatalyst materials have been found to efficiently decompose and remove a variety of pollutants: bisphenol A [42], natural organic matter [43], persistent pharmaceutical compounds [44], phenol [45], o-cresol [46], etc. Taking advantage of this inherent ability of TiO_2, the degradation processes of HA involving TiO_2 samples has become an important topic of research in recent years.

This review considers recent developments in the research and application of adsorption and photocatalyst TiO_2 for HA removal from aqueous solution. During this work, the effects of photoreactor operating parameters on the photocatalytic process are listed in addition to mineralization and disinfection kinetics associated with their modelings.

Mechanism and Limitations

Mechanism

It has been agreed that the basic process of photocatalytic reactions are initiated by the absorption of illumination with energy equal to or greater than the band gap of the TiO_2 semiconductor surface, usually 3.2 eV (anatase) or 3.0 eV (rutile), creating an hole in the valence band. The light wavelength for such photon energy usually corresponds to λ<400 nm.

The simplified mechanism:

$$TiO_2 + hv \rightarrow e_{CB}^- + h_{VB}^+ \qquad (1)$$
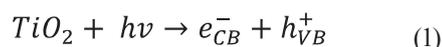
…where CB is the conduction band and VB is the valence band. Thus, upon UV irradiation, the electron-hole pairs (e_{CB}^-/h_{VB}^+) are generated by the TiO_2 particle. The electron and hole can recombine and emancipate the absorbed light energy with no chemical reactions occurring. On the other hand, due to the VB hole strongly oxidizing while the CB electron is strongly reducing, the redox

reactions can occur between them and the adsorbed species. The mineralization of HA on the surface of TiO_2 is occurring by the participation between excited electron and the hole in redox reactions with water, hydroxide radical ('OH) organic compounds, or oxygen. Therefore, the ('OH) radical can be formed by both of two reactions of the valence band holes with adsorbed H_2O or with the surface groups on the TiO_2 particle. The reactive ('OH) radical can hydroxylate the aromatic compounds, leading to a successive oxidation/addition and ring opening. The resulting intermediates will be further carboxylated to produce innocuous carbon dioxide (CO_2) and water (H_2O). The overall photocatalysis reaction of HA to generate intermediates that ultimately lead to CO_2 and H_2O are depicted in the following equations:

e_{CB}^- reactions:

$$O_2 + e_{CB}^- \rightarrow O_2^- \qquad (2)$$

$$O_2^- + H^+ \rightarrow HO_2^. \qquad (3)$$

$$HO_2^. + HO_2^. \rightarrow H_2O_2 + O_2 \qquad (4)$$

$$H_2O_2 + e_{CB}^- \rightarrow {}^.OH + OH^- \qquad (5)$$

$$H_2O_2 + O_2^- \rightarrow {}^.OH + OH^- + O_2 \qquad (6)$$

$$H_2O_2 + hv \rightarrow 2\ {}^.OH \qquad (7)$$

h_{VB}^+ reactions:

$$h_{VB}^+ + H_2O \rightarrow H^+ +\ {}^.OH \qquad (8)$$

$$OH^- + h_{VB}^+ \rightarrow\ {}^.OH \qquad (9)$$

The redox reactions:

$$HA +\ {}^.OH \rightarrow H_2O + CO_2 + other\ degradation\ products \qquad (10)$$

$$HA + TiO_2(h_{VB}^+) \rightarrow oxidation\ products \qquad (11)$$

$$HA + TiO_2(e_{CB}^-) \rightarrow reduction\ products \qquad (12)$$
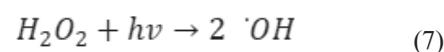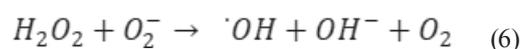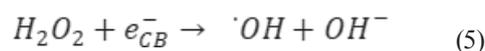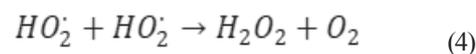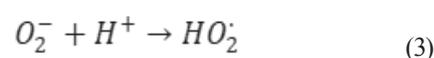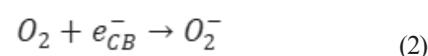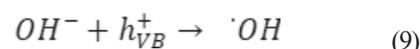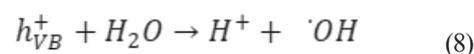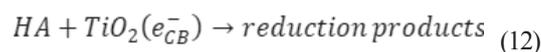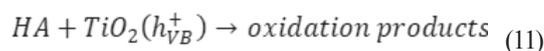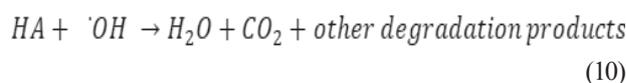
In summary, the molecular structures of HA can be broken down or rearranged by the photocatalysis process, which can convert the nonbiodegradable organics to more biodegradable forms.

The Limitations

Although it has been considered one of the most popular photocatalysts, the TiO_2 material still has some of important limitations:

Table 1. Comparative study on the efficiency of humic acid removal by using modified TiO_2 photocatalyst.

