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Recent progress in air treatment with combined photocatalytic/plasma processes : A review

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30 Abstract

31 Nowadays, air pollution is an increasingly important topic, as environmental
32 regulations require limiting pollutant emissions. This problem requires new
33 techniques to reduce emissions by either improving the current emission control
34 systems and processes or installing new hybrid treatment systems. These are of
35 broad diversity, and every system has its advantages and disadvantages. The
36 tendency is, accordingly, to combine various techniques to achieve more acceptable
37 and suitable treatment. Recent studies suggest that the combination of
38 photocatalysis and plasma in a reactor can offer attractive pollutant treatment
39 efficiency with a minimum of partially oxidized by-products than that of these
40 processes taken separately. However, there is little review of the capability of this
41 pairing to treat different brands of pollutants. Besides, available data concerning
42 reactor design with flows treated 10 to 1000 times higher than those studied at the
43 lab scale. This review paid particular attention to determine the reaction mechanisms
44 in terms of engineering and design of combination reactors (plasma and catalysis).
45 Likewise, we developed the effect of critical parameters such as pollutant load,
46 relative humidity, and flow rate to understand the degradation kinetics of specific
47 pollutants individually by using plasma and photocatalysis. Additionally, this review
48 compares different designs of cold plasma reactors combination with heterogeneous
49 catalysis with special attention on synergistic and antagonistic effects of using
50 plasma and photocatalysis processes at the laboratory, pilot, and industrial scales.
51 Therefore, the elements discussed in this review stick well to the first theme on
52 pollution prevention of the special issue concerning pollution prevention and the
53 application of clean technologies to promote a circular (bio) economy.

54 **Keywords:** Process extrapolation, Air pollution; Non-thermal plasma; photocatalysis;
55 Synergetic effect

56 **1. Introduction**

57 The increasing emission of volatile organic compounds (VOCs) into the
58 atmosphere is a major public health concern today (Zhang, 2018; Tong, 2019; Li et
59 al., 2018). Many studies have shown that exposure to VOCs can be toxic,
60 carcinogenic, mutagenic, or teratogenic (Zhang, 2018; Sun et al., 2021; Tong, 2019;
61 Li et al., 2018). Air pollution causes respiratory illnesses, allergies, cardiopulmonary
62 diseases (e.g., asthma and myocardial infarction), reduced fertility, increased infant
63 mortality, weakened immune system, and several other health hazards in humans.
64 However, the adverse impacts of air pollution on public health depend on the
65 magnitude of pollution, contaminant type, age group of exposed individuals,
66 geographical region, and climatic/weather conditions, to name a few. It should be
67 noted that the elderly individuals, children below 12 years and immunocompromised
68 persons, and people with underlying medical conditions are more acute to illnesses
69 caused by air pollution (Annesi-maesano et al., 2011).

70 In addition to their direct effects on health, many compounds have low odour
71 thresholds in the polluted air and cause a significant nuisance to the exposed
72 personnel and neighbourhood. Eliminating odour nuisance is a complex subject
73 because the principle often lies in treating a low-load high-flow effluent, but is made
74 up of many chemical compounds, each of which contributes to the odorous color.
75 The prominent families are sulfur derivatives (e.g., hydrogen sulfide, mercaptans, and
76 sulfides), nitrogen (e.g., ammonia and amines), and oxygen (e.g., volatile fatty acids,
77 alcohols, aldehydes, and esters).

78 Different techniques for eliminating pollution in gaseous discharges are divided
79 into two main classes : (i) pollutant adsorption or absorption and (ii) pollutant
80 degradation. Adsorption and/or absorption chiefly capture the contaminant from the
81 atmosphere or a specific gas phase by re-encrypting them in another fluid phase (via
82 absorption) or solid support (via adsorption). Pollutants are captured and concerted in
83 one location. Nonetheless, this necessitates an operation of regeneration of the
84 transfer medium for the second cycle. The latter can be realized, for example, by
85 coupling the transfer of pollutants by absorption with a biological treatment unit. On
86 the other hand, the destructor techniques or the oxidation processes, based on
87 chemical reactions to eliminate pollution, are marked by forming sub-intermediate
88 products of H₂O and CO₂. This reaction is carried out under controlled conditions
89 such as those involving high temperatures (e.g., combustion) or mild to moderate
90 temperatures (e.g., cold plasma and catalytic oxidation).

91 This review focuses on (i) comparing different designs of cold plasma
92 combined reactors with heterogeneous catalysis (ii) to the synergistic and
93 antagonistic effects of using plasma and photocatalysis processes at the laboratory,
94 pilot, and industrial-scale (iii) reasons of this synergistic effect. To our knowledge, no
95 review papers approach these aspects with a comprehensive vision at different
96 scales. Furthermore, particular attention has been paid to determining the reaction
97 mechanisms in engineering and combined reactors design (plasma and catalysis).
98 Moreover, we have developed the effect of critical parameters such as pollutant load,
99 relative humidity, and flow rate to understand the degradation kinetics of specific
100 pollutants individually using plasma and photocatalysis.

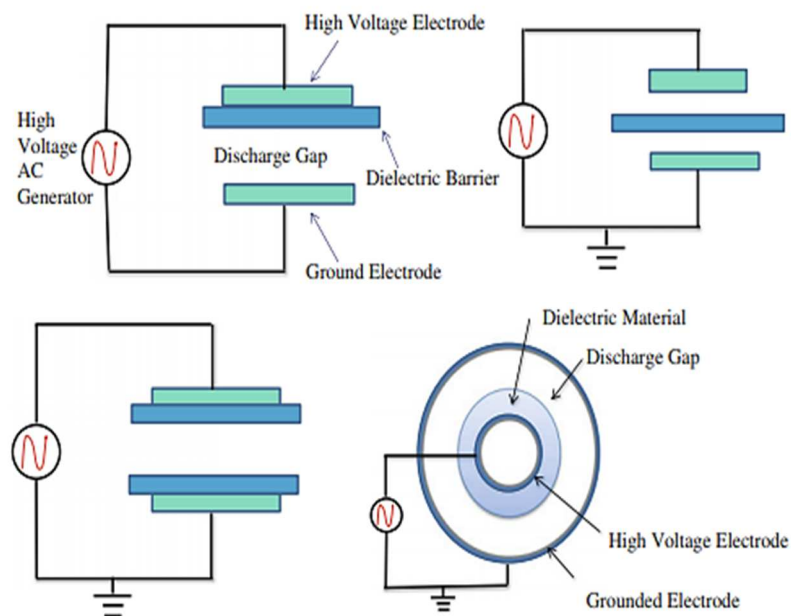
101 **2. Non-thermal plasma technology**

102 A state of matter, plasma, consists of ionizable gases obtained by heat, excitation, or
103 electromagnetic conditions. The plasma is generated through the combination of
104 neutral species, positive ions, and electrons. Plasma in air produces filamentary
105 plasmas, which are excellent sources of radicals and excited species that form a
106 globally oxidizing medium, even at low injected energy. The reactivity of these
107 plasmas is demonstrated here too on a considerable number of organic molecules,
108 i.e, thermal plasma exhibits extremely high equilibrium temperatures. Moreover, the
109 temperature of the electrons can be greater than that of the gas phase, which has an
110 almost ambient temperature (e.g., cold plasma). At high ionization energy, the
111 electrons react directly with the molecules and ions existing, ensuring the formation
112 of excited compounds and radicals that, in turn, allow them to oxidize the pollutants
113 present in the air at room temperature (Tong, 2019). Various categories of discharge
114 are used to generate cold plasmas. Plasma with dielectric barrier discharge (DBD)
115 and corona discharge are commonly applied to mitigate air pollution (Zhang, 2018;
116 Tong, 2019).

117 **(i) Plasma with Corona discharge:** This discharge occurs by applying a
118 difference in high potential (some tens of kV) of two electrodes with
119 variable curvatures. Wire-plane, point-plane, and fill-cylinder type
120 geometries are mainly used for plasma with corona discharge. The curved
121 electrode initiates the electric discharge, which further progresses in the
122 proximity of the planar counter electrode.

