



Review

Review on electrical discharge plasma technology for wastewater remediation



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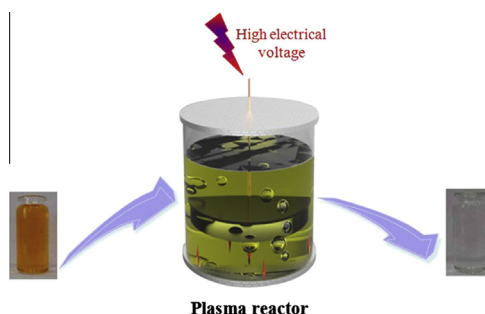
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HIGHLIGHTS

- Various plasma reactors available for water remediation are addressed.
- Combination of plasma with catalysts for pollutant removal is reviewed.
- Some factors in pulsed electrical discharge are systematically discussed.
- Further researches and challenges for plasma technology are presented.

GRAPHICAL ABSTRACT

Electrical discharge plasma can be generated in a reactor with introducing high electrical voltage. After plasma treatment, wastewater can be remediated with fast treatment rate and environmental compatibility.



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ABSTRACT

As wastewater remediation becomes a global concern, the development of innovative advanced oxidation processes for wastewater treatment is still a major challenge. With regard to its fast removal rate and environmental compatibility, plasma technology is considered as a promising remediation technology for water remediation. The principles of electrical plasma with liquids for pollutant removal and the reactors of various electrical discharge types are outlined in this review. To improve energy efficiency, combination of plasma technology with catalysts has attracted significant attention. The present review is concerned about present understanding of the mechanisms involved in these combined processes. Further on, detailed discussions are given of the effects of various factors on the performance of pulsed electrical plasma technology in water treatment processes. Finally, special attention is paid to the future challenges of plasma technology utilized for industrial wastewater treatment.

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Contents

1. Introduction	349
2. Plasma technology	349
2.1. Introduction to plasma	349
2.2. Application of plasma for water treatment	349
2.3. Type of discharge	351
2.3.1. Pulsed corona/streamer/spark discharge	351

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2.3.2.	DC pulseless corona discharge	353
2.3.3.	Dielectric barrier discharge	354
2.3.4.	Gliding arc discharge	355
2.3.5.	DC glow discharge	356
2.3.6.	DC arc discharge	357
3.	Plasma for wastewater remediation	359
3.1.	Combined with catalysts	359
3.1.1.	Carbon materials	359
3.1.2.	Metal oxide	360
3.1.3.	Metal ions	361
3.1.4.	Other catalysts	362
3.2.	Factors affecting plasma efficiency	362
3.2.1.	Reactor system	362
3.2.2.	Electrode	362
3.2.3.	Energy input	363
3.2.4.	Solution pH	363
3.2.5.	Temperature	363
3.2.6.	Gas input	363
3.2.7.	Conductivity	364
3.3.	Target compounds	364
4.	Further researches	364
5.	Summary	365
	Acknowledgments	365
	References	365

1. Introduction

Organic compounds as a major group of pollutants in wastewater are of concern worldwide due to their severe problems for the environment and human health [1]. Thus, in the cases of unavoidable pollutant emissions, these emerging compounds must be treated to satisfy the stringent water quality regulations before discharging into aquatic ecosystem.

Advanced oxidation processes (AOPs) are innovative tools that involve an introduction of energy (e.g., chemical, electrical and radiative) into the reaction zone to generate highly reactive species, especially hydroxyl radicals whose standard potentials are up to 2.8 V ($E_{\text{OH}^\bullet/\text{H}_2\text{O}}^0$) in acidic media [2]. Interest in the utilization of electrical plasma technology, as one of the AOPs, for organic pollutants removal has increased enormously, mainly because of environmental compatibility and high removal efficiency. The electrical discharge plasma technology leads to various physical and chemical effects, such as primary formation of oxidizing species: radicals (H^\bullet , O^\bullet , OH^\bullet) and molecules (H_2O_2 , O_3 , etc.), shockwave, ultraviolet light and electrohydraulic cavitation [3–5]. Consequently, plasma degradation process is generally regarded as a combined process of some other AOPs including ozonation, UV photolysis and pyrolysis, etc. and has the advantages of no demands on temperature and pressure, insensitive to contaminants and environmental friendliness.

