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REVIEW ARTICLE

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A review of prospects and challenges of photocatalytic decomposition of volatile organic compounds (VOCs) under humid environment

Girma Masresha[1] | **S. Anuradha Jabasingh**[1] | **Shimelis Kebede**[2] | **David Doo-Arhin**[3] | **Mekdim Assefa**[1]

[1]Process Engineering, School of Chemical and Bio-Engineering, Addis Ababa Institute of Technology, Addis Ababa University, Addis Ababa, Ethiopia

[2]Environmental Engineering, School of Chemical and Bio-Engineering, Addis Ababa Institute of Technology, Addis Ababa University, Addis Ababa, Ethiopia

[3]Department of Materials Science and Engineering, School of Engineering Sciences, University of Ghana, Legon-Accra, Ghana

Correspondence
Girma Masresha, Process Engineering, School of Chemical and Bio-Engineering, Addis Ababa Institute of Technology, Addis Ababa University, Addis Ababa, PO Box 385 Ethiopia.
Email: girma.masresha@aait.edu.et

Abstract

Volatile organic compounds (VOCs) are harmful for humans and the surrounding ecosystem. Emissions from these pollutants have caused a significant reduction in air quality, which has an effect on people's health. Alkanes, alkenes, alcohols, aromatics, and other VOC pollutants have all been broken down by TiO_2 photocatalytic processes. Due to several operating inefficiencies and deactivation issues in humid environments, the practical application of photocatalysis has not been realized on a broader scale. The effectiveness of photo-oxidation of VOCs is impacted by a variety of environmental conditions. In the photocatalytic oxidation of the VOCs, relative humidity (RH) is critical. Therefore, it is important to review the recent findings on how humidity affects the photocatalytic breakdown of VOCs in air. To satisfy this need, this work provides a critical review of the related literature with focus on the fundamentals of photocatalysis, photocatalytic degradation of air pollutants, and the influence of humidity on the photocatalytic process degradation for selected air pollutants. It also highlights the kinetic models and typical photocatalytic reactor and supports for VOC removal.

KEYWORDS

air quality, photocatalysis, pollutants, titanium dioxide, volatile organic compounds

1 | INTRODUCTION

Volatile organic compounds (VOCs) have recently become a major public concern due to their pollution of both indoor and outdoor air. VOCs are primarily produced by the industrial emissions, urban public facilities, and agricultural and animal husbandry emissions. These pollutants can come from a variety of sources, and long-term exposure to them causes sick building syndrome (SBS), a health problem.[1] Currently, a number of methods exist for reducing the emission of gaseous pollutants. These include condensation, adsorption, solvent absorption, porous material adsorption, membrane separation, ozonation, and photocatalytic oxidation (PCO).[2–10] These treatment methods, however, involve more chemicals, high energy requirements, operationally demanding situations, and low efficiencies. In this regard, heterogeneous photocatalysis can be an appropriate choice when contaminants cannot be removed properly or efficiently using other treatment methods. Furthermore, because the catalyst is inexpensive and capable of mineralizing the majority of VOCs, photocatalytic treatment is less expensive than other most common methods, such as chemical scrubbers or activated carbon adsorbers.[11]

Photocatalysis is a type of chemical process in which light energy is used to drive two chemical reactions.[12] The pioneer work by Fujishima and Honda[13,14] has motivated profound interests on the photocatalytic processes applied to environmental issues. Several studies have shown that TiO_2 based photocatalysis with a UV light source can be successfully applied to water and air purification processes in outdoor settings.[15,16] This is due to TiO_2's unique properties, which include its inexpensiveness, chemical and biological stability, non-toxicity, and relatively high photoactivity (especially in its anatase or anatase-rutile combination forms).[17]

UV photocatalytic treatment techniques are presently employed extensively for the degradation of VOCs. Figure 1 depicts the photocatalytic mechanism for the VOC mineralization. The PCO processes of the catalyst on the degradation of VOCs have been frequently attributed to two major photochemical oxidants: OH radical and reactive oxygen species (ROS). In general, removing VOCs in high concentrations has proven to be tedious. However, photocatalysis can be effective for some low concentrations of indoor VOCs such as trichloroethylene (TCE), acetone, methanol, and toluene, as well as carbon monoxide (CO) and nitrogen oxides (NOx).[11,15,18–21] The efficiency of PCO is primarily influenced by several factors such as light source, catalyst, temperature, humidity, and residence time.[22,23] Among these factors, many authors have focused on the effect of relative humidity (RH) on the photocatalytic degradation of gaseous VOCs.[24] The influence of water on the kinetics of photocatalytic degradation and the lifetime of the catalyst is still up for debate. In real-world applications, it was discovered that a high concentration of water vapour in the feed stream had a negative impact on the removal efficiency of VOCs from the catalysts. The effect of water's inhibition has been discussed by a number of authors. Re-engineering the catalyst's natural structure and enhancing VOCs' ability to adsorb on the TiO_2 surface are two potential solutions to this issue. The objective of this work is to review and evaluate the existing literature related to the effect of water vapour on the PCO process of VOCs and to propose strategies for photocatalyst modification to improve the adsorption capacity.