Type of modified TiO_2 photocatalyst	Removal efficiency (%)	Time	Kinetics model	References
$Fe_2O_3/TiO_2/GO$ membrane	98	2 hour	-	[20]
ZnO coupled TiO_2/bamboo charcoal (ZnO-TiO_2/BC)	≥99	3 hour	Langmuir–Hinshelwood	[51]
TiO_2/GAC composite	99.5	3 hour	Langmuir–Hinshelwood	[52]
TiO_2-coated ceramic foam filte (TCF)	83	12 hour	-	[53]
TiO_2-coated membranes	≈ 100	80 min	Pseudo first-order kinetic	[54]
TiO_2-coated nanofibre membranes	83	2 hour	-	[55]
Photocatalytic Membrane Reactor (PMR)	95	48 hour	-	[56]
Ag-TiO_2/HAP/Al_2O_3	88.3	1 hour	-	[57]
Fe-doped TiO_2	50	1 hour	Pseudo first-order kinetic	[58]
Ag-doped TiO_2 (Z-Na-TiO_2-Ag)	32	2 hour	-	[59]
$(Cr^{3+} + Ce^{3+})$ modified TiON (Cr–Ce/TiON)	≈ 99	4 hour	Pseudo first-order kinetic	[60]
$(TiO_2)_{0.7}(RuO_2)_{0.3}$	65	3 hour	-	[61]
TiO_2 thin film electrodes	70	5 min	-	[62]

– TiO_2 powder, called TiO_2 Degussa P-25, is the most common commercial photocatalyst applied in the photocatalytic process. However, in the form of powder, TiO_2 is not only easy to agglomerate but also difficult to recycle. It required a complication in the separation of powdered TiO_2 after the treatment, which instantly raises the system's economic viability [47-49]. Alternatively, the catalyst may be attached to the suitable solid support without the need for separation from the effluent streams [50].

– Only ultraviolet light photons, which account for 4-5% of the solar spectrum, have enough energy to displace valence band electrons due to the wide band gap of TiO_2. Thus, photocatalytic activity is quite limited in visible, solar, and fluorescent light [51].

– During photocatalytic treatment processes, the rapid recombination of photogenerated electron-hole pairs is also a limitation that affects photocatalytic efficiency.

Enhancement of HA Removal by the Modification of TiO_2 Photocatalytic

To overcome those limitations, in terms of removing HA, many studies involving modified TiO_2 photocatalytic have been carried out with certain success. The comparison of using a modified TiO_2 photocatalyst for the removal of HA under various experimental conditions is compared in Table 1 [20, 51-62].

Fixation of TiO_2 onto the Support Matrix

To solve the problem of TiO_2 particle separation and recovery after the treatment, various techniques were done for the fixation of TiO_2 onto the support matrix,

e.g., dip-coating, sol-gel technique, filtration membrane, electrochemical oxidation, and chemical vapour deposition. When a photocatalytic film is used, most of the slurry drawbacks may be avoided.

Bamboo charcoal (BC) was used by Wang et al. [51] to invest in an effective photocatalyst for HA removal. ZnO coupled TiO_2/BC with high adsorption-photocatalytic activity were synthesized by a microwave-assisted sol-gel method. The results showed that the ZnO-TiO_2/BC had relatively higher photodegradation efficiency for HA under visible-light irradiation as compared with TiO_2/BC. The synergistic relationship between surface adsorption characteristics and photocatalytic potential was **also** investigated by Xue et al. [52]. The nano-sized TiO_2-coated granular activated carbon composite (TiO_2/GAC) was prepared by a sol-dipping-gel route using tetra-*n*-butyl titanate as the precursor. Due to its high surface area feature and high adsorption capacity, a suitable pore structure has proven the extensive exhaustive activated carbon as a supporter of TiO_2 photocatalytic. Additionally, Mori et al. [53] investigated the photodecomposition of aqueous HA by a TiO_2-coated ceramic foam filter (TCF) reactor. A remarkable result was given and high stability in consecutive operation cycles was also shown by the TCF reactor.

Along with the aim of enhancing photoactivity, the nanoscale of TiO_2 has also been widely studied [63] due to its high specific surface area and sorption capacity for ionic and nonionic species [64]. Re-designing TiO_2 structured photocatalytic material as well as incorporating TiO_2 into the membrane, the slurries' drawbacks could be solved. The TiO_2 membrane can provide unique multifunctional concurrent separation and photocatalytic degradation, thus no extra separation is needed. Besides, membrane fouling caused by

NOM such as HA has been one of the major obstacles inhibiting the wide application of membrane technologies for water treatment. By confining the photocatalysts by means of a membrane, not only the above drawbacks of suspended nanoparticles can be overcome, it may also save energy, reduce the size of installation for catalyst separation, and reuse the photocatalyst in further runs [65]. The HA removal was increased by using membranes coated with TiO_2 under UV_{254} (ultraviolet light of $\lambda = 254$ nm) irradiation in the investigation of Zhang et al. [54]. Via a concurrent filtration and photocatalytic oxidation, the TiO_2 nanowire membrane achieved near 100% and 93.6% removal rates of HA and total organic carbon (TOC), respectively. It can be explained by molecular weight cut-off of membranes becoming smaller with the presence of TiO_2, which increased adsorption of HA. Additionally, the concurrent photocatalytic degradation led to a decrease of TiO_2 nanowire membrane fouling caused by HA accumulation. Nanofiber membranes containing TiO_2 nanoparticles were also used by Daels et al. [55], which stated that the removal of HA achieved 83% after 2 h of illumination. Taking a step forward, Patsios et al. [56] investigated the performance of a hybrid photocatalysis-membrane system that combined suspended TiO_2 particles and an ultrafiltration submerged module for the removal of HA and control of membrane fouling. The efficiency of HA mineralization rate reached rather high – almost 74% at optimum pH near 5.5. In addition, the formation potential of DBPs was reduced because HA aromatic rings were degraded very high, resulting in more than 95% of specific $UV-A_{254}$ removal efficiency in almost all cases studied. To further improve the effectiveness of the membrane process and reduce membrane fouling, Ma et al. [57] employed $Ag-TiO_2$/hydroxiapiate (HAP, $Ca_{10}(PO_4)_6(OH)_2)/Al_2O_3$), which is a highly reactive photocatalytic membrane to carry out microfiltration (MF) coupling photocatalysis for removing HA. In this study, the HA removal of the membrane was improved but cannot be sustained because a limiting of transmembrane pressure seems to exist beyond. Additionally, the transition in fouling mode from initial pore blocking to cake filtration occurred much slower as UV irradiated.