Up to present, previous reviews involving plasma technology have covered in detail plasma chemistry and physics, mathematical modeling and its environmental applications, etc. [6–14]. In this review, the contribution focuses on a detailed review of plasma reactors available for water remediation, plasma-catalytic oxidation processes and the factors influencing plasma process as well as future researches of plasma technology for industrial scale application.

2. Plasma technology

2.1. Introduction to plasma

Plasma is a partially or fully ionized gas consisting of electrons, free radicals, ions and neutrals. And it can be produced by a variety of electrical discharges. All varieties of plasma systems are traditionally defined into two major categories, namely thermal

and non-thermal, in terms of electronic density or temperature [4]. Thermal plasma (usually arc discharges, torches or radio frequency) is associated with sufficient energy introduced to allow plasma constituents to be in thermal equilibrium. While non-thermal plasma is obtained using less power (usually corona discharge, dielectric barrier discharge, gliding arc discharge, glow discharge and spark discharge), which is characterized by an energetic electron temperature much higher than that of the bulk-gas molecules. In this plasma, the energetic electrons can collide with background molecules (N_2 , O_2 , H_2O , etc.) producing secondary electrons, photons, ions and radicals [7].

2.2. Application of plasma for water treatment

Thermal plasma is sustained with introducing high electrical energy, so that a high flux of heat is created, which can be used in processing even the most recalcitrant wastes via thermal incineration processes [15]. As for non-thermal plasma, it does not express a local thermodynamic equilibrium, which, therefore, offers high selectivity and energy efficiency in plasma chemical reactions. In view of these facts, applications of atmospheric pressure electrical plasma technologies for water treatment attract the increasing interest and emerge as technological opportunities for the plasma community.

Based on the plasma-phase distribution, electrical discharges with liquids can be subdivided into three main groups, namely, electrical discharges above liquid surface, direct electrical liquid discharges and discharges in bubbles/vapor in liquids [5].

In the cases of electrical discharges above liquid surface, the plasma generation and gas phase breakdown above liquid surface are mostly similar to the gas electrical discharge due to their analogous breakdown strength in the atmospheric gas. But, as to electrical discharges above liquid surface with the liquid as an electrode, the existence of the liquid surface affects the physical aspects of the discharge, as well as the chemical processes occurring in the gas–liquid interface. The reason is that the discharge current is transported through the water electrode by ions which have a much smaller mobility than electrons in metals. Additionally, water has a smaller secondary electron emission coefficient and is easier to deform and evaporate than most metals

[8]. On the other hand, bulk-phase reactions in the liquid can in turn be influenced by the plasma formed at the gas–liquid interface. Strongly oxidative reagents (OH^\cdot , O^\cdot , O_3 , etc.) generated in the gas–liquid interface can diffuse into water and initiate chemical reactions.

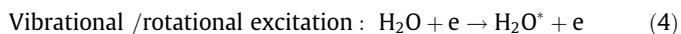
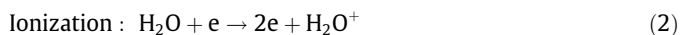
The mechanism for direct discharge in liquid is very intricate since water as a discharge medium is much denser than gases and does not express the long periodic range of the atomic and molecular as in most solids. In electrical liquid discharge, the current is transferred by slow ions in water that is strongly affected by liquid conductivity. Moreover, the purity, such as dissolved gases which form micro-bubbles in the liquid, plays a significant role in the breakdown process. So some physical principles are difficult to determine. For instance, regarding liquid electrical breakdown in liquids under pulsed excitation, The detailed mechanism is still not fully understood and there are primary two principal competing schools, namely, an electron multiplication theory and a phase change mechanism breakdown theory [5].

Electrical discharges in bubbles/vapor in water are completely surrounded by the liquid which serves as an electrode. Normally, electrical discharges with external gas bubbling or in the vapor phase at metal electrode surface can be categorized into this group. The basic chemistry of this type is generally similar to that in gas-phase discharge with liquid as an electrode [16]. But electrical discharges in bubbles own large contact surface area of gas and liquid increasing the efficiency for gaseous phase species diffusing into the liquid and require lower energy to generate the plasma than directly in the liquid.