123 **(ii) Plasma with dielectric barrier discharge (DBD):** To generate DBD,
124 dielectric barriers such as specific isolating material or supports (Annesi-
125 maesano et al., 2011; D.P. Subedi, U.M. Joshi, 2017), e.g., ceramic,
126 quartz, glass, or Teflon are used to separate the two electrodes. Various

127 configurations are available for DBD, such as coaxial cylinders, plane-
128 plane, plane-wire, and plane-point type. Depending on the type of dielectric
129 barrier and the electrodes' offset arrangement, DBD can be classified into
130 volume DBD plasma or a surface DBD plasma depending on the type of
131 dielectric barrier and the electrodes offset arrangement. In Fig. 1, a non-
132 exhaustive list of some different configurations of cylindrical and planar
133 plasma DBD reactors is provided.



134

135 **Figure 1.** Some configurations of DBD plasma (Zhang, 2018)

136 Ideal and conducive to prevent the generation of undesired and toxic by-
137 products, the pollutants must be oxidized with total mineralization marked by the
138 formation of CO₂ and H₂O. However, on a practical level, plasma reactors allow
139 partial degradation with a significant formation of oxidized by-products, which are
140 sometimes not identified in the treated emanation, likely generating additional
141 problems than the initial pollutant (Zhang, 2018; Durme et al., 2008). Moreover, non-
142 thermal plasma alone has drawbacks regarding energy efficiency and by-product
143 generation presented with poor CO₂ selectivity even at high conversion rates (Zhang,

144 2018). The presence of ozone and nitrogen oxides in the effluents leaving non-
145 thermal plasma air treatment systems constitutes this technology's biggest drawback,
146 which will require post-treatment to eliminate these toxic by-products and more,
147 particularly, ozone. The association of another remediation method and the plasma
148 makes it possible to combine their destruction efficiency and to limit the drawbacks of
149 each process (Jiang et al., 2017; Schiavon et al., 2017).

150 Recently, many investigators have focused on evolving the mineralization to
151 have complete oxidation while combining cold plasma with catalysts (Jiang et al.,
152 2017; Schiavon et al., 2017). Numerous catalysts have been experienced, in the
153 literature, using diverse categories with different pollutants (e.g., ammonia, hydrogen
154 sulfide, and VOCs). Undeniably, the coupling of the cold plasma and the photo-
155 catalyst has shown better performance than the efficiency of each process when
156 taken separately. Consequently, this review explores the synergistic effects of using
157 the combination of photocatalysis and cold plasma techniques for pollutant
158 degradation.

159 **3. Photocatalytic reactors**

160 A semiconductor can absorb light radiation to promote an electron from the
161 valence state to the conduction band while creating a hole (h⁺) in the valence band
162 as a photo-catalyst. Most of the resulting electron-hole (e⁻/h⁺) pairs recombine,
163 whereas a few others can oxidize or reduce the compounds adsorbed on the catalytic
164 surface (Neyts, 2016). These reactions can occur directly in the presence of the
165 specific pollutant or indirectly with the aid of oxygen and water in the atmosphere to
166 yield their radicals such as O₂^{•-} and HO[•] (Saoud et al., 2020 & 2021; Almomani et al.
167 2020). These reactive oxygen species (ROS) are highly selective for oxidation and

168 mineralization of the pollutants (Assadi, 2012; Boyjoo et al., 2017). The most
 169 commonly investigated photo-catalyst is TiO₂ that absorbs the wavelength of
 170 ultraviolet (UV) radiation of less than 388 nm (Elfalleh et al., 2017). Table 1
 171 summarizes some notable studies on eliminating various volatile organic compounds
 172 (VOCs) in a photocatalytic reactor, such as aromatics, aldehydes, and mercaptans.

173 **Table 1. Reactor configuration for pollutant removal**

Target pollutants	Reactor design	References
Acetylene	Continuous reactor	(Thevenet et al., 2014)
Tetrachloroethylene and Decane	Annular reactor	(Monteiro et al., 2015)
Ethanol et Benzene	Batch reactor	(Andryushina and Stroyuk, 2014)
Isopropanol	Tubular reactor	(Hou and Ku, 2013)
Cyclohexane	Fixed bed reactor	(Murcia et al., 2013)
Benzene	Fixed bed reactor	(Zhuang et al., 2014)
Toluene	Continuous and batch reactors	(Pham and Lee, 2015, Almomani et al., 2020)
Acetone and benzene	Batch reactor	(Xie et al., 2015)
Dichloromethane	Batch system combined with (bio)reactors	(Almomani et al., 2021)
Trimethylamine	Annular reactor	(Assadi et al., 2012)
Isovaleraldehyde	Planar and cylindrical reactor	(Assadi et al., 2014c; Palau et al., 2015)
Formaldehyde	Fixed bed reactor	(Han et al., 2013)
Butyraldehyde	Planar reactor	(Ghaida et al., 2016)
Dimethyl disulfide	Planar reactor Cylindrical reactor	(Chuang and Luo, 2013; Saoud et al., 2017)
Dimethyl sulfide	Annular reactor	(Lin et al., 2016)
2, 3 Butadione	Planar reactor with luminous	Saoud et al., 2021

	textiles	
NO_x	Tubular reactor, Fixed bed reactor Rectangular reactor	Hu et al., 2015; Ma et al., 2015; Szatmáry et al., 2014)
	Tubular reactor	(Alonso-tellez et al., 2014)
H ₂ S	Planar reactor	(Portela et al., 2010)
SO ₂	Fixed bed reactor	(Liu et al., 2014)
NH ₃ & H ₂ S	Rectangular reactor	(Maxime and Amine, 2014)

174

175 Some inorganic pollutants such as ammonia, NO_x, SO_x, CO, and H₂S, mainly from
 176 the industrial sector, are also eliminated by the photocatalysis reactor. Nevertheless,
 177 compared to previous studies (Table 1), these ranges of molecules are less studied.

178 An advantage of heterogeneous photocatalysis is its ability to mineralize a
 179 wide range of organic compounds in water and air. Several researchers have widely
 180 studied its efficiency in degrading different molecules (Assadi, 2012; Boyjoo et al.,
 181 2017; Saoud et al., 2020). The most commonly studied families of organic
 182 compounds are chlorinated compounds (Monteiro et al., 2015), phenols (Bechec et
 183 al., 2015; Murcia et al., 2013; Pham and Lee, 2015; Xie et al., 2015; Zhuang et al.,
 184 2014), nitrogen compounds (Assadi et al., 2012) and sulfur compounds (Chuang and
 185 Luo, 2013; Lin et al., 2016; Saoud et al., 2017). The photocatalytic reaction can be
 186 activated by photon irradiation and operate at room temperature and atmospheric
 187 pressure with reasonable installation requirements (Andryushina and Stroyuk, 2014;
 188 Assadi et al., 2012, 2014c; Bechec et al., 2015; Chuang and Luo, 2013; Ghaida et
 189 al., 2016; Han et al., 2013; Hou and Ku, 2013; Lin et al., 2016; Monteiro et al., 2015;
 190 Murcia et al., 2013; Palau et al., 2015; Pham and Lee, 2015; Saoud et al., 2017;
 191 Thevenet et al., 2014; Xie et al., 2015; Zhuang et al., 2014). However, the

192 advantages of photocatalysis are hampered by some significant drawbacks. The
193 photo-catalyst is only activated by UV irradiation, limiting its effectiveness in the
194 visible and interior applications (Palau et al., 2015). The recombination of
195 photogenerated charges between their formation and diffusion on the semiconductor
196 surface can also decrease the process efficiency.

197 Abou Saoud et al. confirmed the poisoning of photocatalysis for sulfur and
198 nitrogen pollutants at the pilot-scale (Saoud et al., 2017). The authors showed that,
199 after many photocatalysis self-regeneration procedures, the photocatalytic efficiency
200 reduced considerably (Saoud et al., 2017). Therefore, a poisoning phenomenon may
201 be evident during a continuous and prolonged photocatalytic oxidation process. To
202 remedy these problems and increase photocatalytic activity, a combination of photo-
203 catalyst and other processes such as non-thermal plasma could be helpful (Ramaraju
204 and Subrahmanyam, 2014; Dou et al. 2016; Mei et al. 2016; Assadi et al. 2016;
205 Aouadi et al. 2016; Maciucă et al. 2012; Karuppiah et al. 2013; Huang et al., 2010; Jo
206 et al., 2016; Karuppiah et al. 2014; Assadi et al. 2015; Pham Huu et al. 2017).