Due to immobilization and TiO_2-induced photodegradation, it can be concluded that membranes containing TiO_2 nanoparticles provided several obvious advantages:
(i) Faster degradation of HA.
(ii) No requirement for separating and recycling catalyst particles.
(iii) Anti-fouling ability as a result of effective photocatalytic degradation of aromatic rings.

Enhance Light Absorption

With the limitation on the wide band gap of TiO_2, numerous studies have been recently performed to improve photocatalytic activity and utilize solar energy more efficiently. To increase visible light absorption and TiO_2 photocatalytic properties on HA removal, the doping of TiO_2 with transition metal ions as well as with Ag and Fe have been studied to substitute O_2^- in TiO_2 to reduce the energy band-gap.

A great increase in the efficiency of solar light photocatalysis was explained by the extension of TiO_2 absorption band from the UV into the visible region [66]. In a study by Birben et al. [58], a reduction in band gap energy of both bare P-25 and UV-100 TiO_2 specimens to 2.55 eV and 2.43 eV, respectively, was caused by Fe doping. In terms of solar photocatalytic activity in a period of 1 h, approximately 50% of HA in UV absorbance at 254 nm was degraded by Fe-doped TiO_2 specimens.

The expansion of absorption bands shifting to the visible range of TiO_2 also was proved by Lazau et al. [59], who successfully synthesized the hybrid materials based on natural zeolite and undoped ($Z-Na-TiO_2$) and Ag-doped TiO_2 ($Z-Na-TiO_2-Ag$) by using solid-state reaction in microwave-assisted hydrothermal conditions. The result from UV–vis diffuse reflectance spectroscopy (DRUV-VIS) showed that $Z-Na-TiO_2-Ag$ exhibited absorption within the range of visible light (400–500 nm), which is stronger than undoped TiO_2 onto zeolite. In addition, under both ultraviolet and visible light irradiation, $Z-Na-TiO_2-Ag$ had an enhanced photocatalytic activity on degradation and mineralization of HA in comparison with $Z-Na-TiO_2$.

Another significant modification in the doping of TiO_2 should be mentioned by Rashid et al. [60]. In this study, N-doped TiO_2, (TiON) was co-doped with bimetal (Cr^{3+} and Ce^{3+}). The bimetal-modified TiON (Cr–Ce/TiON) catalyst with an evaluated bandgap of 2.1 eV was successfully synthesized. The degradation of HA on exposure to visible light was done by the synthesized Cr–Ce/TiON catalyst.

These representative experiments verified that transition metal ions as well as with Fe, Ag doping of TiO_2, shifts the TiO_2 absorption band from the UV into the visible region and enhances the redox reaction.

Delaying the Recombination of Photogenerated Electron-Hole Pairs

Another general concern for TiO_2 photocatalytic materials is the fast recombination of photogenerated electron-hole pairs, which would lead to the loss of photocatalytic activity [67-68]. Adjusting its structure or processing compositions is one way to delay the recombination of photogenerated electron-hole pairs, thus improving photocatalytic activity.

Graphene oxide (GO) was introduced into the TiO_2 membrane matrix to improve the photocatalytic activity of TiO_2 by functioning as an electron sink, suppressing the recombination of electron-hole pairs. Besides that, GO also showed strong adsorption of certain organic compounds in water, which may facilitate the photo-degradation process [67]. Over 98% HA removal in

a short-term test (2 h) and 92% removal in a 12 h test under solar irradiation were the significant results when a membrane made of interconnecting TiO_2 nanowires, Fe_2O_3 nanoparticles, and graphene oxide (GO) sheets was used by Rao et al. [20]. With $Fe_2O_3/TiO_2/GO$ compositions, the greater adsorption of HA improved photocatalytic activity of TiO_2, the recombination of electron-hole pairs could be delayed, thus resulting in HA removal being enhanced and suggesting the anti-fouling ability of this novel membrane.

Another concept for developing TiO_2-based photocatalytics (PC) is called photoelectrocatalytic (PEC). The photoelectrocatalytic treatment process is the combination of electrochemical and photocatalytic treatment processes [69-70]. In this method, a coating semiconductor onto a metal foil creates a photoanode that is biased by an external potential under illumination. The recombination of electron (e^-_{CB}) and hole (h^+_{VB}) is decreased by photoanode since the biasing potential applied, thus photocatalytic performance is improved. At the same time, photoexcited electrons can be withdrawn to a counter electrode in a cathode cell. Pinhedo et al. [61] used a titanium anode coated with 70% TiO_2 + 30% RuO_2 $((TiO_2)_{0.7}(RuO_2)_{0.3})$ in electrochemical and PEC oxidation methods for degradation of HA in aqueous solution. It stated that thermally prepared oxide electrodes exhibit photoactivity and may be used for photo-assisted electrolysis for the degradation of HA in aqueous effluents. By assisting electrolysis with photocatalysis, an increase in the HA degradation rate was observed. Taking over the conduct of the matter, Selcuk and Bekböle [62] continued to compare PC and PEC processes at acidic, neutral, and alkaline pH values. Once again, the effectiveness of PEC was more clearly confirmed. HA removal in the PEC process achieved two times under acidic conditions and four times under neutral conditions higher than the conventional PC process. After the lag phase, the TOC degradation rate of both PC and PEC process followed pseudo first-order kinetics. Rate constant in the PEC process was 2.4 times higher than in the PC process. Results of these studies proved that the PEC process was a safe and effective technique for decreasing DBP formation significantly in the removal of HA.