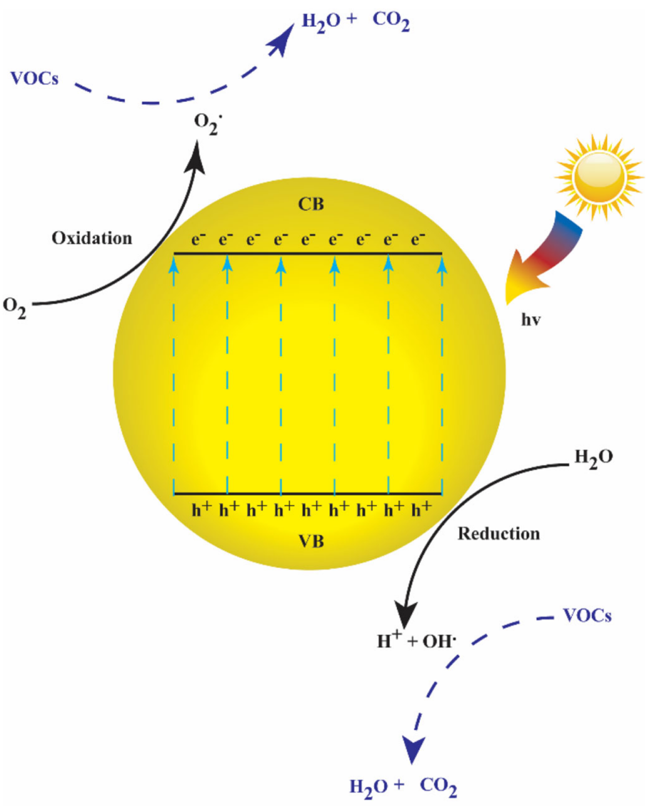

FIGURE 1 Photocatalytic mechanism for volatile organic compounds (VOCs) mineralization. CB, conduction band; VB, valence band.

2 | PRINCIPLE OF PHOTOCATALYTIC DEGRADATION

In PCO, a semiconductor catalyst (oftentimes TiO_2) is used in the presence of a light source to degrade pollutants into primarily oxidation products (usually CO_2 and H_2O).[25] Photocatalytic reaction primarily depends on the wavelength or light (photon) energy and the catalyst. Under the influence of photons, the catalyst generates free radicals that obliterate the contaminants that have bonded to its surface.[26]

Light absorption, the formation and separation of electron (e) and hole (h^+) pairs, and oxidation–reduction surface reactions between electrons (e^-) and adsorbed oxygen molecules (O_2), which can produce superoxide radicals ($^{\cdot}O_2^{-}$), are all photocatalytic reaction mechanisms for air treatment. Subsequently, additional electron holes (h^+) and water (H_2O) molecules can generate hydroxyl radicals ($OH^{\cdot}$). Thus, given that both O_2^- and $OH^{\cdot}$ radicals are powerful oxidants, they can mineralize harmful chemical species (i.e., VOCs) in air, converting them into CO_2 and H_2O in the case of complete mineralization.[27] As demonstrated in Figure 2, the basic mechanism of the electron–hole generation in TiO_2 photocatalysis involves three major steps: (i) light absorption and generation of electron–hole pairs; (ii) separation of charge carriers; (iii) oxidation and reduction reactions; and (iv) recombination of electron and electron–hole at the surface of semiconductor.

TiO_2 as a photocatalyst is used to produce electron (e^-) and holes (h^+), subsequently facilitating the redox (reduction and oxidation) reactions. UV radiation can stimulate electrons and holes, resulting in the generation

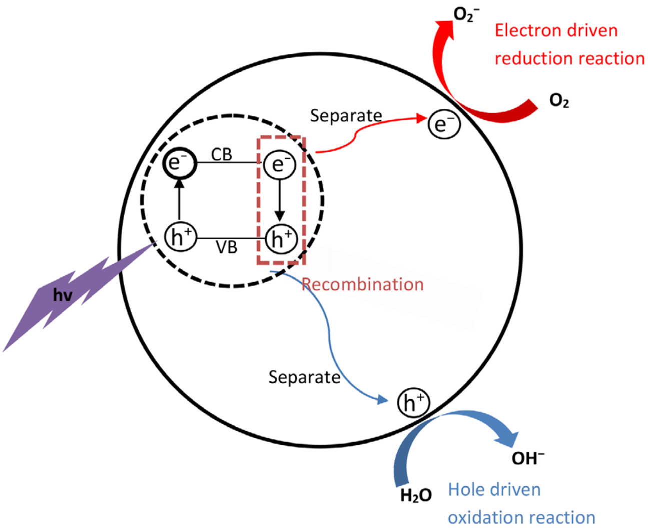

FIGURE 2 The electron–hole generation in a photocatalyst particle. CB, conduction band; VB, valence band.

of radical OH^- and O^{-2} ions, which transform the desired pollutant into CO_2 and H_2O.[28] An electron (e^-) may be promoted from the valence band (VB) to the conduction band (CB), creating an electron vacancy-hole (h^+), when a semiconductor absorbs a photon with energy equal to or greater than the band gap energy ($h\nu \geq EG$) (Equation (1)). In redox processes (Equations (2)–(6)) involving various species adsorbed on the catalyst surface, the electron and the hole can migrate to the catalyst surface. Surface-bond H_2O or OH and holes can react to form the hydroxyl radical OH (Equations (2) and (3)), whereas electrons during reaction with oxygen can generate superoxide radical anion O_2^- (Equation (4)). Hydroxyl radicals can be also formed following the path represented by reactions in Equations (5)–(9).[29] Investigating the photocatalytic elimination of a specific pollutant requires a thorough understanding of the reaction mechanism and mineralization yield.[30] The electrons can also react with organic compounds to provide reduction products (Equations (1)–(9)). Since oxygen (Equation (4)) can interact with the photogenerated electrons, its involvement is crucial.

Electron–hole pair formation is as follows:

$$\mathrm{TiO_2} + h_\nu \rightarrow h^+_{\mathrm{VB}} + e^-_{\mathrm{CB}} \tag{1}$$

$$\mathrm{H_2O\,(Ads)} \rightarrow \mathrm{OH^-} + \mathrm{H^+} \tag{2}$$

Hole trapping is as follows:

$$\mathrm{OH^-} + h^+_{\mathrm{VB}} \rightarrow \cdot\mathrm{OH} \tag{3}$$

$$\mathrm{O_2} + e^-_{\mathrm{CB}} \rightarrow \mathrm{O_2^-} \tag{4}$$

$$\mathrm{O_2^-} + \mathrm{H_2O} \rightarrow \cdot\mathrm{OOH} + \mathrm{OH^-} \tag{5}$$

$$2\cdot\mathrm{OOH} \rightarrow \mathrm{O_2} + \mathrm{H_2O_2} \tag{6}$$

Electron removal from the CB is as follows:

$$\cdot\mathrm{OOH} + \mathrm{H_2O} + e^-_{\mathrm{CB}} \rightarrow \mathrm{H_2O_2} + \mathrm{OH^-} \tag{7}$$

$$\mathrm{H_2O_2} + e^-_{\mathrm{CB}} \rightarrow \cdot\mathrm{OH} + \mathrm{OH^-} \tag{8}$$