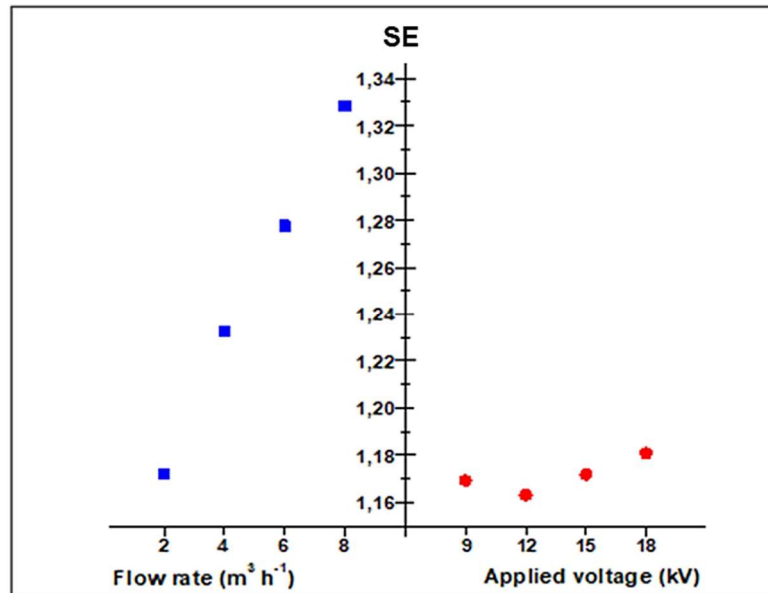
207 **4. Plasma/photocatalytic hybrid systems**

208 Based on each process considered alone (plasma or photocatalysis), TiO₂ is a
209 catalyst capable of oxidizing many organic molecules with excellent selectivity to
210 CO₂, thanks to its quantum efficiency and the redox potentials of its valence and
211 conduction bands. In recent years, many studies combining the non-thermal plasma
212 (e.g., dielectric barrier discharge - DBD, corona discharge, and surface discharge)
213 and catalysts are carried out on different types of effluents, thus highlighting the
214 existence of a synergistic effect due to the coupling process (Karuppiah et al. 2014;
215 Assadi et al. 2015; Pham Huu et al. 2017). TiO₂ is a catalyst capable of oxidizing

216 many organic molecules into CO₂ with excellent selectivity. Plasma DBD in air
217 produces ionized filaments that are excellent sources of radicals and excited species
218 that form a globally oxidizing environment even at room temperature and low input
219 energy (Saoud et al., 2017). Non-thermal plasma presents remarkable performances
220 (e.g., conversion efficiency and energy cost) for low polluted effluents (Saoud et al.,
221 2017; Dou et al. 2016; Mei et al. 2016). The major challenge with the plasma is to
222 avoid the formation of oxidation by-products and to pursue the reactions towards total
223 mineralization (Zhang, 2018; Trinh and Mok 2015a; Liu et al., 2014; Maxime and
224 Amine, 2014). TiO₂, due to its adsorption capacity, tends to maintain the by-products
225 in an adsorbed state, thus exposing them to the long-lived radicals to achieve their
226 full degradation (Trinh and Mok 2015a). It is interesting to correct these types of
227 plasma defects by supplying TiO₂ (Schiavon et al., 2017).

228 Considering the ability of photocatalysis to reach a high mineralization rate,
229 various investigations have been performed combining the later and non-thermal
230 plasma, to heighten the elimination with consistently complete mineralization. A few
231 studies in this area have recently shown the application of a broad set of reactor
232 configurations permitting the association of the plasma and photocatalytic processes
233 for pollutant denaturation. The different reactor configurations reported in the
234 literature are summarized in this section. Some recent studies (Saoud et al. 2019;
235 Patil et al. 2016; Jo et al. 2016; Nguyen Dinh et al. 2015; Li et al., 2015; Ramaraju
236 and Subrahmanyam, 2014; Saoud et al., 2017; Trinh and Mok, 2015a) on the
237 catalyst performance and its association with the plasma discharge have remarkable
238 impacts on the rate of VOCs elimination and the mineralization effectiveness (Zadi et
239 al., 2018). Nevertheless, the in-situ characterization of these hybrid processes with
240 an active plasma is rarely investigated due to the convoluted experimental reactor

241 configurations to associate the plasma, performance monitoring tools and analytical
242 facilities (Figure 2)



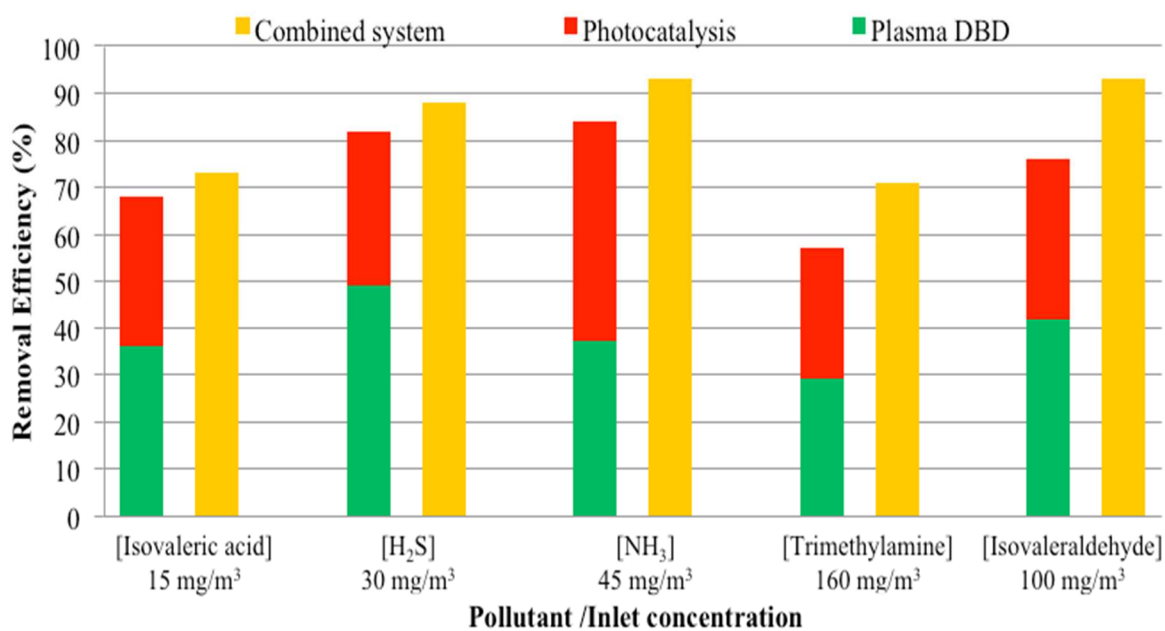
243

244 **Figure 2:** Example of Variation of synergetic effect (SE) with flow rate (at V= 15 kV)
245 and applied voltage (at Q= 2 m³ h⁻¹) using three processes (Zadi et al., 2018)

246 4.1 Design of hybrid plasma/photocatalytic systems

247 Several investigations show that the interesting reactors configurations about
248 plasma combined with photocatalysis were about DBD (Schiavon et al. 2017; Huang
249 et al., 2010; Jo et al., 2016; Ramaraju and Subrahmanyam, 2014; Zhu et al., 2015a;
250 Shi et al., 2016; Jiang et al., 2017a; Chen et al., 2016; Jo et al., 2016; Bahria et al.,
251 2016) and corona discharge (Shirjana et al 2020; Nan et al 2016; Changming et al
252 2019; Wan et al. 2011; Mikhail et al. 2016; Fada et al. 2015; Sultana et al. 2019 ;
253 Vandenbroucke et al. 2016; Nguyen Dinh et al. 2015). Moreover, some authors have
254 extensively documented that DBD release is relatively more effective compared to
255 corona release because of the uniformity in plasma discharge on the catalyst surface
256 (Ramaraju et al., 2013). Several configurations are promising to provide a solution to

257 this problem. The coupling between plasma by dielectric barrier discharge (DBD) and
 258 TiO₂/UV photocatalysis reveals exciting configurations in terms of synergy to destroy
 259 VOCs with low energy consumption (Aouadi et al., 2016). Recent work on model
 260 compounds indicates that this association needs to be explored and developed.
 261 Associating a photo-catalyst in a DBD that produces filamentary plasmas in the air,
 262 which are excellent sources of radicals and excited species, will make it possible to
 263 intensify the oxidizing environment with the same injected energies. The reactivity of
 264 these systems has been demonstrated on a large number of organic molecules (Fig.
 265 3) (Assadi et al. 2018; Chen et al. 2016; Karuppiah et al. 2014).