Operational Parameters

It has been demonstrated that the adsorption and the efficiency of the photocatalytic system are highly dependent on the operational parameters. Some reviews have been written regarding the mechanistic and kinetic details as well as the influence of experimental parameters [65, 71-73]. An understanding of the parameter effects not only aids in assessing the feasibility of using photocatalytic oxidation to HA removal but also allows for a thoughtful photocatalytic oxidation design. The most important operating parameters that govern the degradation rate and affect the photocatalytic

Table 2. Optimum dosage of TiO_2 loading for degradation of HA from aqueous solution.

Photocatalyst	Optimum dosage or optimal thickness	References
Degussa P25	1.5 - 2.0 (g/L)	[19]
$Fe_2O_3/TiO_2/GO$ membrane (weight ratio of 50:100:10)	$15\pm1\mu m$	[20]
ZnO-TiO_2/BC	2 (g/L)	[51]
TiO_2/GAC	2 (g/L)	[52]
TiO_2 coated ceramic foam filter (TCF)	0.01% g^{-1} TiO_2	[53]
TiO_2 nanowire membranes	15 μm	[54]
Degussa P25	0.75 (g/L)	[56]
Ag-TiO_2 layer	10-20 nm	[57]
Fe-doped P-25	0.25 (g/L)	[58]
Fe-doped UV-100	0.25 (g/L)	[58]
Ag-Doped TiO_2	1 (g/L)	[59]
TiO_2 thin film electrodes	0.5 mm	[62]
Degussa P25	0.1 (g/L)	[71]
Degussa P25	0.25 (g/L)	[75, 76]

performance of TiO_2 in HA removal can be summarized in the following sections.

TiO_2 Loading

The amount of catalyst loading is directly proportional to the overall photocatalytic reaction rate [74]. Generally, it is necessary to determine the optimum catalyst concentration in any given photocatalytic application in order to avoid excess catalyst and ensure total absorption of efficient photons. There is a higher surface area of the catalyst that is available for adsorption and degradation when the TiO_2 catalyst loading is increased, leading to a corresponding increase in the decomposition process. The linear dependency is held to a certain extent when the amount of TiO_2 reaches a certain level (saturation stage), causing an independence of reaction rate with TiO_2 loading. It is understood that an increase of the photocatalyst concentration increases the solution opacity, leading to a reduction of light penetration in the solution, the surface area of TiO_2 being exposed to light illumination and photocatalytic efficiency. Therefore, the optimum dosages of TiO_2 loading selected below the saturation level, under given conditions, is very important to avoid excess catalyst and ensure efficient photon absorption. There are many studies given in Table 2 [19-20, 51-54, 56-59, 62, 71, 75-76] that have reported the effect of TiO_2 loadings on the HA removal process efficiency. The optimal TiO_2 catalyst dosage is mostly independent and it is difficult to make

a direct comparison due to the experiment conditions, radiation fluxes, intensity, and wavelengths, and the dimension of the photoreactor used were different. For TiO_2 immobilized systems, the optimal thickness of the catalyst film should also be considered due to TiO_2 thin-film electrode being immobilized as a ceramic film. An excess increase of catalyst film thickness will increase the recombination possibility of the electron/hole pair and the degradation performance is reduced, as an inevitability.

Nature of the TiO_2 Photocatalyst

TiO_2 has three different crystalline forms, with anatase and rutile being the most common while brookite forms are uncommon, unstable, and hence are not discussed in terms of catalyst materials [66]. Degussa P-25, a powder including both forms of approximately 25% rutile and 75% anatase crystallites, is the most common commercially available form of TiO_2 that has been used in many studies of photocatalytic degradation. By heating to temperatures above 700ºC, anatase TiO_2 can be converted to rutile form. It is generally accepted that anatase is a better photocatalyst than rutile [77]. In addition, a number of different forms of TiO_2 such as Degussa P-25, Hombikat UV100 (100% anatase) have been synthesized to perform the desired characteristics of the photocatalyst. It was noted that the actual photocatalytic rate did not necessarily require the dependency on the higher surface area of Hombikat UV-100, but rather to the available or active sites or centers taking place in the course of the reaction. The probable reason for this occurrence could be explained by the unified crystal characteristics of Degussa P-25. In fact, Degussa P-25 composed of small nanocrystallites of rutile being dispersed within an anatase matrix. Thus, electron-hole pairs are generated by the smaller bandgap of rutile "catches" the photons. The transmission of the electron from the rutile conduction band to electron traps in the anatase phase takes place. This transmission inhibits the recombination and allows the hole to move to the surface of the particle and join the reaction. The better efficiency of Degussa P25 may also be explained by "quantum size effect" [78]: when the particles become too small, there is a "blue shift" with an increase of the band gap energy, detrimental to the near UV-photon absorption, and an increase of the electron-hole recombination. Not only that, in the report of Zhang et al. [79], two types of TiO_2 obtained by the post-calcination of hydrothermally derived titanates were found to be more efficient than Degussa P-25 in the degradation of HA. In summary, morphological and crystallographic properties of TiO_2 might play important roles in the photocatalytic efficiencies.

Effect of pH

There are many reports about the effect of pH on photocatalytic degradation of organic compounds in aqueous solution [65, 72-73]. In fact, the interpretation of the pH-dependent photodegradation of HA on TiO_2 is a very difficult task because of its multiple roles.