Oxidation of organic pollutant molecules is as follows:

$$\cdot\mathrm{OH} + \mathrm{Pollutant} + \mathrm{O_2} \rightarrow \mathrm{Products\,(CO_2,\,H_2O,\,etc.,)} \tag{9}$$

3 | FACTORS AFFECTING THE PHOTOCATALYTIC ACTIVITY

Several environmental factors have an impact on the efficiency of PCO processes used to degrade VOCs. The incoming gas concentration, gas flow rates, gas flow type, and RH are all factors that influence how effective the process is.[31–35] Understanding the relationship between photocatalytic degradation rate and substrate concentration is required for the PCO system to function properly.[36] How much of the reaction will degrade is determined by how many organic pollutants are adsorbed onto the photocatalyst's surface. Adsorption on the photocatalyst is also influenced by the initial concentration of the pollutant, and this typically decreases as pollutant concentration increases.

The intensity of light radiation also has an impact on the rate of photodegradation reaction. The likelihood of electron excitation increases as the light intensity increases.[37] The pollutant gas flow rate has a significant impact on the rate of PCO because it affects the mass transfer of pollutants from the gas phase to the catalyst surface, where oxidation occurs. The airflow rate, on the other hand, is an important factor in the PCO of VOCs. The airflow rate of a reactant can influence the rate of the reaction. The PCO response is affected differently by low and high airflow speeds.[38] In terms of surface chemistry, the photocatalytic efficiency and lifetime of the photocatalyst depends on how the target gas molecules interact with the photocatalyst, as well as how they adsorb and desorb intermediates and products.[39]

Although photocatalysis technology is an effective treatment method for VOC degradation, it suffers from an unknown reaction mechanism and photocatalyst deactivation, which severely limits its practical application.[40] The effects of humidity on catalytic activity were thoroughly examined and addressed in the sections that follow.

4 | EFFECT OF HUMIDITY ON PCO OF VOCS

Water's role in VOC catalytic oxidation is quite complex and is determined by a number of variables such as the type of VOC, the catalyst, and the reaction conditions. Humidity is frequently required in gas phase photocatalysis to maintain photocatalytic activity. The presence of water molecules on the photocatalyst surface can increase the activity of the catalyst in two ways.[41] First, it acts as a precursor for the formation of OH radicals ($OH^{\cdot}$), and second, it improves oxygen adsorption. When exposed to light, surface oxygen reacts with photogenerated electrons to form oxygen radicals, which are important for oxidizing the contaminants.

The impact of water vapour on gas phase PCO varies greatly depending on the substance to be oxidized, the shape of the photocatalyst, and the amount of water vapour present.[42] As a result of excessive humidity, hydroxyl groups cover the titanium dioxide surface, and the material active sites are occupied, reducing catalytic activity.[43] A VOC molecule needs to get through this layer of water molecules on the photocatalyst's surface and be able to diffuse to the photocatalytic surface for a reaction to happen.[44] Depending on the type of pollutant, water can have a positive or negative impact on a gas phase photocatalytic degradation reaction. The best condition for humidity for each of the contaminants was suggested in the following sections, and details on the impact of humidity on photocatalytic degradation during the removal of this pollutant is presented as well.

4.1 | Saturated alkanes

Boulamanti and Philippopoulos[45] reported that the reaction rate decreased by an increase in humidity in the system, leading to more adsorption of water vapour molecules on the surface catalyst and a lowering of the reaction rate. Debono et al.[46] investigated the effect of RH on decane PCO by conducting the experiment at two levels of water vapour content: 0% RH and 50% RH. They observed that water vapour had no effect on the PCO of the decane conversion. Figure 3 illustrates the general PCO mechanism of decane proposed by Debono et al., which indicates that decane is first converted to aldehydes and then to CO_2.[46] Zhang and Liu[47] investigated how RH affected the PCO of hexane. The results showed that hexane conversion increased dramatically with an increase in RH up to 20%, then nearly stabilized until 45%, but decreased significantly when RH exceeded 45%.

4.2 | Unsaturated alkenes and alkynes

Researchers studied ethylene breakdown and discovered that as water vapour mole fractions increased, the reaction rate decreased.[48] Jimenez-Relinque and Castellote[49] investigated the PCO of isobutylene at 50%, 75%, and 90% RH. They observed an increase in PCO up to 75% RH, followed by a minor decrease at 90% RH, indicating that 75% RH is the optimal humidity level for this device to degrade VOCs. Acetylene was removed at a rate of 27 ppm/min in dry air, and 16, 10, and 8.5 ppm/min when the amount of water vapour was increased to 4000, 8000, and 10,000 ppm, according to Thevenet et al.[42]

4.3 | Aromatic hydrocarbons

According to Zhang et al.'s[50] study of PCO of toluene, the amount of eliminated toluene decreased sharply as RH increased. This is consistent with the findings of Park et al.,[51] who discovered that when toluene is decomposed using TiO_2 at higher humidity, the competing adsorption of water and toluene reduces the effectiveness of toluene removal. Sun et al.[52] discovered that increasing the RH from 0% to 60% improves the removal rate of toluene, but only slightly when the RH is raised to 80%. Cui et al.[53] chose RH levels ranging from 10% to 60% in their study. They discovered that as RH increased

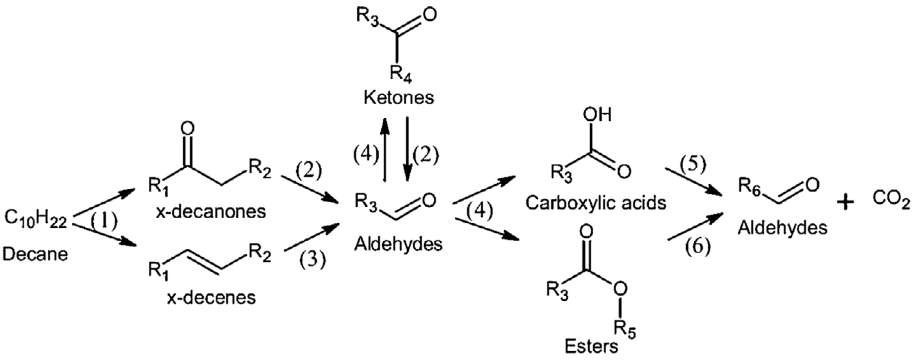

FIGURE 3 Photocatalytic oxidation (PCO) mechanism of decane as proposed by Debono et al.[46]

up to 35%, degradation efficiency increased significantly, before gradually declining under more humid conditions.