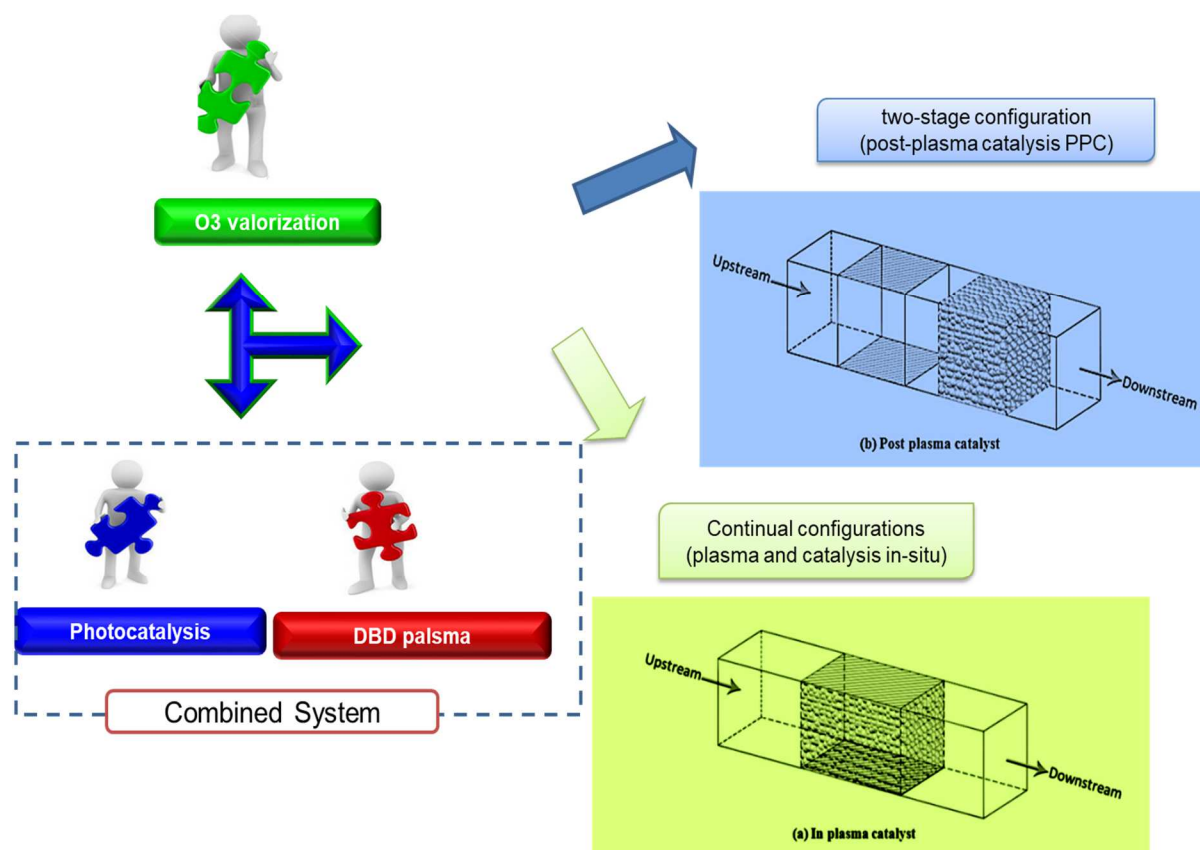


266
 267 **Figure 3:** Example of the synergistic effects of plasma-photocatalysis for the
 268 degradation of isovaleric acid, hydrogen sulfide, ammonia, trimethylamine and
 269 isovaleraldehyde (Assadi, 2012)

270 4.2 Catalyst type and its function in plasma discharge

271 The catalysts have been positioned in two important ways to elucidate the
 272 functionality of different active species generated by plasma upon catalyst activation.

273 Firstly, the catalyst is introduced into the discharge zone (in-plasma catalysis, IPC)
274 (Patil et al. 2016; Jo et al. 2016; Xu et al. 2016; Chen et al. 2016; Pham Huu et al.
275 2017; Zhu et al. 2015a). Secondly, the gas phase moves to the discharge zone
276 before encountering the catalyst, which is then installed downstream (post-plasma
277 catalysis, PPC) (Assadi et al. 2018; Huang et al., 2010; Nguyen Dinh et al. 2015; Li et
278 al. 2015; Vandenbroucke et al. 2016). According to some reports, the IPC configurations
279 demonstrate better performance because of the transitory components on the
280 catalyst surface (Fig. 4). However, the configuration enactment is a function of the
281 catalyst type and VOCs in the gas stream. Both the configurations have the flexibility
282 to load the catalyst within the reactor, especially in a packed bed reactor (PBR) or are
283 positioned only on its surface (Chen et al. 2016; Huang et al., 2010; Saoud et al.,
284 2019; Mei et al. 2016; Li et al. 2015; Jo et al. 2016). However, studies have
285 presented a configuration with an inner electrode covered with a thin TiO₂ film
286 (Subrahmanyam, 2009; Subrahmanyam et al., 2007).



287

288 **Figure 4:** Typical process flow diagrams and description of the main functions of
 289 Post Plasma Catalyst (PPC) and In Plasma Catalyst (IPC) system (Assadi, 2012)

290 In most reactor configurations with packed beads, the catalysts are deposited
 291 on glass beads, which also play the role of a dielectric barrier of the plasma reactor.
 292 Furthermore, TiO₂ can be used in a pure state (Guaitella et al., 2005; Rousseau et
 293 al., 2005) or doped on a support such as silica gel (Futamura et al., 2004), Al₂O₃
 294 (Kang et al., 2006; Lee et al., 2004) or other porous materials. It is also reported that
 295 TiO₂ can be deposited on Ni/Al₂O₃ foam (Huang and Ye, 2009; Huang et al., 2010),
 296 activated carbon (Sun et al., 2007; Taranto et al., 2007), and zeolite of ZSM-5
 297 monolith and Raschig rings (Annesi-maesano et al., 2011). A powdered form of the
 298 catalyst can be used to cover the surface of the reactor (Futamura et al., 2004; Sano
 299 et al., 2006). Furthermore, the catalyst can also be doped onto a support such as
 300 glass fibers (Guaitella et al., 2008; Thevenet et al., 2008, 2007) or activated carbon

301 material (Hou and Ku, 2013). It is interesting to note that a block of $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{SiO}_2$
 302 placed in the reactor has also been used (Durme et al., 2007), as presented in Table
 303 2. Despite their photocatalytic activity, the porosity of these materials has compelling
 304 adsorption capacities

305 **Table 2.** Different catalysts used in the combined systems.

Target pollutant	Reactor design	Catalyst and positions	References
Toluene	DBD	Co-MCM-41 (IPC)	(Xu et al., 2016)
	Photocatalytic DBD	TiO_2/SMF (IPC)	(Chen et al., 2016)
	Pulsed DBD	$\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ (IPC)	(Huu et al., 2017)
Formaldehyde	Packed bed DBD	NaNO_2 (IPC)	(Liang et al., 2010)
	DBD	Cu/CeO_2 (IPC)	(Zhu et al., 2015a.)
	Packed bed DBD	Ag/CeO_2 (IPC)	(Huixian and Zengfeng, 2009)
	Corona discharge	$\text{MnO}_x/\text{Al}_2\text{O}_3$ (PPC)	(Wan et al., 2011)
Benzene	DBD	$\text{TiO}_2/\text{MnO}_x/\text{SMF}$ (IPC)	(Linga et al., 2014)
	Packed bed DBD	Ag/TiO_2 (IPC)	(Kim et al., 2005)
	Packed bed DBD	$\text{Ag}_0.9\text{Ce}_0.1/\gamma\text{-Al}_2\text{O}_3$ (IPC)	(Jiang et al., 2015)
Trichloroethylene	Corona discharge	Pd/LaMnO_3 (PPC)	(Vandenbroucke et al., 2016)
	Corona discharge	CeMn_4 (PPC)	(Dinh et al., 2015)
	DBD	Au-mesoporous silica (PPC)	(Magureanu et al., 2007)
Propionic acid and benzene	DBD	$\text{SiO}_2\text{-TiO}_2$ (IPC)	(Zadi et al., 2020)
Mixture VOCs	DBD	MnO_x/SMF (IPC)	(Ramaraju and Subrahmanyam, 2014)
Mixture VOCs	DBD	$\text{AgO}_x/\text{MnO}_x/\text{SMF}$ (IPC)	(Karuppiyah et al., 2013)
Mixture VOCs	Corona discharge	$\text{MnO}_x/\text{Al}_2\text{O}_3$ (PPC)	(Wan et al., 2011)

306

307 4.3 Plasma/photocatalytic operation mode

308 The plasma DBD reactors combined with photo-catalyst have been tested for
309 the removal of numerous VOCs and NO_x. Nonetheless, we are limited in our review
310 to present only the VOCs tested in lab-scale and pilot-scale operations. For instance,
311 the central part of the investigations has been devoted to the habitually available
312 VOCs such as toluene (Jo et al., 2016; Sun et al., 2007), Butadione (Saoud et al.,
313 2020) acetylene (Guaitella et al., 2008), benzene (Futamura et al., 2004; Lee et al.,
314 2004; Zhu et al., 2009), chloroform (Zadi et al., 2020), fatty acids (Zadi et al. 2018)
315 and butyraldehyde (Saoud et al., 2019).