These above discharge types have been reported distinct discharge characteristics and very large magnitude differences in gas temperature and electron density and temperature [8]. However, these electrical discharges have certain common chemical reaction mechanisms and physical phenomena, such as formation of molecular and radical species and UV light generation.

(1) Hydroxyl radical

The addition of water molecules into electrical discharge process leads to generating OH^\cdot and H^\cdot via dissociation, ionization and vibrational/rotational excitation of water molecules [3]. For example, the pulsed streamer discharge process produces charged particles having energies of about 5–20 eV, which can initiate the reactions of vibrational/rotational excitation of water (threshold energy <1 eV), dissociation of water (threshold energy ≈ 7.0 eV) or even ionization energy of water (threshold energy ≈ 13 eV) as Eqs. (1)–(4) [3,11,17].



Eqs. (5)–(7) demonstrated that vibrationally/rotationally excited water molecules relax into a lower energetic state through which some active radicals can be produced.

Hydroxyl radicals are the vital oxidants that dominate the plasma oxidations in water treatment. Their reactions with organic compounds may be differentiated into three different mechanisms: abstraction of hydrogen atom, electrophilic addition to unsaturated bond and electron transfer. In the case of saturated aliphatic hydrocarbons or alcohols, hydrogen abstraction is primary for organic abatement with yielding H_2O and an organic radical. As for olefins or aromatic hydrocarbons, C-centered radical with a hydroxyl group at the α -C atom can be formed with OH^\cdot radical addition to unsaturated double carbon–carbon bonds of organic compound. Besides, reduction of hydroxyl radicals to hydroxide anions by an organic substrate is of particular interest in the cases where hydrogen abstraction or electrophilic addition reactions may be disfavored by multiple halogen substitution or steric hindrance [18].

(2) O-based species

When oxygen is exposure to electrical discharge, O atom ($E_{\text{O}/\text{H}_2\text{O}}^0 = 2.42$ V) can be generated via dissociation of O_2 and boosts the rate of production of OH^\cdot as Eq. (8) [9].



Furthermore, O atom can directly react with contaminants and also takes part in the reactions with O_2 resulting in the formation of O_3 ($E_{\text{O}_3/\text{O}_2}^0 = 2.07$ V) [9].

Ozone as a strongly oxidizing allotropic form of oxygen reacts best when it can act as an electron transfer acceptor for the oxidation of metal ions, as an electrophile for the oxidation of phenol and other activated aromatics, and as a dipole addition reagent by addition to carbon–carbon multiple bonds [19].

Ozone is unstable and decomposes through a cyclic chain mechanism to produce hydroxyl radicals in neutral and basic solutions [19]. Moreover, with the presence of H_2O_2 in plasma system, ozone can react with HO_2^- giving OH^\cdot as Eqs. (9), (10) [20].



(3) Hydrogen peroxide

Due to its very short lifetime (3.7×10^{-9} s), the diffusion of OH^\cdot radicals (diffusion distance: approximately 6×10^{-9} m) from the plasma zone into the surrounding water seems implausible [21]. Thus, a long-lived plasma chemical product, hydrogen peroxide ($E_{\text{H}_2\text{O}_2/\text{H}_2\text{O}}^0 = 1.77$ V) can be formed via the recombination of OH^\cdot radicals, especially in the cases of underwater plasmas.

Hydrogen peroxide does not significantly react with most organic compounds, at least at appreciable rates for water treatment. Nevertheless, H_2O_2 increases the collective oxidizability of the plasma and affects significantly plasma chemistry. In presence of H_2O_2 , much more OH^\cdot can be directly or indirectly generated via various reactions (e.g., dissociation, photolysis and metal-based catalytic reactions).

(4) Reduction species

In addition to the contributions of oxidizing species to pollutant removal, the presence of reductive species in electrical plasma provides the possibility that aqueous contaminants are removed by reductive degradation pathways.

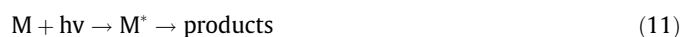
In plasma chemistry, aqueous electron, as a strong reducing agent ($E_{\text{H}_2\text{O}/e_{\text{aq}}}^0 = -2.77$ V), can be formed by the irradiation of water with high energy electrons, which thereby plays an important role in the degradation of compounds due to its high electron affinity [14].