Fang et al.[54] investigated the effect of water vapour on the photocatalytic decomposition of toluene in another study. The results demonstrated that the addition of water vapour significantly reduced the catalysts' ability to catalyze reactions. The results showed that the addition of water vapour significantly reduced the ability of the catalysts to catalyze reactions. Kuo et al.[55] investigated the toluene removal efficiencies at RH = 15%, 30%, 45%, and 65%. They discovered that for all tested inlet toluene concentrations, the toluene removal efficiency at RH = 30% was the best in the tested RH conditions. However, at high RH levels, water adsorption on the photocatalysts prevented toluene adsorption on the catalyst.

Lin et al.[56] investigated the photocatalytic degradation of benzene under different humidity conditions. C_6H_6 degraded from 1.25 to 0.12 ppm in 45, 35, 45, 60, and 65 min as humidity increased from 33% to 60%, according to their findings. The highest degradation efficiency of C_6H_6 was achieved at a humidity of 41%. When the humidity increased from 33% to 41%, the degradation efficiency of C_6H_6 increased significantly, thus indicating the favourable effect of increasing the humidity on C_6H_6 degradation. However, as the humidity increased from 41% to 60%, the degradation efficiency continued to decline, indicating that high humidity has a negative impact on the photo-catalytic degradation of C_6H_6.[56]

Wang et al.[57] examined how humidity concentration affected the UV/TiO_2 technique used to break down gaseous benzene. The air stream utilized in this experiment had a RH between 0.5% and 80%. With a RH of 0.1%–10%, benzene removal and mineralization increased rapidly. According to the experiment results, a RH level of 10% was required to achieve the highest reaction rate. However, when RH levels were greater than 10%, the effect of increasing RH shifted in the opposite direction.

Ao et al.[58] reported that at 2100 ppm humidity, the conversions of benzene, toluene, ethylbenzene, and *o*-xylene (BTEX) were 24.9%, 35.6%, 55.2%, and 61.4%, respectively. As the humidity increased to 2200 ppm, the conversions of BTEX dropped to 2.2%, 3.8%, 7.9% and 10.5%, respectively. The experimental results clearly showed that the increase in humidity levels reduced the conversion of BTEX.

Jo and Kim[41] investigated the efficacy of target VOC degradation at three RH levels: 10%–20%, 50%–60%, and 80%–90%. The rate of decomposition slowed for the majority of chemicals as RH increased. For two RH ranges of 10%–20% and 50%–60%, four compounds (ethyl benzene, *o*, *m*, and *p*-xylenes) had a degradation efficiency of more than 90%.

4.4 | Oxygen-containing VOCs

Zhang et al.[50] investigated the nano-TiO_2/diatomite composite's ability to degrade ketone and alcohol VOCs. They found that the optimal RH for isopropanol, isobutanol, and 1-heptanol degradation was 5%, 15%, and 50%, respectively. When the humidity increased from 34% to 41%, Lin et al.[56] discovered that the concentration of formaldehyde HCHO decreased quickly after 25 min; however, when humidity increased from 47% to 57%, the concentrations of HCHO decreased rather slowly. In trials on the elimination of HCHO, Xu Liu et al.[59] used an initial HCHO concentration of 5.5 0.2 ppm and a range of RH values between 40% and 80%. The outcomes showed that for the highest reaction rate (3.47 ppmv/h), a RH of 55% was found to be ideal. According to Hager and Bauer,[60] 2-propanol photooxidation increased marginally with increasing water vapour concentrations and decreased with increasing water content. Boulamanti and Philippopoulos[61] investigated the effects of water vapour on methyl tert-butyl ether (MTBE) PCO at various RH values (0%–68% RH). Higher concentrations of water vapour were discovered to be inhibitory.

Circumstantiae et al.[34] investigated the effects of humidity photocatalysis on the oxidation of NO_2 from vehicle exhaust by TiO_2 immobilized on cement-based road materials. According to the study's findings, as the humidity increased, the effectiveness of PCO of NO_2 decreased significantly. Similarly, Nguyen et al.[62] on photocatalytic NO conversion found that increasing RH from 40% to 90% decreased the effectiveness of PCO. From the RH range of 40% to 60%, there was no significant change of the PCO efficiency. The maximum value of degradation of NO efficiency was obtained at about 75% RH after 5 min of irradiation.

4.5 | Chlorinated VOCs

Using pre-treatment TiO_2 sol gel sheets, the degradation process of TCE in gas phase was studied to determine the impact of humidity. No matter how the photocatalyst was treated, they discovered that when the RH was over 50%, the reaction rates dropped.[63] Similar result were also reported by Kazemi et al.[64] A significant change in degradation efficiency was not observed as the RH increased from 10% to 15%, but when RH increased up to 30%, degradation efficiency increased to approximately 99%. Further increasing of RH reduced the degradation efficiency due to competitive adsorption of perchloroethylene (PCE) and water molecules on the photocatalytic surface.

4.6 | Sulphur-containing VOCs

Ramakrishna et al.[65] reported that the PCO efficiency of diethyl sulphide (DES) decreases with the change of humidity from 87% (RH = 34%) to 78% (RH = 88%). Water vapour has two opposing effects, competing with fimethyl sulphide (DMS) adsorption on the one hand and producing hydroxyl radicals that speed up surface reaction kinetics on the other, according to Demeestere et al.[66] The former effect dominates at RH > 22%; the latter at lower RH. Table 1 shows the literature reports mentioning the optimal RH of humidity on photocatalysis for various VOCs.