316 TiO₂ photo-catalyst is typically activated by using UV radiation at wavelengths
317 typically less than 388 nm. This fact requires the arrangement of UV lamps outside
318 the photocatalytic reactors for ensuring uniform illumination and activation of the
319 photo-catalyst (Assadi et al., 2018; Jo et al., 2016; Ramaraju and Subrahmanyam,
320 2014). The plasma-driven photocatalysis UV light is widely utilized in hybrid plasma-
321 photocatalytic systems (Sivachandiran et al., 2013; Shi et al., 2016; Palau et al.,
322 2015; Subrahmanyam, 2009; Saoud et al., 2018). The ability of plasma radiation for
323 TiO₂ activation is discussed below.

324 (Rousseau et al., 2005) studied the combination of TiO₂ and a low-pressure
325 plasma discharge to oxid acetylene using a batch reactor. In this study, the authors
326 presented the synergistic interactions between the volumetric plasma discharge and
327 an externally illuminated TiO₂ catalyst. (Thevenet et al., 2008, 2007) studied the
328 elimination of acetylene in a recirculation reactor loaded with a TiO₂/SiO₂ catalyst.
329 The authors reported that the plasma discharge on porous catalytic material results in
330 more CO and oxidized components. Nonetheless, in the presence of an externally
331 illuminated UV lamp, they noted an increase in the acetylene removal potency with
332 an increase in the mineralization efficiency (Thevenet et al., 2008, 2007).

333 Subsequently, it can be deduced that, regardless of the operational mode,
334 laboratory-scale experiments have shown that a hybrid photocatalytic plasma
335 discharge can increase the elimination performance of VOCs due to the existence of
336 synergistic effects (Thevenet et al., 2008, 2007).

337 Some key factors that lead to the synergetic effects are mentioned below:

338 (i) The by-products attached to the photo-catalyst surface (especially TiO₂)
339 can be desorbed using the plasma for mineralization (Assadi et al., 2014c;
340 Ghaida et al., 2016; Palau et al., 2015; Saoud et al., 2019; Zadi et al.,
341 2020).

342 (ii) TiO₂ activation occurs through the plasma ion bombardment and
343 generation of electron-hole pairs (Assadi et al., 2018, 2014c, 2014b).

344 (iii) Plasma can generate ionic products, radicals, high-energy electrons to
345 promote the mass transfer of the pollutants from the bulk phase to the solid
346 phase (Ghaida et al., 2016).

347 **5. Plasma discharge and photo-catalyst combination: actives species and** 348 **reaction mechanism**

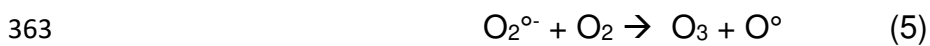
349 **5.1 Plasma discharge**

350 The electrons formed can collide directly with the existing molecules when a
351 plasma discharge occurs in the air (Annesi-maesano et al., 2011; Visscher et al.,
352 2008; Wang and Chen, 2009). This collision reaction results from different reactions
353 patterns like dissociation or excitation and reactive species (e.g., O[°], O₂[°] and N₂[°]).
354 While atomic oxygen O[°] is short-lived for lower than a millisecond (Allegraud, 2009),
355 N₂[°] and O₂[°] can be reactive and short-lived for about a few microseconds.





359 It is important to note that these unstable ROS and RNS rapidly undergo
360 reactions for re-institution to their ground states. They could also generate some
361 long-lived species like ozone (Futamura et al., 2004).



365 ROS can degenerate with the generation of intermediate by-products followed by
366 their oxidation. Besides, Eq. (7) illustrates the complete oxidation of a VOC, where
367 the intermediate products are CO and other VOCs with a carbon number less than
368 that in P.



370 For conventional VOCs such as the BTEX family (benzene, toluene,
371 ethylbenzene and xylene), the elimination of these pollutants by applying ozone is
372 insignificant in contrast to the oxidation by O° (Zadi et al., 2018). Moreover, cold
373 plasma makes the reaction possible between VOCs and electrons. However, the
374 treatment of acetylene by plasma is insignificant (Rousseau et al., 2005).

375 (Chang and Lin, 2005) reported that a reactor filled with glass beads led to an
376 increase in the removal efficiency of toluene and acetone when compared to that of
377 the empty reactor. Regardless of the residence time due to the glass beads packing

378 inside the reactor, the formation of plasma on their entire surface efficiently leads to
379 the VOCs denaturation.

380 The mineralization (CO₂ selectivity) may not result from the use of glass
381 beads. A tenuous rise in the selectivity of CO₂ has been noticed with neutral packing
382 in the case of acetone treatment (Chang and Lin, 2005). It has been suggested that
383 the presence of an oxygen atom in the pollutant structure would promote the
384 formation of CO and CO₂. It should be noted that the plasma can form specific long-
385 lived molecules, such as NO, N₂O, and NO₂, as shown in Eq. (8) to Eq. (12).



391 As shown in Eq. (11) and Eq. (12), a rise in NO_x concentration, as well as that
392 of NO and NO₂ as a result of catalytic reactions, can lead to a reduction in the levels
393 of ozone concentration (Annesi-maesano et al., 2011).

394 **5.2. Plasma and photocatalysis (without external UV light)**

395 An extrinsic UV light illumination on the photocatalytic surface is responsible
396 for the formation of electron-hole pairs. Under these conditions, the material does not
397 have any photo-catalytic activity to participate in the oxidation of the pollutant.
398 Nevertheless, other reactions should not be disregarded that could considerably
399 involve the VOC oxidation process. Under certain conditions, even without being

400 activated, the photo-catalyst can play the role of an adsorbent of the pollutant present
401 in the gas phase, mainly when carried on porous supports with a very high specific
402 surface area (Guaitella et al., 2005). The pollutant adsorption on the photo-catalyst
403 surface makes it possible to increase its adequate residence time in the reactor,
404 which argues in favour of increasing the pollutant-ROS contact produced by the
405 plasma (Guaitella et al., 2008; Thevenet et al., 2007).

406 Furthermore, the deposition of the photo-catalyst in the plasma zone (IPC)
407 can lead to oxidation being intervened by the ROS. The short-lived components
408 could recombine before reaching the plasma downstream (PPC) where the catalyst is
409 loaded. Consequently, ROS such as ozone with a relatively long lifetime can react
410 with the pollutant adsorbed on the photo-catalyst surface.

411 It is well known that the loading of TiO_2 in the discharge zone illuminated with an
412 external UV can increase the generation of ozone at the reactor exhaust. This
413 phenomenon is because TiO_2 furnishes additional surface area in the reactor as
414 indicated in Eq. (4) (Allegraud, 2009).