Additionally, H radicals are formed directly by the electron collision with water molecules and from the reaction of hydrated electrons with acids [22]. The H radicals are strong reducing agents ($E_{\text{H}_2\text{O}/\text{H}}^0 = -2.30 \text{ V}$) and undergo two general types of reactions with organic compounds: (i) hydrogen addition to unsaturated bond and (ii) hydrogen abstraction saturated compounds [22].

(5) UV light

All plasmas containing water have UV light emission as a result of excited species relaxation to lower energetic states, which are generated from the collisions between electrons and neutral molecules.

In organic degradation processes, when an organic molecule (M) is irradiated by UV light, it absorbs the radiation and gets promoted to an excited state (M^*). Then, the excited molecule M^* immediately returns to the ground state due to its short lifetime (10^{-9} – 10^{-8} s) through which excited molecule can decompose into new molecules [11,23]:



Not only can the UV light photolytically degrade organic compounds, it also dissociates the hydrogen peroxide and ozone thereby causing hydroxyl radicals generation in plasma system [24,25]. These supplementary hydroxyl radicals in turn destroy the pollutants and thus enhance the utilization of input electrical energy.

(6) Shockwave

In electrical discharge processes, the expansion of the plasma channel against the surrounding water generates an intense shockwave. Thus, shockwave can be produced by high electric energy only introduced directly in the liquid or in bubbles [26]. For example, streamer-like discharges in liquid produce shock fronts, and diaphragm-like discharges in bubbles in the liquid can generate weaker shockwaves at the moment of bubble implosion [27,28]. While gas-phase plasmas normally do not induce any shockwaves in the liquid, but they can affect the liquid motion under three plasma generation situations, namely, cold plasma jets or plumes, ionic wind and the formation of Taylor cones in plasma–water interface [29,30]. The resulting shockwave can induce pyrolytic and chemical reactions in bulk liquid indirectly via electrohydraulic cavitation. For example, more OH^\cdot and H_2O_2 in the bulk liquid can be produced via dissociation of water induced by shockwaves [31].

(7) Pyrolysis

Pyrolysis is the degradation of organic molecules with heat alone in the absence of oxygen. In non-thermal plasma generation process, high electrical discharge induces the production of localized regions of high temperature. Example is that Bruggeman et al. [32] estimated $\text{N}_2(\text{C-B})$ bands rotational and vibrational temperatures of $550 \pm 50 \text{ K}$ and $3860 \pm 200 \text{ K}$, respectively for dc-excited corona discharges in air bubbles. This temperature does not only dissociate water molecules into radicals but also induce pyrolysis of pollutants. And these effects are more intensive for electrical thermal plasma cases due to its high temperature of 10^4 K in whole discharge zone [33].

In summary, the degradation of organic compounds using electrical plasma technologies is primarily depended on chemical active species, and the presences of other physical effects intensify this process.

2.3. Type of discharge

In the application of electrical plasma technology for water treatment, designing an energy-efficient plasma reactor has been

receiving great attentions. And a variety of different reactors with liquid phase or gas–liquid phase electrical discharges have been developed. The representative reactors among these will be discussed in this section according to the classification of discharge types. Phenol and phenolic compounds are the commonly studied organic compounds in such electrical discharges with liquids, and some experiment results are provided in Table 1 for straightforward efficiency comparisons.

2.3.1. Pulsed corona/streamer/spark discharge

For pulsed electrical discharge, the reactor is driven by a pulsed electric generator able to create very sharp high voltage pulse with a nanosecond or microsecond range duration time. Thus, in this discharge process, only free electrons gain high energy with producing energetic electrons leading to non-thermal plasma generation [9]. The typical pulsed electrical discharge configurations involve two asymmetric electrodes, one is very high curvature electrodes (e.g., needles [34,35], rings [36] or wires [37] and the other one is small curvature such as a plate. This configuration reduce the discharge inception voltage because of the fact that uniform electric field generated on the large curvature electrode can induce a high potential gradient.

With pulsed voltage input, the point-plate configuration reactor is the most studied object, which consists of a high-voltage point electrode placed at a certain distance from the grounded plate electrode [34,35,38–44]. The diagrammatic sketch in Fig. 1a is a typical reactor of electrical liquid discharge. The benefit of this reactor is that active species generated in liquid can directly interact with target pollutant. However, the relatively low rates of transport in the liquid phase induce the sharp gradients in temperature and concentration between the plasma region and the bulk solution, resulting in recombination and quenching of active radicals within the discharge zones [6]. Similarly, steep boundary transition regions can also exist in the gas–liquid interface in the gas electrical discharge reactor (Fig. 1b) [34,35].