According to the above review, water vapour has both a negative and a positive influence on the activity of catalysts for the catalytic oxidation of VOCs. The effect will differ depending on the chemical and physical properties of the contaminants and catalyst materials, as well as the pollutant type, concentration, and possibly other experimental factors. For some pollutants, humidity had little effect on PCO, including for example benzene, ethyl benzene, *o*-, *m*-, and *p*-xylenes, TCE, and PCE. The absence of water for some chemicals hinders the reaction rates common in toluene and formaldehyde PCO. The result of the PCO of ethylene indicated an inverse correlation between water vapour concentration and reaction rate. PCE degradation efficiency increased when RH increased. Further increasing of RH reduced the degradation efficiency due to competitive adsorption of PCE and water molecules on the photocatalytic surface. For NO, increasing decreased the effectiveness of PCO. For toluene at high RH levels, the adsorption of water on the photocatalysts prevented the adsorption of toluene on the catalyst, which decreases toluene removal efficiency.

5 | KINETIC MODELS

Equation (2) in a mathematical form shows that as humidity rises from zero, it always has a negative impact on the photocatalytic activity. In contrast, there are two additional ways to increase the humidity: (a) by continuously promoting the reaction, or (b) by having no effect at all. It is therefore evident that Equations (9) and (11) cannot universally represent the influence of humidity as reported in literature.

$$r = k\frac{K_B C_B K_W C_W}{(1 + K_B C_B + K_W C_W)^2} \tag{10}$$

$$r = k\frac{K_B C_B}{(1 + K_B C_B + K_W C_W)} \tag{11}$$

where C_B is the concentration of the organic reactant B (ppm), C_W is the concentration of water (humidity) (ppm), k is reaction rate coefficient (ppm/min), and K_B is adsorption coefficient of the organic reactant B (ppm^{-1}).

Zhang et al.[44] investigated the influence of humidity on photocatalytic degradation of chlorobenzene. They developed correlation based on the semi-empirical Langmuir–Hinshelwood bimolecular model. Use of the model with experimental data indicates that the reaction rate coefficient of chlorobenzene is linearly related to the reciprocal of humidity. According to Lin et al.,[56] HCHO

TABLE 1 Summary of literature reports mentioning the optimal relative humidity (RH) of humidity on photocatalysis for various volatile organic compounds (VOCs).

Pollutant	Concentration (ppm)	Catalyst used	Light source	Optimal RH (%)	Removal efficiency (%)	References
Toluene		Carbon-TiO_2	15 W mercury	60	86.8	Guo et al.[67]
NO_x	350	Iron chloride	150 W xenon	40	77	Nguyen et al.[62]
Dimethyl sulphide	275	TiO_2	18 W UV	22	22.6	Demeestere et al.[66]
Formaldehyde	5.5	$TiOSO_4$ TiO_2	8-W UV	55	-	Xu Liu et al.[59]
Diethyl sulphide	1200	Mn $(NO_3)_2$		34	87	Ramakrishna et al.[65]
Trichloroethylene	3000	TiO_2-C	4-W UV	30	99	Kazemi et al.[64]
Benzene	20	TiO_2 P-25	20-W UV	5	80	Wang and Ku[68]
Hexane		The TiO_2 film	UV lamp	45		Zhang and Liu[47]
Toluene	100	Mo-TiO_2	UVC		35	Jeong et al.[69]
Isopropanol	10	TiO_2/diatomite	UVA lamps	5	-	Zhang et al.[50]
1-Heptanol	10	TiO_2/diatomite	UVA lamps	50	-	Zhang et al.[50]
Isobutylene	4	TiO_2 P-25	UV lamp	75	-	Jimenez-Relinque and Castellote[49]

degradation conformed to a pseudo-first-order kinetic reaction since the fitting plots of $\ln(C_0/C_t)$ versus the degradation time t were linear at any humidity and had correlation coefficients (R^2) above 0.98.

Toluene photocatalytic removal at the ppb level is likely a pseudo-first-order process, according to Debono et al.[70] However, it is difficult to precisely quantify the boost through toluene reaction rates. In contrast to the dispersion of the experimental data, the favourable effect of water vapour on toluene disappearance is minimal.

6 | STRATEGIES FOR IMPROVING PHOTOCATALYTIC EFFICIENCY AIMING AT REMOVING POLLUTANTS FROM THE HUMID ENVIRONMENT

The kind of photoreactor, catalyst modification, and solvent selection are only a few of the variables that have been taken into account for the optimization of the photocatalytic process. The catalytic performance of the nano-catalyst is considerably improved by the surface modification, which is advantageous for the degradation of VOCs.[71]

6.1 | Novel cocatalytic LnOCl/BiOCl composite photocatalysts

Okumura et al.[72] investigated nitric oxide (NO) photo removal using the novel cocatalytic effects of mechanically grafted new-type lanthanide oxychloride LnOCl (Ln = Sm, Nd) photocatalysis. They discovered that the maximum NO photoremoval rate of the powder composite is approximately five times greater than that of pure BiOCl, or 20 times greater if BiOCl were the only active photocatalyst.

6.2 | Noble metal supported photocatalysts

In the catalytic combustion of VOCs, precious metals and base metal oxides are widely used. Due to their increased activity, the noble metals, particularly platinum and palladium, are recognized as the most common species of precious metal catalysts. Fu et al.[14] investigated the effect of Pt/TiO_2 catalysts on the rate of ethylene oxidation over UV-illuminated TiO_2. They discovered a significant increase in simultaneous heterogeneous catalytic oxidation for the illuminated Pt/TiO_2 catalyst at temperatures ranging from 40 to 110°C. You et al.[73] investigated the removal efficiencies of aromatic hydrocarbons by platinized TiO_2 (Pt/TiO_2) (e.g., benzene, toluene, *m*-xylene, and styrene). They discovered an increase in catalytic oxidation.