415 **5.3 Plasma and photocatalysis (with external UV light)**

416 External UV illumination is required outside the reactor to ensure proper
417 activation of TiO_2 for processes involving photocatalysis and cold plasma. As
418 indicated in Eq. (6), plasma discharge could emit photons for activating the photo-
419 catalyst. The energy necessary to yield electron-hole pairs on the photo-catalyst
420 surface could be directly provided by the reaction of nitrogen radical with the photo-
421 catalyst, i.e. N_2° with TiO_2 (Durme et al., 2007). Several authors have proposed that it
422 is theoretically possible to activate TiO_2 by UVs of the plasma (Saoud et al., 2019;
423 Subrahmanyam, 2009; Zadi et al., 2018). Some studies suggest that the activation by

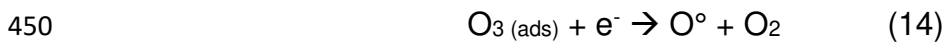
424 an external UV lamp generates important photocatalytic activities (Jo et al., 2016;
425 Subrahmanyam, 2009; Subrahmanyam et al., 2007; Sun et al., 2007; Zhu et al.,
426 2009), while a few other studies suggest otherwise (Bao et al., 2007; Futamura et al.,
427 2004; Guaitella et al., 2008; Rousseau et al., 2005; Sano et al., 2006; Thevenet et
428 al., 2007). It is, therefore, ambiguous to ascertain the reason for these paradoxical
429 results.

430 It should be noted that after the activation of the photo-catalyst by an external
431 UV light source, the reactions independent of light are also conceivable during the
432 plasma discharge. Moreover, an external source of UV light could also lead to
433 photolysis to denature the adsorbed VOCs and ozone into ROS provided the emitted
434 radiation has a wavelength of 200-308 nm, as indicated in Eq. (13) (Huang and Ye,
435 2009).

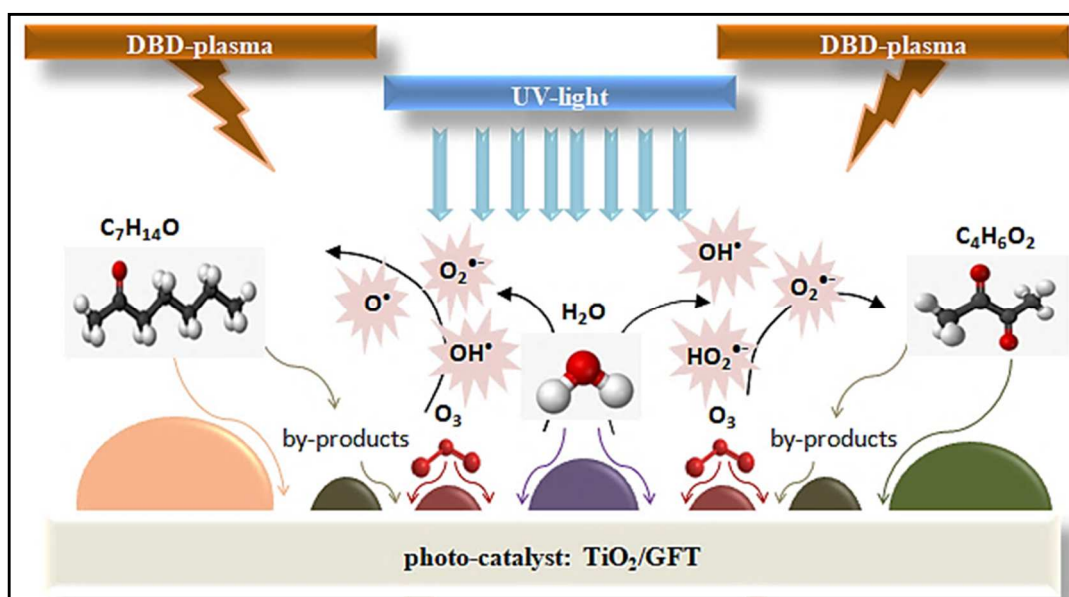


437 As mentioned previously, the generation of electron-hole pairs on the photo-
438 catalyst surface area is due to the irradiation of the photo-catalyst. Subsequently,
439 along with the photo-catalyst, the electron-hole pairs and the species produced by
440 the plasma discharge react with the adsorbed pollutant leading to its denaturation.
441 Atomic oxygen is a resilient oxidizing agent responsible for VOC decomposition
442 (Durme et al., 2008; Ghaida et al., 2016; Subrahmanyam et al., 2010; Trinh and Mok,
443 2015; Visscher et al., 2008). It is produced by the degradation of ozone adsorbed on
444 the photo-catalyst surface (TiO₂). This synergistic effect is evident with the
445 association of plasma discharge, a suitable photo-catalyst, and an external UV
446 illumination, preferably in an IPC configuration (Assadi et al., 2014b; Saoud et al.,
447 2017; Zadi et al., 2018). This result indicated that the effectiveness of pollutant

448 degradation by an individual process is relatively lower than that of the hybrid
 449 process (Assadi et al., 2017; Saoud et al., 2017; Zadi et al., 2020).



451 As previously mentioned in Eq. (14), the ozone decomposition on the photo-
 452 catalyst surface aids in the decay of its residual concentration in a hybrid process
 453 involving plasma discharge and the UV-activated photo-catalyst. Besides, the
 454 pollutant removal rate increase is observed because of the O° species reaction with
 455 the adsorbed VOCs (Assadi et al., 2014b; Saoud et al., 2017; Zadi et al., 2020).
 456 Since the only reactive component inside the photocatalytic zone is ozone, PPC
 457 reactors make the former reaction more apparent. In contrast, plasma discharge in
 458 the IPC reactors facilitate the formation of short-lived species in its photocatalytic
 459 zone. In the next step, the short-lived species are adsorbed on the surface of the
 460 photo-catalyst for selective reaction with pollutants present in the gas phase (Durme
 461 et al., 2007). Such type of reactor configurations makes ozone dissociation relatively
 462 insignificant (Fig. 5).



463

464 **Figure 5.** A suggested mechanism for ROS interaction with pollutants under
465 simultaneous DBD-plasma/photocatalysis (TiO₂ deposited on glass fiber tissue (GFT))
466 (Saoud et al., 2020).

467 The coupling of plasma discharge and the photo-catalyst could favor both the
468 conversion/decomposition of the pollutant and the mineralization of the by-products
469 compared to each process performed separately (Futamura et al., 2004; Guaitella et
470 al., 2008; Lee et al., 2004; Saoud et al., 2018, 2017; Subrahmanyam, 2009). For
471 example, a packed bed of TiO₂, in the post-discharge zone, conducts more
472 significant mineralization than any packing material of a similar size (Chang and Lin,
473 2005). Hence, a photo-catalyst is responsible for mineralization instead of porous
474 material. The hybrid process also reduces the type and amount of intermediate
475 degradation products and by-products (Sun et al., 2007).

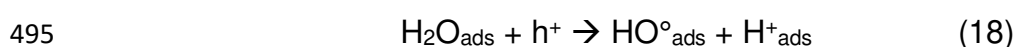
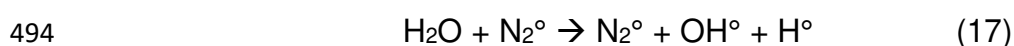
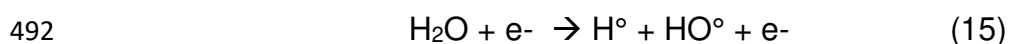
476 Some authors have confirmed that plasma has an appealing impact on photo-
477 catalyst life. TiO₂ is gradually poisoned in the photocatalysis process alone
478 (Futamura et al., 2004). This fact is because of the non-reversible adsorption of
479 HNO₃ (Durme et al., 2007) and H₂SO₄ (Portela et al., 2007). A plasma discharge can
480 regenerate the photocatalytic activity by uptaking a portion of the compounds (e.g.,
481 sulfur-containing species) responsible for the poisoning of photo-catalyst and loss of
482 its effectiveness (Futamura et al., 2004; Huang and Ye, 2009; Sun et al., 2007).

483 **6. Effect of some key parameters on VOCs removal efficiency**

484 **6.1 Relative Humidity (RH) effect**

485 We note that all the mechanisms mentioned above are compatible with
486 plasma DBD beneath dry air. Nevertheless, the water molecule is naturally
487 accompanying pollutants in the air. Water vapour present in the system alters the
488 ROS and RNS resulting from plasma discharge substantially. This phenomenon

489 happens when it reacts with the electrons liberated from plasma discharge or with
490 some active species (D.P. Subedi, U.M. Joshi, 2017) originating from the
491 photocatalytic reactions (Abidi et al., 2020; Saoud et al., 2020).