The pioneering and landmark work done by the group of B.R. Locke in point-plate reactors design is noteworthy [40–43,45]. Based on the separated features of gas and liquid phase discharge, they originally proposed a hybrid gas–liquid reactor (Fig. 1c) with the high voltage electrode submerged in liquid while the ground suspended in gas phase. In this reactor, substantial short lived radicals and hydrogen peroxide are produced in the liquid phase for organic abatement. In addition, electrical discharge can also occur above liquid surface, which enhances the productions of active species and provides ozone under oxygen-containing gas atmosphere thereby intensifying contaminants removal via diffusing into liquid phase. As a result, hybrid gas–liquid reactor expresses the superiority for water treatment over liquid discharge reactor and gas discharge reactor [40,41,44].

Although, utilizing a matrix of needles has proved its usefulness in wastewater remediation, design makes it hard to implement on larger and more efficient scale. Recently, some attracting reactor configurations with large plasma zone are developed and applied for water treatment.

A water-circulating wires-plate reactor was manufactured with pulsed corona discharge above flowing water film as depicted in Fig. 1d [37]. In this reactor, there is always fresh solution exposure to plasma due to liquid film flowing, which compensates mass transfer resistance to some extent. To upscale this reactor, four units can be connected in series and parallel driven by a power supply. The experiment results for 1 mM phenol solution treatment were that removal efficiency of 14% was achieved after passing one reactor and increased to 27%, 35% and 38% after two, three and four reactors, respectively at liquid flow rate of 0.3 L min^{-1} [46].

Table 1
Summary of the typical reactor configurations of various plasma technologies for phenol and phenolic compounds removal.