Iwanaga et al.[74] investigated ethylene photocatalytic decomposition. They discovered that humidity has a significant effect on the elimination of ethylene. They discovered that co-depositing Pd and Pt on glass-immobilized TiO_2, as well as heating the immobilized photocatalysts, accelerated the breakdown of ethylene. Belver et al.[75] investigated Pd/TiO_2 photocatalysts for toluene vapour removal. They claimed that the Pd/TiO_2 impact was reduced in dry conditions, but no discernible loss of photoactivity was observed during the study. Palladium is used to protect catalysts from deactivation caused by partially oxidized products of the reaction.

Tu et al.[76] developed a Me/TiO_2-zeolite Y (Me = Au, Pd) photocatalyst for the gas phase PCO of toluene under highly humid conditions to overcome. Toluene photooxidation was enhanced as water vapour concentration increased from 5.91 to 17.9 mg/L. Venezia et al.[77] investigated a variety of Pd-based catalysts for the oxide.

6.3 | Titania coated carbon and silica-titania composite

NiO nanoparticles were synthesized by Park et al.[51] and integrated into mesoporous silica for toluene oxidation at temperatures between 250 and 350°C. They discovered that dampness had both favourable and unfavourable impacts on catalytic activity. They found both positive and negative effects of humidity on catalytic activity. Stokke and Mazyck[78] studied the effect of RH (12% and 95%). Due to competition with water vapour for adsorption sites in a high humidity environment (RH I = 95%), the adsorption capacity of the silica titanium composite (STC) (1.2 mg/g) and titania coated activated carbon (AC) (1.9 mg/g) was decreased.

6.4 | Fabrication of hydrophobic TiO_2 photocatalyst

Surface modification has received a lot of attention recently since TiO_2 particle surfaces are hydrophilic, while the majority of organic molecules are hydrophobic. Silanization, surfactant absorption, and hydrophobic substrates might make it easier for organic molecules to move from the solution to the surface of TiO_2 particles. Another approach for creating hydrophobic supports has been disclosed, and it comprises a number of silylation techniques employing organosilanes.[79] Kuwahara et al.[80] proposed a method for creating hydrophobic surfaces utilizing triethoxyfluorosilane, an inorganic functional group containing silylation agent (triethoxyfluorosilane [TEFS]). Lee et al.[81] created films with superhydrophobic characteristics and photocatalytic activity by combining SiO_2 and N-TiO_2 in the right proportion, which is 5:5. Wang et al.[82] synthesized SiO_2–TiO_2–polydimethylsiloxane (PDMS) ternary compound, and sol–gel composite SiO_2–TiO_2 particles were first modified with PDMS. They discovered that the coating was practically superhydrophobic and that SiO_2–TiO_2–PDMS had some photocatalytic activity.

Likewise, Liu et al.[83] linked PDMS with the surface of metal-oxide photocatalysts. The photocatalytic activity is enhanced for the superhydrophobic TiO_2 with PDMS layer of 2.2 nm compared with bare TiO_2. The PDMS layer reduces the photocatalytic activity of the superhydrophobic TiO_2 when it is thicker than 5 nm.

Widati et al.[84] synthesized from SiO_2, TiO_2, and methyltrimethoxysilane (MTMS) precursors. The addition of TiO_2 to SiO_2–MTMS coated glass increased the surface roughness and improved the hydrophobicity. Rocha Segundo et al.[85] used TiO_2 and ZnO in combination to promote the ultra-hydrophobic photocatalytic reaction. Xing and colleagues[79] synthesized carbon-doped TiO_2/methyltrimethoxysilane flourine doped (MCF-F) hydrophobically modified photocatalysts by the hydrothermal method. Dioxin was degraded effectively using the synthesized catalyst.[86]

6.5 | Substrate/supported types

Numerous studies have found that choosing the right substrate is the best way to address these issues. The application of different substrates used in gas photocatalysis is depicted in Table 2.

In order to immobilize photocatalytic powders on various substrates for photoreactor design, many strategies have been used. Titanium dioxide (TiO_2) immobilization on various support materials (e.g., silica gel, zeolites, glass beads, activated carbon, and alumina quartz optical fibres, glass fibres, or wool) and coating of TiO_2 on walls of the reactor as a thin film are two common forms of TiO_2 handling in reactors.[98–100] It would be crucial to create a TiO_2 photocatalyst supported on materials with a wide surface area to clean the environment of storage facilities where the ethylene concentration is low under low-temperature, high-RH circumstances.[101]

Shiraishi et al.[102] studied the effect of humid air on the photocatalytic decomposition of ethylene. Under both humid and dry conditions, the glass support, scarcely adsorbs ethylene, while the glass-immobilized photocatalyst can continuously degrade ethylene quickly due to its reduced sensitivity to humid air. TiO_2 is advantageously deposited on glass fibres and glass frits because it increases the surface area exposed to active surfaces and the interfacial charge carrier transfer rates, both of which are essential to the effectiveness of photocatalytic systems.[74]

Obuchi et al.[103] studied the use of porous silica as a support for TiO_2. They reported that the use of Pt-TiO_2/SiO_2 catalyst enables us to construct a multifunctional reaction process for air purification, in which VOCs are photocatalytically decomposed. de Chiara et al.'s[104] investigation of silica support revealed that it had poor ethylene adsorption performance and that the silica-

TABLE 2 Summary of support and immobilized method reported in the literature.