496 It should be noticed that the HO[°] radical produced by the above reactions is a
497 more potent oxidant than those investigated so far (Portela et al., 2007). For
498 example, the kinetic constant of toluene oxidation by HO[°] is greater than that by O[°].
499 Hence, the degradation aided by ozone is trivial compared to that with HO[°] radicals
500 (Durme et al., 2007; Maxime and Amine, 2014). Besides, HO[°] also stabilizes the
501 activity of a photo-catalyst by decelerating its deactivation (Thevenet et al., 2008).
502 Even if humidity considerably increased the efficiency of plasma photocatalysis, few
503 studies have shown adverse effects. On the one hand, studies proposed that it
504 reduces the discharge in the case of gas-phase release. Thus, the energy and
505 concentration of the electrons, then the ROS formed by the plasma (D.P. Subedi,
506 U.M. Joshi, 2017; Durme et al., 2007; Ye and Tian, 2006). Besides, upon its
507 adsorption at higher amounts, it can create a layer preventing the access to
508 pollutants and reagents, thus reducing the efficacy of pollutant decomposition by the
509 photo-catalyst (D.P. Subedi, U.M. Joshi, 2017; Durme et al., 2007).

510 Relative humidity of the gas phase can influence the degradation of pollutants
511 and the harmful effects associated with the recombination of free radicals. However,

512 this depends mainly on the operating conditions, such as the co-concentration of the
513 contaminant. The occurrence of HO° radicals depends on the concentration of water
514 in the reaction; hence, the degradation rate of pollutants can rise with the
515 concentration of water (Huang and Ye, 2009). In contrast, an increase in the relative
516 humidity is found to lower the rate of pollutant conversion or decomposition
517 regardless of the coupling configuration (i.e., IPC or PPC type reactors) (Durme et
518 al., 2007; Thevenet et al., 2008). Some studies have confirmed that HO° radicals
519 promote the conversion of CO into CO₂, thus leading to a higher mineralization rate
520 at greater water concentrations (Kim et al., 2015; Ye and Tian, 2006). However, an
521 inadequate fraction of water can inhibit the photo-catalyst, thereby reducing its
522 selectivity for CO₂ mineralization (Huang and Ye, 2009).

523 The existence of water vapor, particularly in PPC reactors, can reduce ozone
524 emissions at the reactor outlet (Durme et al., 2007). However, the same study
525 (Durme et al., 2007) reported that, at a humidity below 30%, the ozone concentration
526 is unaffected in the IPC system compared to the configuration of plasma alone.
527 Besides, they have shown that humidity diminishes the emanation of NO₂ and,
528 afterword, raises the catalyst service life (Durme et al., 2007).

529 **6.2 Effect of the applied voltage**

530 Increasing the input energy density can lead to an increase in the discharge of
531 the plasma and a rise in the concentration of released electrons and their
532 corresponding energies (Lu et al., 2014). Subsequently, more collisions occur with
533 the other species/pollutants existing. Consequently, the concentrations of ROS, like
534 the radicals O° and HO°, are also increased, principally in charge of the degradation
535 and mineralization of pollutants (Costa et al., 2016; Visscher et al., 2008). Therefore,

536 it is compelling to indicate that the feeding energy density is not affected by the
 537 association of plasma discharge and a photo-catalyst under steady process
 538 parameters (Bao et al., 2007; Chang and Lin, 2005; Durme et al., 2007; Futamura et
 539 al., 2004; Guaitella et al., 2008; Huang et al., 2010; Subrahmanyam, 2009; Zhu et al.,
 540 2009). Nonetheless, CO₂ selectivity can elevate with amplification in energy density
 541 (Futamura et al., 2004; Lee et al., 2004; Maxime and Amine, 2014; Sano et al., 2006;
 542 Subrahmanyam, 2009; Subrahmanyam et al., 2007). Additionally, it should be
 543 mentioned that the concentrations of ozone (Bao et al., 2007; Durme et al., 2007;
 544 Huang and Ye, 2009; Huang et al., 2010; Maxime and Amine, 2014) and NO₂
 545 (Durme et al., 2007), at the reactor exit behave proportionally as well as the input
 546 energy. Thus, an optimal feeding energy density and an appropriate photo-catalyst
 547 are essential to enhance the pollutant decomposition and reduce the concentrations
 548 of ozone and NO_x at the reactor outlet.

549 **6.3 Other significant parameters**

550 Table 3 summarizes the different effects of other keys parameters on plasma
 551 combined with photocatalysis.

552 **Table 3.** Impacts of widely studied parameters for the decomposition of pollutants in
 553 the hybrid plasma-photocatalytic process

	Flow rate	Pollutant concentration	Amount of photo-catalyst	Level of oxygen in the gas phase
Elimination efficiency	(-) (D.P. Subedi, U.M. Joshi, 2017;	(-)	(+)	(-/+ Optimum 1-5%
Selectivity of CO ₂	Thevenet et	(D.P. Subedi, U.M. Joshi,	(Monteiro et al., 2015)	(D.P. Subedi, U.M. Joshi, 2017)

554

555 As shown in Table 3, increasing the effluent gas flow and the concentration of
556 pollutants decreases the elimination efficacy and the CO₂ selectivity. Therefore, more
557 research is necessary for optimizing process parameters and operating conditions.

558 As explained previously, a hybrid of the plasma and photocatalytic processes
559 can surpass the efficacy of the two processes assessed individually. The coupling of
560 both processes has many synergistic effects.

561 Coupling both the processes promotes pollutant decomposition and
562 mineralization while diminishing the chances of undesirable by-product formation.
563 Such mechanisms remain less understood; hence the inferences from various
564 studies available in the literature in certain aspects are contradictory owing to a wide
565 variety of the investigated systems and the involved process variables.

566 Owing to these reasons, the comparison of the reactors performance
567 considered in proportion to their configurations is not possible, which given their great
568 diversity, would have been interesting. Nevertheless, coupling plasma and
569 photocatalytic processes seem to be promising, except for the deficiency of available
570 data in the literature, concerning pollutants other than VOCs.

571 **7. Hybrid plasma/photo-catalytic reactor design**

572 Traditionally, the studies concerning dielectric barrier discharges involved
573 inserting materials (e.g., BaTiO₃) having a high relative permittivity into the plasma
574 discharge zone to enhance their electrical properties. The electric field at the
575 circumference is strengthened through micro-discharges upon the particles of matter

576 polarization at the plasma discharge zone. (Ray and Subrahmanyam, 2016) have
577 proposed that the properties of the material incorporated into the plasma reactor
578 enhance both the pollutant decomposition and the selectivity of CO₂. The changes
579 also influence the increased effectiveness of the plasma reactor in the operating
580 conditions leading to plasma discharge and material characteristics. A coaxial
581 cylindrical reactor is a commonly used reactor, both in the laboratory- and industrial-
582 scale processes. This characteristic is a type of PBR reactor in which the discharge
583 space is packed with pellets of catalysts (Assadi, 2012).

584 (Holzer et al., 2002) have studied the oxidation of VOCs using an
585 amalgamation of heterogeneous catalysis and non-thermal plasma discharge. The
586 study demonstrated the benefits of adding a porous material with non-photocatalytic
587 activity to a dielectric barrier discharge. The accessibility of short-lived active
588 components generated from plasma discharge was feasible because of their diffusion
589 into the porous structure of σ -alumina and silica gel. Introduction of photocatalytic
590 materials (e.g., TiO₂, ZnO, and SnO₂) in the plasma discharges can offer several
591 benefits of the higher specific surface area and potentially reactive compounds
592 (Holzer et al., 2002; Li et al., 2001). (Li et al., 2001) observed that TiO₂ addition into a
593 corona discharge considerably enhanced toluene denaturation. The authors
594 suggested a possible surface activation by the active component. However, the
595 approach of photocatalytic activation by UV rays generated in the corona discharge is
596 required to be well understood.