First, relating to the ionization state, the surface of the TiO_2 can be protonated or deprotonated under acidic or alkaline conditions [74], respectively, according to the following reactions:

$$\text{At pH} < \text{PZC:} \quad TiOH + H^+ \leftrightarrow TiOH_2^+ \quad (13)$$

$$\text{At pH} > \text{PZC:} \quad TiOH + OH^- \leftrightarrow TiO^- + H_2O \quad (14)$$
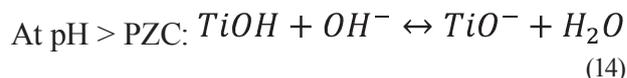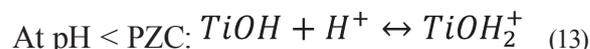
The change of pH value can influence the adsorption modes of HA molecules onto the TiO_2 surfaces, and the amount of produce (˙OH) can lead to a modification of the overall photocatalytic oxidation rate. The pH value at which the number of the positively and negatively charged surface sites are equal is defined as the point of zero charge value (pH_{pzc}) or isoelectric point. The PZC for TiO_2 varies in the pH range of 6.0-7.5 [80], depending on the catalysts used. This means that the surface of the TiO_2 is positively charged if pH is lower than the PZC, while it is negatively charged if pH is higher than PZC. According to Teow et al. [18], it was clear that the coverage of HA on the TiO_2 catalyst surface was obviously pH-dependent. A strong ability to absorb HA on TiO_2 particles is demonstrated at low pH condition (pH < 3.0 or 5.0), whereas high solution pH, the adsorption of HA, becomes very difficult. Teow et al. [18] showed that there is less than 5% of absorbance occurring at each PVDF-TiO_2 mixed-matrix membrane (MMMs) at pH 9.0. The negative influence on the permeate flux and HA removal at alkaline conditions (pH 9.0) was confirmed by Szymański et al. [19], while at pH 3.0 and pH 6.5 no membrane fouling was noticed. In acidic solution (close to pH_{zpc}), HA molecules are easily adsorbed on the surface of TiO_2 and are more quickly mineralized. A near optimum pH at approximately 5.5 was also identified by Patsios et al. [56], with high mineralization rate of HA as well as high mineralization efficiency (almost 74 %). Palmer et al. [81] also observed that the maximum mineralization rate was close to pH 7.

In the case of doped or coated photocatalysts, a change in pH may change the interfacial structure. Both of ZnO-TiO_2/BC and TiO_2/BC composites in Wang et al. [51] showed that the removal efficiency of HA decreased as pH increased from 2.0 to 10.0. In addition, at pH > PZC 7.2 and 8.1, HA could not adsorb onto the negatively charged ZnO-TiO_2/BC and TiO_2/BC surfaces, respectively. Xue et al. [52] also confirmed that HA cannot adsorb onto the negatively charged TiO_2/GAC surface at high pH values.

Secondly, the pH affects not only the adsorption of charged contaminants but also alters the concentration of surface hydroxyls and shifts the position of conductance and valence bands [80]. It is hard to predict the effect of pH on the band edges of the TiO_2 and the oxidation potential of HA [81].

The third role is hydroxyl radicals (·*OH*) can be formed by the reaction between hydroxide ions and positive holes (Eq. (9)). At neutral or high pH levels, ·*OH* radicals are considered the pre-dominant species, which means are more easily generated due to more ions being available on the TiO_2 surface, and thus the efficiency of the process is enhanced [82]. On the other hand, the positive holes act as the major oxidation species at low pH. However, ·*OH* radicals can also be generated following the pathway presented by Eqs. (3)-(7), and this mechanism at lower pH should also be taken into consideration [65]. The importance of ·*OH* in the photocatalytic oxidation of HA was emphasized by Liu et al. [83]. At low pH, the overall HA removal process was not improved by the enhancement of HA adsorption. The reaction rate could be enhanced by the addition of H_2O_2 further due to the increased generation of ·*OH*.

Finally, TiO_2 particles tend to agglomerate at low pH and the surface area available for adsorption of contaminants and photon absorption would be reduced, which finally influences the photodegradation rate [80]. The aggregation of TiO_2 nanoparticles in an aquatic environment under UV irradiation at different pH levels was investigated by Wang et al. [84]. With the same period of UV, the highest aggregation was observed at pH 3.0. Furthermore, the results illustrated that the removal of the HA was in accordance with the TiO_2 aggregation time. Because of this reason, pH plays an important role both in the characteristics of the aqueous solution and in the reaction mechanisms such as hydroxyl radical attack, direct oxidation by the positive hole, and direct reduction by the electron.

Since the effect of pH is very complicated and complex, as can be seen from the above discussion, the optimal pH value for a specified application should be selected on the basis of preliminary investigations.

Effect of Reaction Temperature

In fact, photocatalytic systems in most cases are operated at room temperature and do not require heating. Although it is well known that the minor changes in temperature do not much affect the photocatalytic oxidation rate, many researchers are establishing experimental evidence for the dependence of photocatalytic activity on temperature. At room temperature, low thermal energy (0.026 eV) is inadequate to activate the TiO_2 surface, but it is quite close to the activation energy of hydroxyl radical formation. Thus, it can be assumed that the photodegradation rate of HA is governed by hydroxyl radical reactions, and the effect of temperature on the rate of oxidation may be dominated by the rate of interfacial electron transfer to oxygen.

At a reaction temperature greater than 80ºC and that tends to the boiling point of water, the recombination of charge carriers would be enhanced and the adsorption of HA compounds onto the TiO_2 surface is disfavored and becomes the rate-limiting step, resulting in a decrease of photocatalytic activity [74]. On the contrary, a low temperature below 80ºC actually favors adsorption, which enhances the adsorption of final reaction products. At very low temperatures (below 0°C), the photocatalytic activity would be decreased and desorption becomes the rate-limiting step of the process. As a consequence, the temperature range between 20-80ºC has been regarded as the desired temperature for effective photomineralization of organic content.