Model compound	Support	Immobilization method	References
Dichloromethane	Activated carbon powder		Torimoto et al.[87]
Trichloroethylene	Silica gel	Sol–gel impregnation	Dibble and Raupp[88]
Toluene	SiO_2 support	Sol–gel	Jeong et al.[69]
Propionaldehyde	Silica/ferrite/zeolite	Sol–gel	Takeda et al.[89]
Formaldehyde	Activated carbon	Sol–gel	Huang and Saka[90]
Toluene	SiO_2	Chemical vapour deposition	Yao and Kuo[91]
2-Propanol	X-Zeolite/Porous glass	Hydrothermal dip coating	Yasumori et al.[92]
Acetylene	Pyrex glass/organic fibres	Dip coating	Thevenet et al.[93]
Ethylene	Glass/silica/activated carbon	Hydrothermal method	Iwanaga et al.[74]
Toluene	Aluminium sheets	Dip coating	Tasbihi et al.[94]
Isopropanol	Mesoporous silica powders	Sol–gel impregnation	Tasbihi et al.[95]
Toluene	Activated carbon	Chemical vapour deposition	Kuo et al.[55]
NOx	Silica gel	Sol–gel	Matsuda and Hatano[96]
Ethylene	Glass plate	Sol–gel	Lin et al.[97]

immobilized photocatalyst decomposed ethylene slowly. However, the dried silica-immobilized photocatalyst significantly improved ethylene adsorption performance and increased the photocatalytic activity for ethylene decomposition. Thevenet et al.[93] investigated the photodegradation of acetylene (C_2H_2) over powder, Pyrex glass-supported, and non-woven fibre-supported titanium dioxide in air into static conditions. The maximum activity was achieved using fibre-deposited photocatalysts, and the chemical composition of the fibre had no effect on the photodegradation.

6.6 | Support immobilization techniques

Aqueous or gaseous methods can be used to deposit TiO_2-based catalysts on structured substrates. Sol–gel and electrophoretic deposition (EPD) are some examples of aqueous methods given in Table 2, while spray pyrolysis deposition, chemical vapour deposition (CVD), physical vapour deposition, and other processes are examples of gas phase methods.[105] EPD is a coating method using the principle of generating movement of electrical charges to anode or cathode by applying an electric field to particles having each positive charges and negative charges in a colloidal phase.[106] CVD is a technique where a solid material is deposited from a vapour by some chemical reaction occurring on or in the vicinity of a normally heated substrate surface.[107] The hydrothermal process is used in the autoclave under regulated temperature and/or pressure, with the reactions taking place in aqueous solution to create nanoparticles.[108]

Dip coating is a process in which the substrate is gently and steadily removed from a precursor solution of TiO_2. Dip coating is a procedure in which a precursor solution of TiO_2 is slowly and carefully withdrawn from the substrate. The hydrothermal method of nanoparticle synthesis is carried out in the autoclave. The reaction requires an aqueous medium, and controlled temperature and pressure are achieved. This technique is utilized for synthesizing nanoparticles of TiO_2.[109] Among various common photocatalysts immobilization method, the sol–gel method is common. This method has the characteristics of a controllable process, simple operation, high purity, and normal temperature.[83–86]

6.7 | Reactor configuration

The effectiveness of the catalytic process for the degradation of VOCs is significantly influenced by reactor design. Numerous types of laboratory scale photocatalytic reactors have been developed, each with its own advantages and disadvantages, such as flat plate, multi-plate, paper-based immobilized TiO_2, annular, corrugated plate, multi-annular, monolith, packed bed, foam packed bed, and fluidized bed, as per Raza et al.[18]

Using computational fluid dynamics, Wang et al.[110] modelled the photocatalytic breakdown of formaldehyde in a honeycomb monolith reactor. It is frequently used in the reduction of NOx in power plant flue gases by catalytic reduction and the control of vehicle exhaust emission. For the acceleration of gas-phase photocatalytic oxidative dehydrogenation of cyclohexane, Palma et al.[111] used a fluidized bed reactor.

Amama et al.[112] used a cylindrical batch reactor for photocatalytic degradation of TCE. The batch reactor is the simple type of photo reactor used for VOC degradation. The batch reactor typically consists of a Pyrex glass chamber.

A novel packed bed reactor was proposed by Arabatzis et al.[113] for the photocatalytic destruction of VOCs. The packed bed reactors are straightforward, simple to build, and effective. A cylindrical tube constructed of Pyrex glass, metal, or another material makes up this kind of reactor. The photocatalyst is located in the central part of the reactor. Shiraishi et al.[102] investigated the effect of photocatalytic decomposition of ethylene concentration in a spiral-type reactor. They showed a spiral-type photocatalytic reactor that can decompose ethylene at low concentrations and used it to preserve the quality of agricultural products. A plug-flow, fixed-bed annular reactor that was operated continuously was used to study the decomposition of gaseous acetone by the UV/TiO_2 reaction at room temperature (between 20 and 25°C).[102]

Using a lab-scale continuous-flow annular photoreactor that was filled with glass beads, Kazemi et al.[64] examined the PCO of PCE in the gas phase. In this study, a lab-scale continuous-flow tubular UV-photoreactor filled with coated glass beads was used to analyze photocatalytic degradation of PCE in air utilizing titanium oxide base catalysts. Table 3 below shows common types of photocatalytic reactors usually used for the air treatment.

6.8 | Catalyst regeneration

Any use of photo-oxidation requires catalyst regeneration.[138] Recent research has examined the electrochemical regeneration of saturated activated carbon by Ti/SnO_2 anode.[139] The PCO process, which promotes the breakdown of organic substances when exposed to UV radiation, is another means of regeneration.[140] Satter et al.[141] used heat treatment of

TABLE 3 Summary of the catalyst used and reactor type in heterogeneous photocatalysis reported in the literature.