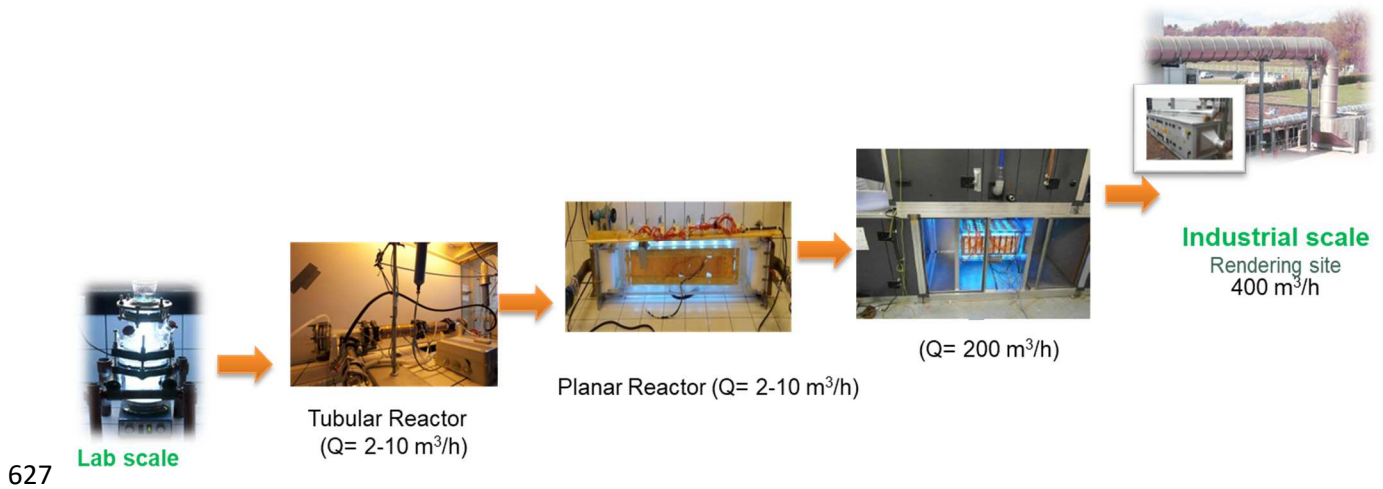
597 (Kang et al., 2002) reported a transition in the decomposition rate for toluene
598 under a pulsed oxygen discharge from 40% to 70%. This result was possible upon
599 loading TiO₂ on a glass substrate through a sol-gel technique for a plasma discharge.
600 The authors also reported that the rise in the pollutant conversion rate is a function of

601 the voltage employed to each pulse. However, the interaction between the two
602 processes is not well understood.

603 Some notable findings of the hybrid plasma/photocatalytic processes for VOC
604 removal are summarized in Table 4. (Andersen et al., 2013) reported eliminating
605 methanol, styrene, and butyl acetate in the shale oil treatment plant exhausts and a
606 hull production site. They observed nearly 71% and 74% decomposition of butyl
607 acetate, methanol, and styrene under specific input energy (SIE) of 220 and 300 J/L,
608 respectively (Andersen et al., 2013). Some field tests have been carried out for spice
609 plants and rubber with a prototype plasma deodorant intended for remedying a gas
610 flow up to 10 m³/min (Mizuno, 2007). The efficiency of gas deodorization was
611 quantified by odours concentration utilizing an olfactive measurement method. The
612 elimination efficiency of toluene at a level of 10 ppm in the ambient air and a catalytic
613 combustion system assisted by plasma reached almost 90% with a gas flow rate of
614 60 m³/min. (Beckers et al., 2013) investigated the denaturation of H₂S, NH₃, NO_x,
615 limonene, toluene, along with the elimination of fine dust particles in a semi-industrial
616 scale facility using a pulsed corona system. The system demonstrated the feasibility
617 of air purification on a large scale as the efficiency reaches 90-100% for all the tested
618 target pollutants.

619 Different technologies are commonly used that can produce corona discharge
620 (plasma generated by electrical discharges) (Beckers et al., 2013), dielectric barrier
621 discharge (Martin et al., 2008; Murali et al., 2019), and non-thermal plasma. An
622 amalgamation of photocatalysis and plasma discharge can provide high treatment
623 performance with many synergistic effects (Assadi et al., 2015, 2014a; Dou et al.,
624 2016; Mei et al., 2016; Murali et al., 2019). As illustrated in Fig. 6 the pilot-scale

625 reactor can operate solely as a DBD plasma system and photocatalytic system or as
 626 a hybrid system (photocatalysis coupled with DBD plasma).



628 **Figure 6.** Industrial pilot combining plasma and in situ photocatalysis.

629

630 The coupled reactor configurations illustrated by (Martin et al., 2008) have the
 631 following advantages:

- 632 (i) pollutant oxidation facilitated by ions and free radicals generated by the activated
 633 species under a dielectric barrier discharge, and
- 634 (ii) pollutants/by-products adsorption on a mineral bed.

635 **Table 4. Pollutant removal with photocatalytic-plasma oxidation on an**
 636 **industrial scale.**

Reactor configuration	Pollutant	Operating condition	Catalysts	performance	Ref.
Corona discharge reactor	Indole	Concentration of pollutant: 2 ppb Flow rate: 45 and 70 m ³ /h	None	90% for both pollutants	(Andersen et al., 2013)
Pulsed corona	Toluene	Concentration: 10 ppm Flow rate: 60 m ³ /min	Zeolite	90% of toluene	(Mizuno, 2007)

discharge					
Pulsed corona discharge	NH ₃ , H ₂ S, limonene, and fine dust	Concentration:15-70 ppm Flow rate: 150-528 m ³ /h	None	90% of NO _x 90-100% of toluene, limonene, H ₂ S and fine dust	(Beckers et al., 2013)
Dielectric Barrier Discharge (DBD)	Isobutyraldehyde, isovaleraldehyde	Concentration:30 mg/m Flow rate: 250 m ³ /h	Glass Fiber Tissue	60-75% for the three aldehydes	(Murali et al., 2019)
Dielectric Barrier Discharge (DBD)	Naphthenic and paraffinic bitumen fume	Flow rate: 40-50 m ³ /h	Adsorbent (Mineral filters)	Complete removal	(Martin et al., 2008)
Corona discharge	Toluene	Concentration: 8.2–1000 ppbv Flow rate: 3-9 m ³ /h	None	98.2% at 8.2 ppbv	(Ondarts et al., 2016)
DBD surface discharge	Acetone and toluene	Concentration: 0.2 ppm Flow rate : 38.42 m ³ /h	Pt/TiO ₂ and MnO ₂ /Cu O ₂ /Al ₂ O ₃	100% toluene and acetone abatement with 0.2 ppm and 0.46 ppm, respectively.	(Jia et al., 2015)
Dielectric Barrier Discharge (DBD)	Butyl acetate, styrene, and methanol	Concentration:30-110 ppm Flow rate: 2.5 and 5 m ³ /h	None	71% of butyl acetate 74% of styrene and methanol	(Schmidt and Jo, 2015)

GlidArc discharge	TNT, o-xylene sarin	Concentration:160 ppm; 1,38 ng/m ³ (of TNT/Sarin) Flow rate : up to 200 m ³ /h	None	81,25% at 160 ppm 97% at 1,38 ng.m ⁻³	(Czernichowski and Czernichowski, 2009)
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637

638 **8. Practical applications and future research prospects**

639 Among the gas phase processes, there are promising zero waste & zero reagent
640 technologies such as the coupling between dielectric barrier discharge plasma (DBD)
641 and catalysis. These processes are very interesting prospects in terms of synergy,
642 with low energy consumption. However, the by-products are reduced with the plasma
643 coupling and photo-catalyst, the quantity of NO_x and ozone at the outlet of the
644 reactors remains non-negligible. All of these present a significant challenge requiring
645 more investigations to be conducted within the framework of a post-discharge
646 treatment.

647 **9. Conclusions**

648 In this review, for each operating condition and tested key parameter, a synergetic
649 effect could be observed at the laboratory, and pilot scales were unambiguously
650 confirmed. Based on the review of available literature, the combined photocatalysis
651 and plasma processes can present an improved efficiency for pollutant reduction
652 compared to their functionalities realized individually. The enhancement in
653 performance can be to (i) the scavenging of plasma active species by catalytic
654 surface (ii) surface regeneration with discharge (iii) ozone decomposition with UV
655 radiation. From our point of view, the expenditures associated with VOC treatment
656 can be mitigated by applying cutting-edge technologies.

657

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664

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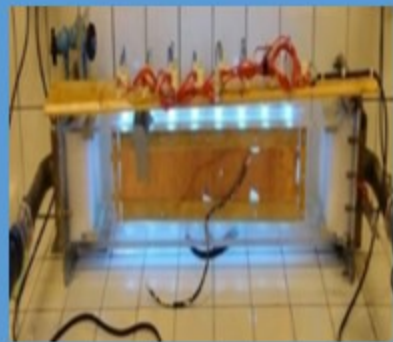
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From Initial Idea...



Tubular Reactor



Planar Reactor



Photocatalysis+Plasma