The Van't Hoff-Arrhenius equation (Eq. (15)) has been applied to describe the effect of reaction temperature on the rate constant k, which is linearly proportional to the exponential $(-1/T)$:

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{15}$$

…where E_a is the energy of activation, R is the universal gas constant, and k_1 and k_2 are the constants for temperatures T_1 and T_2, respectively. However, the data in Palmer et al. [81]'s experiment did not fit the Arrhenius equation well.

Light Wavelength

In the photocatalytic process, depending on the types, the crystalline phase or modifications state of photocatalysts used, radiation sources with different wavelength-emitting ranges is an important ingredient in the reaction rate. With TiO_2, which absorbs irradiation below the visible range of the light spectrum, a light wavelength at least near UV light is needed. The band gap of anatase TiO_2 is 3.2 eV and the irradiation portion is below 380 nm, which is sufficient for photonic activation. Depending on the band gap threshold of the type used, the rutile TiO_2 can be activated with the light wavelength of up to 400 nm due to its band gap being 3.02 eV.

The light sources might be solar irradiation or artificial lamps. Solar light can also activate TiO_2 given that the TiO_2 activation spectrum overlaps with the solar spectrum. Unfortunately, only 4-5% of the total irradiated natural sunlight reaching the earth's surface is in the 300-400 nm near ultraviolet (UV) range that has sufficient energy that can be used to power photocatalytic reactors. This wavelength-emitting range is suitable for photocatalytic degradation of water pollutants. Several experiments were carried out for removing HA in solar photoreactors. By using UV light and artificial sunlight (ASL), Dziedzic et al. [85] studied the effects of wavelength on photocatalytic degradation of HA. It was stated that the removal efficiency of HA under ASL irradiation was only 18%, whereas the removal under UV irradiation was found to be 100% as measured by the UV_{254} absorption technique. It means that the energy of the ASL appeared not to be high enough to cause the degradation of humic substances in a photocatalytic process at the TiO_2 surface.

However, a drawback of solar energy is its intermittency and variability, with both factors being geographically dependent. Therefore, numerous investigations have

recently been focused on the preparation of novel photocatalysts that are able to utilize the visible range of the solar spectrum [86]. To increase the efficiency of solar light photocatalysis, doping of TiO_2 with transition metal ions has been considered an effective method that to red-shift the TiO_2 absorption band from the UV into the visible region. It was demonstrated through Fe-doped TiO_2 and $Fe_2O_3/TiO_2/GO$ compositions in the study of Rao et al. [20] and Birben et al. [58], respectively.

It could be concluded that the range of light absorbed is one of the most important factors for photocatalyst. Although UV-based photocatalysts perform better than visible light-based photocatalysts due to the higher photon energy, visible light reaches the Earth's surface much more than UV light. Thus, a less efficient photocatalyst that absorbs visible light may ultimately be more useful than a more efficient photocatalyst absorbing solely light with smaller wavelengths.

Light Intensity

Light intensity has a determinant role in the kinetics of the photocatalysis process. The review of Konstantinou and Albanis [82] reported that during a photocatalytic process:

i.   In the case of low light intensities (0-20 mW/cm^2), the rate would increase linearly with increasing light intensity (first order), because the electron-hole was mainly formed from the reactions involved, while electron-hole recombination is negligible.

ii. In the case of intermediate light intensities beyond a certain value (approximately 25 mW/cm^2), the rate would depend on the square root of the light intensity (half order), because there is a lower effect on the reaction rate caused by the competition between electron-hole pair separation and recombination.

iii. In the case of high light intensities, the rate is independent of light intensity, which is explained as follows: due to the surface coverage of the catalyst being saturated, resulting in a mass transfer in the adsorption and desorption being limited, it thus prevents the effect of light intensity from setting in.

In recent studies, the enhancement of reaction rate in HA removal in the presence of TiO_2 and UV wavelength as the light intensity increased was also observed [57, 71, 82]. By using nominal TiO_2 particles without modifications, Palmer et al. [81] showed that due to the increasing number of oxidizing species, the rate of degradation of HA also increases as light intensity increases, and there were two regions of light intensity increase results in differing degrees of the rate increase. Pansamut et al. [71] used commercial TiO_2 Degussa P-25 as a photocatalyst for investigating the effect of light intensity to the kinetics of photocatalytic degradation of HA. The results reported that 99% of HA removal efficiency was found and the removal efficiency increased with increasing light intensity and then become asymptotic. Under given feed water composition,

increasing light intensity, which is helpful for HA removal from aqueous solution, also was proved by Ma et al. [57] with a highly reactive photocatalytic membrane (Ag-TiO_2/hydroxiapiate(HAP, $Ca_{10}(PO_4)_6(OH)_2$)/Al_2O_3).

In summary, intensity increase proportionally with the reaction rate until it reaches the mass transfer limit (case (iii)). At higher irradiation intensities the electron transfer from the catalyst to oxygen present in the solution, which results in the generation of , is the rate-limiting step, especially in the case of larger TiO_2 particles and photocatalyst agglomerates.

Dissolved Oxygen

Dissolved oxygen (DO) has been essential to semiconductor photocatalytic degradation of organic compounds. It was found that the presence of DO might restrict or improve the photodegradation rate depending on the degradation mechanism of the pollutant. DO is strongly electrophilic, which serves as the electron scavenger to trap the excited conduction-band electron from recombination in the photodegradation processes [87]. But higher concentrations of DO may lead to decreasing the reaction rate due to the TiO_2 surface becoming highly hydroxylated to the extent of inhibiting the adsorption of pollutants at active sites. Generally, Henry's Law can be simulated to find an approximation of the amount of DO under the experimental conditions, provided the oxygen sparging rate and the photoreactor gas holdup is known [88]. Photoreactor sparging with pure oxygen in the TiO_2 slurry reactor is usually a cost-ineffective solution, as the amount of DO being held-up is a function of photoreactor geometry [72]. Therefore, it should be considered for operating the photoreactor under ambient conditions in order to prevent raising the cost of air or oxygen sparging for enhanced degradation rates.