Pollutant	Type of catalyst	Reactor	References
Toluene	TiO_2 on the activated carbons	Fluidized bed	Kuo et al.[55]
Propionaldehyde	Silica, alumina, activated carbon, mordenite, femerite, X-type zeolite	Pyrex reaction cell	Takeda et al.[89]
Toluene	(TiO_2/c-MDF) carbonized medium density fibreboard	Batch reactor	Lee et al.[114]
Dichloromethane	TiO_2-1oaded activated carbon	Pyrex reaction cell	Torimoto et al.[87]
Toluene	TiO_2	Batch reactor	Jeong et al.[69]
NOx	TiO_2/silica gel	Fluidized bed system	Matsuda and Hatano[96]
Formaldehyde	TiO_2 crystallite-activated carbon	Batch reactor	Huang and Saka[90]
2-Propanol	TiO_2-zeolite-porous-glass composite	Batch reactor	Yasumori et al.[92]
Toluene	TiO_2 Degussa P25	Fluidized bed photoreactor	Prieto et al.[115]
Trichloroethylene		Fluidized bed	Dibble and Raupp[88]
Dimethyl Sulphide	Titanium dioxide P25	Flat-plate reactor	Demeestere et al.[66]
Diethyl Sulphide	MnO/Zeolite-13X	Batch reactor	Ramakrishna et al.[65]
Acetone/acetaldehyde/toluene	Commercial TiO_2	Pyrex glass cylindrical reactor	Bianchi et al.[116]
Ethanol	Nano-MnO_2 decoration of TiO_2 microparticles	Batch reactor	Stucchi et al.[117]
Benzene	$BiPO_4$	Fixed bed tubular reactor	Long et al.[118]
Benzene	Pt/TiO_2 catalyst	Fixed bed annular	Fu et al.[119]
Benzene	Ga_2O_3	Fixed bed tubular	Hou et al.[120]
Acetone, benzene, toluene	Indium hydroxide nanocrystals In_2O_3	Batch reactor	Yan et al.[121]
Benzene	Pt/TiO_2	Batch reactor	Li et al.[122]
Benzene	TiO_2 ~ P25	Batch reactor	Einaga et al.[123]
2-Butanone	Gallium oxide/reduced graphene oxide	Batch reactor	Ibrahim and Sreekantan[124]
No	Degussa P-25 titanium dioxide	Annular	Lim et al.[125]
Trichloroethylene	TiO_2/SiO_2	Annulus fluidized bed reactor	Lim and Kim[126]
Acetaldehyde	Ternary g-C_3N_4/Ag-TiO_2 composites	A continuous gas flow reactor	Wang et al.[127]
N-Butanol	Degussa P25	Cylindrical reactor Batch	Kirchnerova et al.[128]
1-Propanol	TiO_2 P25 Degussa	Annular reactor	Vincent et al.[129]
Propene	TiO_2	Batch reactor	Bouazza et al.[130]
Toluene	TiO_2	Fixed-bed cylindrical	Augugliaro et al.[131]
Benzene	TiO_2/Sr_2CeO_4	Closed stainless steel	Zhong et al.[132]
Ethylene	Zirconia-titania catalyst	Batch reactor	Tibbitts et al.[133]
Trichloroethylene, isooctane, acetone	Degussa P-25 TiO_2 powder	Plug flow reactor	Alberici and Jardim[134]
Ethylene	TiO_2 obtained by plasma modification of Ti foil and oxidation	Batch reactor	Kajita et al.[135]
Toluene	Commercial TiO_2	Annular reactor	Tomašić et al.[136]
Cyclohexane	Pt doped-TiO_2	Fluidized bed photoreactor	Murcia et al.[137]

the spent catalyst in a He flow and regenerated the original activity for subsequent reaction. Another group of investigators demonstrated the use continuous adsorption and electrochemical regeneration using an air-lift reactor.[142]

6.9 | Photodegradation by vacuum ultraviolet (VUV) light

Using VUV degradation as an alternate method to break down gaseous organic molecules shows promise.[69] The key processes used in the technique are direct photolysis, photocatalysis, and ozone oxidation, which is formed by the byproduct ozone and may effectively destroy organic molecules.[143]

The photodegradation of ethylene was studied using UV (254 + 185 nm) irradiation and a TiO_2 photocatalyst. It was observed that using UV irradiation considerably improved the photodegradation of ethylene by Chang et al.[144] Jeong et al.[145] studied the degradation of NO_x and toluene by means of UV-C254 + 185 nm/TiO_2 irradiation and reported that NO_x and toluene were effectively degraded to HNO_3 and CO_2, respectively.

The effectiveness of palladium-modified TiO_2 coatings in the simultaneous breakdown of formaldehyde under UV254 + 185 nm illumination was studied by Fu et al.[146] According to the findings, UV 254 + 185 nm photocatalysis has a greater rate of HCHO breakdown and a longer lifetime of photocatalysts than conventional photocatalysis.

6.10 | Conclusions and future opportunities

Since photocatalysis acts at room temperature, creates no secondary pollutants, and has a high removal activity, it is becoming acknowledged as a reliable and healthy treatment approach for VOC elimination. This article summarizes the PCO of VOCs focusing on the differing pollutant types. Significant progress has been made in the development of photocatalysts for air purification. From what was discussed, the following conclusions can be drawn: Humidity will have a significant impact on VOC adsorption, because water molecules and reactants compete for space on the catalytic active sites, and water vapour often inhibits the oxidation of VOCs. To solve these concerns, different approaches have been developed for removing VOCs from humid environment. One was the use of hydrophobic supports to alleviate such inhibition. Selection of the right substrate and reactor type also helps for the optimal removal of VOCs.

The use of noble metal supported catalysts, such as Pt and/or Pd supported catalysts, for VOC removal at relatively low temperatures is the alternative technique. Based on our current knowledge about the limitations of PCO technology in removing VOCs in high humidity environments, we can make some suggestions for future research: these include (1) improving the properties of the nano-catalyst to enhance its photocatalytic activity, adsorption of VOCs, and resistance to deactivation, (2) investigating more reliable and effective photocatalyst materials by combining various techniques including heterojunctions and co-catalysts, and (3) designing new reactor configurations to minimize humidity effect and enhance photocatalytic activity. New techniques for creating catalysts and enhancing their overall performance should therefore be managed and given more focus in the future research.

AUTHOR CONTRIBUTIONS

Girma Masresha: Conceptualization; writing – original draft; writing – review and editing. **S. Anuradha Jabasingh:** Conceptualization; supervision; writing – review and editing. **Shimelis Kebede:** Conceptualization; supervision; writing – review and editing. **David Doo-Arhin:** Conceptualization; supervision. **Mekdim Assefa:** Conceptualization; writing – original draft; writing – review and editing.

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DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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