In other words, DO is not only one of an electron acceptor but also involves the formation of other reactive oxygen species and the stabilization of radical intermediates, mineralization, and direct photocatalytic reactions [72]. This was evidenced by the research of Palmer et al. [81] for HA degradation and mineralization rates. The degradation occurred with the presence of alternative electron acceptors, but there was no carbon dioxide released, suggesting that oxygen was required for mineralization.

Concentration and Nature of HA

Numerable studies have shown that the rate of photocatalytic degradation of an organic pollutant depends on its concentration, nature such as its structure, molar mass, functional groups, and other existing compounds in aqueous solution [87-88].

In general, under similar operating conditions, organic pollutants increase the photocatalytic degradation rate to a certain level with the increase of its initial concentration. However, a further increase in the concentration creates

the saturation on the TiO_2 surface and the deactivation of the photocatalyst, leading to a decrease of the degradation rate [74, 82]. Yigit and Inan [89] showed that increasing initial HA concentration decreases photocatalytic degradation efficiency. This indicates that the breakdown of some conjugated carbon structures leads to the fragmentation of high molecular weight of organic substances into smaller units. Most researchers have applied the Langmuir–Hinshelwood model to describe the effect of organics concentration on degradation rate. In the case of Palmer et al. [81], the rate of degradation increased with increasing initial concentration of HA until the concentration of 30 ppm carbon, and after this concentration the rate actually decreased. The data did not follow Langmuir-Hinshelwood kinetics model but was actually slightly concave in nature.

Furthermore, the chemical structure of the HA compound also influences the degradation rate of the photocatalytic reactor. HA are organic macromolecules formed with a high molecular weight and that act as natural photosensitizers, which could participate both as electron donor centers (oxidation) and as an electron accepting centers (reduction). Therefore, sequential electron transfer, which from excited HA to the TiO_2 conduction band could lead to mineralization with CO_2 evolution, while that from the TiO_2 conduction band to HA tends to inhibit mineralization. In addition, the structure, molar mass, and functional groups of HA were used in different investigations, which may vary according to the source, age, interactions with the environment, and extraction process. This was well demonstrated in the work of Uyguner and Bekböle [75] and Erhayem and Sohn [90], whereas the adsorption of HA on TiO_2 in various sources and environmental exposures was measured. By using TiO_2 Degussa P-25, Uyguner and Bekböle [75] investigated the photocatalytic removal efficiencies of humic and fulvic acids from different origins (terrestrial and aquatic). Based on the source of origin, whereas diverse chemical and physical properties such as molecular weight, molecular size, and elemental composition, the efficiencies of removal humic and fulvic acids were different for each compound.

On the other hand, synchronous scan fluorescence (SSF) spectroscopy was used to complement the study of HA adsorption onto TiO_2 nanoparticles by Erhayem and Sohn [90]. In this study, there are six kinds of HA that were derived from soils (SLHAs) or sediments (SDHAs), and all originating from the state of Florida. Overall, because of structural differences, the soil HA affected the environmental stability and mobility of nano-TiO_2 differently than did sedimentary HA. The SSF spectra also indicated that there was preferential adsorption of polycondensed structures, which are more prevalent in soil HA than in sedimentary HA.

Inorganic Ions

An aqueous solution is often quite complex and contains a mixture of inorganic and organic solvents as well as dissolved inorganic matter and humic substances. The dissolved inorganic species (as anions and cations) can be adsorbed or compete for the active sites on the TiO_2 surface and, subsequently, affect the photocatalytic degradation rate of the organic pollutants [19, 76, 80] or may lead to voluntary photochemical phenomena. Hence, the influence of inorganic compounds on the TiO_2 photocatalytic properties has become an important research field.

Effect of Inorganic Anions

The inorganic anions naturally occurring in aqueous solution, such as Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, and PO_4^{3-} are known to inhibit the surface activity of the TiO_2 catalyst [64]. These anions behave as holes h^+ and $^\cdot OH$ scavengers, subsequently, the inorganic anion radicals (e.g. $Cl^\cdot$, $NO_3^\cdot$) are formed, whereas the reaction mechanism was obtained as follows:

$$Cl^- + OH^\cdot \rightarrow Cl^\cdot + OH^- \tag{16}$$

$$Cl^- + h^+ \rightarrow Cl^\cdot \tag{17}$$
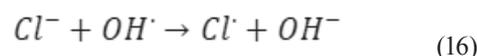
These inorganic anion radicals may initiate oxidation reactions with organic species under CO_2 formation. Although the reactivity of these radicals may be considered, they are not as reactive as h^+ and $^\cdot OH$, thus the observed retardation effect is still thought to be the strong adsorption displacement mechanism, which results in reducing the number of available on the TiO_2 surface [65, 82].

The effect of common inorganic anions on the photocatalytic degradation of HA was studied by Birben and Bekböle [76]. In this study, a representative range of common anions was added to HA solution in the presence of TiO_2 Degussa P-25. The collected data indicated the presence of anions' significantly enhanced initial adsorption on TiO_2 surface, thus the percentage removed of HA decreased. In addition, there was an inhibitory effect on the HA removal in terms of DOC and UV_{254} as increasing anion concentration. The binding of inorganic anions with the catalyst may form fouling, as shown by Szymański et al. [19]. It was found that the presence of HCO_3^-, SO_4^{2-}, and HPO_4^{2-} decreases the flux just at the beginning of the process at both low and high concentrations of these species. In other words, the membrane fouling was formed more severely by these species, resulting in a lower efficiency of HA removal in the feed.

Effect of Inorganic Cations

The metal ion is incorporated into the TiO_2 lattice, therefore impurity energy levels in the band gap of TiO_2 are formed (Eq. (18)-(19)):

$$M^{n+} + h\nu \rightarrow M^{(n+1)+} + e_{CB}^{-} \qquad (18)$$

$$M^{n+} + h\nu \rightarrow M^{(n-1)+} + h_{VB}^{+} \qquad (19)$$
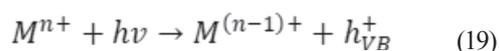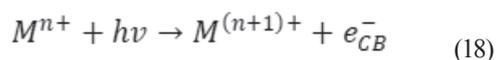
…where M is metal and M^{n+} is metal ion. Moreover, electron (hole) transfer between metal ions and TiO_2 can modify the electron-hole recombination:

$$M^{n+} + e_{CB}^{-} \rightarrow M^{(n-1)+} \qquad \text{as electron trap} \quad (20)$$

$$M^{n+} + h_{VB}^{+} \rightarrow M^{(n+1)+} \qquad \text{as hole trap} \qquad (21)$$
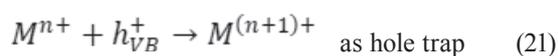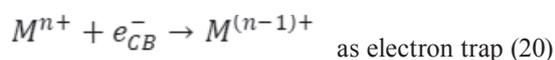
Due to its ability to trap either electrons or holes via oxidizing and reducing reactions, metal ions may increase the photocatalytic rate.

The effect of metal ions Ca^{2+} and Mg^{2+} on the photocatalytic oxidation of HA in TiO_2 suspensions was investigated by Li et al. [91]. They concluded that cation strength was created by adding positively charged metal ions, increasing the efficiency of TiO_2. While the pH of the aqueous solution was close to the PZC of TiO_2, the photocatalytic oxidation could be enhanced by the effect of Ca^{2+} on the adsorption between HA and TiO_2. On the other hand, the rate of HA removal was significantly enhanced in the presence of either Ca^{2+} or Mg^{2+}. It took less than 1 h to achieve the same removal HA efficiency in comparison with more than 2.5 h in the reaction without the addition of Ca^{2+} or Mg^{2+}.

Szymański et al. [19] investigated HA removal by using a ceramic UF membrane in a photocatalytic membrane reactor. They found that there was a more efficient adsorption of HA on TiO_2 particles and reduced membrane fouling in the presence of and .

These experimental results further proved that the existence of divalent cationic ions in HA aqueous solution could enhance the adsorption rate of HA on the TiO_2 surface and therefore improve the photoreduction rate.

Conclusions and Future Prospects

The association between the TiO_2 photocatalytic oxidation process and HA results in modification of the interactions, fate, transport, and toxicity of TiO_2 particles. This review has attempted to summarize most of the literature concerning the removal of HA from aqueous solution by using TiO_2 photocatalytic particles. Although there has been a great number studies that have achieved certain success in this area, the use of the TiO_2-based particles for HA removal has still suffered from some major disadvantages. Further investigations are needed to focus on the key areas to overcome these shortcomings as follows:
– The low quantum efficiency due to the fast recombination of photo-generated charge carriers is one of the major drawbacks of the TiO_2 photocatalyst. Any method that can enhance the lifetime of electron-hole pairs substantially increases the photocatalytic performance that should be devoted to future research.
– Despite so many research papers reporting on the effects of different modifications of the TiO_2 surface to improve its photocatalytic activity, little work has been provided a high photoactivity and thermal stability particle that can utilize visible and/or solar light irradiation. Besides that, TiO_2 under UV irradiation treatment is still considered a pH-dependent process due to the surface-oriented nature of photocatalysis. Each modified TiO_2 photocatalytic method achieves different effects along with certain limitations. Thus, researching an integrated system with wider pH range, with mixtures of the different methods for enhanced photomineralization or photo-disinfection kinetics and utilizing visible and/or solar light irradiation should be expanded further and applied in environmental protection.
– The toxicity of TiO_2 nanoparticles increased in the presence of HA and thus should be considered. Moreover, it has been asserted that photocatalytic oxidation generates superoxide ($O_2^{\cdot-}$), and the hydroxide radical ($^{\cdot}OH$) could be harmful to the human physiological system. Currently, there are no regulations related to the use of nanoparticle TiO_2, which can accumulate and potentially have health impacts on workers exposed to nanoparticle TiO_2 dust. On the other hand, it is difficult to separate the TiO_2 particles from aqueous suspension after treatment. How to reduce the harmful effect both on human health and the environment by keeping its usual microbial activities may be worth further research.
– Most of the studies conducted on HA removal are based on the single HA model solution and therefore might not fully represent their actual efficiency in the real water matrix, where a mixture of the compound exists. More work concentrating on the effect of complex mixtures compound is thus required.
– Although there are large differences in TiO_2 used and reaction operatational parameters (light source, catalyst loading, reaction time and type, the concentration of substrates, etc.), the comparison between each research is little. The respective data analysis was found to be very complex and different from others. Standardization of reactions with further optimization of reaction parameters is one important step that should be considered to get beyond the present level.

In summary, taking together all the above directional prospects in this field, a large-scale photocatalytic treatment process with high efficiency, solar-driven, environmentally friendly, and safe with human health should be realized in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

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