Type of discharge			Application					
Classification	Plasma property	Excitation	Reactor/electrode configurations	Discharge zone	Conditions	Removal efficiency (%)	Energy efficiency	Refs.
Pulsed electrical discharge	Non thermal plasma	DC pulse V: 10 ⁴ kV, F: 10 ⁰ –10 ² Hz	Liquid discharge reactor/ needles-plate	Discharge in bubbles/liquid	Phenol, Vo: 0.25 L, C: 100 pm, t: 120 min, V: 21 kV, F: 50 Hz O ₂ Q: 300 L h ^{−1}	100	0.46 g (kW h) ^{−1}	[38]
			Gas discharge reactor/ pins-plate	Discharge above water surface	Phenol, Vo: 0.1 L, C: 94 ppm, t: 120 min, V: 25 kV, F: 100 Hz, air atmosphere	90	0.13 g (kW h) ^{−1}	[34]
			Hybrid gas–liquid discharge reactor/ needles-plate	Discharge above water surface + discharge in liquid/ bubbles	4-Chlorophenol, Vo: 0.5 L, C: 60 ppm, t: 20 min, V: 16 kV, F: 100 Hz, O ₂ Q: 300 L h ^{−1}	100	1.76 g (kW h) ^{−1}	[39]
			Wires-plate reactor	Discharge above water surface	Phenol, Vo: 0.2 L, C: 94 ppm, Q _L : 0.3 L min ^{−1} , t: 5 min, V: 38 kV, F: 10 Hz, O ₂ atmosphere	38	2.97 g (kW h) ^{−1}	[37]
			Aerosol reactor/wires-wires	Discharge in steam/gas	Phenol, C: 94 ppm, Q _L : 200 L h ^{−1} , residence time: 27 s, P: 900 W, O ₂ atmosphere, 4 nozzles, One pass	62	13 (kW h) ^{−1}	[46]
DC pulseless corona discharge	Non thermal plasma	DC pulseless voltage: 10 ⁰ –10 ² kV	Submerged capillary point electrode reactor	Discharge in liquid	Phenol, Vo:–, C: 2.2 ppm, t: 12 min, V: 5 kV, O ₂ Q: 0.9 L h ^{−1}	100	–	[51]
			Multiple wires-plate reactor	Discharge above water surface	Phenol, Vo: 2 L, C: 50 ppm, t: 240 min, V: 17.5 kV, I: 2.5 mA, 20O ₂ /80N ₂ Q: 30 L h ^{−1}	100	0.57 g (kW h) ^{−1}	[52]
			Wire-cylinder wetted-wall reactor	Discharge above water surface	Phenol, Vo: 0.5 L, Q _L : 1.4 L min ^{−1} , C: 28 ppm, t: 90 min, V: 14 kV; I: 0.5 mA, air Q: 30 L h ^{−1}	82	1.09 g (kW h) ^{−1}	[55]
Dielectric barrier discharge	Non thermal plasma	AC/pulse voltage: 10 ⁰ –10 ² kV, frequency: 10 ² –10 ⁶ Hz	Wires-plate reactor	Discharge above water surface	Phenol, deionized water, Vo: 0.07 L, C: 47 ppm, t: 180 min, V: 16.5–18 kV, F: 50 Hz, air Q: 1.8 L h ^{−1}	97	0.56 g (kW h) ^{−1}	[62]
			Coaxial cylinder type	Discharge above water surface	Phenol, C: 94 ppm, Q _L : 6 mL min ^{−1} , V: 14–16 kV, F: 40 Hz, air Q: 3.6 L h ^{−1}	40	0.88 g (kW h) ^{−1}	[70]
			Coaxial cylinder reactor/ three cylinder type	Discharge above water surface	4-Chlorophenol, Vo: 5 L, C: 20 ppm, Q _L : 150 mL min ^{−1} , t: 19 min, V: 20 kV, F: 50 Hz	94.8	2.6 g (kW h) ^{−1}	[72]
Gliding arc discharge	Dual character of thermal and non-thermal plasma	AC/DC/pulse voltage: 10 ⁰ –10 ² kV, frequency: 10–10 ² Hz	Gas gliding arc discharge reactor	Gas discharge	Bisphenol A, Vo: 0.3 L, C: 28 ppm, t: 30 min, V: 10 kV, I: 100 mA, humid air Q: 800 L h ^{−1}	100	0.016 g (kW h) ^{−1}	[79]
			Gas–liquid gliding arc discharge reactor	Gas–Liquid discharge	Phenol, Vo: 0.1 L, Q _L : 10.5 mL min ^{−1} , COD: 1878 mg O ₂ L ^{−1} , t: 38 min, P: 234 W, air Q: 204 L h ^{−1}	91	12.5 g (kW h) ^{−1}	[74]
DC glow discharge	Non thermal plasma	DC voltage: <10 ⁰ kV	Contact glow discharge reactor/point-plate	Discharge above water surface	Phenol, Vo: 0.15 L, C: 100 ppm, t: 30 min, V: 500 V, I: 100 mA, conductivity: 6.4 mS cm ^{−1}	61	0.34 g (kW h) ^{−1}	[92]
			Submerged glow discharge reactor/point-plate	Discharge in liquid	2,4-Dichlorophenol, Vo: 0.25 L, C: 100 ppm, t: 90 min, V: 600 V, I: 120–150 mA, m (Na ₂ SO ₄): 2 g L ^{−1}	65	0.12–0.15 g (kW h) ^{−1}	[100]
			DC diaphragm glow discharge reactor	Discharge in liquid	Phenol, Vo: 0.25 L, C: 300 ppm, t: 30 min, V: 900 V, I: 110 mA, m(Na ₂ SO ₄): 4 g L ^{−1}	70	1.06 g (kW h) ^{−1}	[104]
DC arc plasma	Thermal plasma	DC voltage: 10 ² –10 ³ V, current: 10 ⁰ –10 ² A	DC arc discharge reactor/ torch	Discharge in steam	Phenol, Q _L : 4.0 × 10 ^{−2} –4.6 × 10 ^{−2} g s ^{−1} , C: 1 mol%, V: 150 V, I: 8 A	100	8.12 g (kW h) ^{−1}	[107]

(1) V: input voltage; F: input frequency; I: electric current; P: input power; Q: gas flow rate; Q_L: liquid flow rate; t: treatment time; Vo: liquid volume; C: concentration; m: amount of addition.

(2) The energy yield of the degradation was calculated from: $Y(g(kW h)^{-1}) = \frac{C(g L^{-1}) \times V(L) \times \frac{1}{100} \times \text{removal efficiency}(\%)}{P(kW) \times t(h)}$.

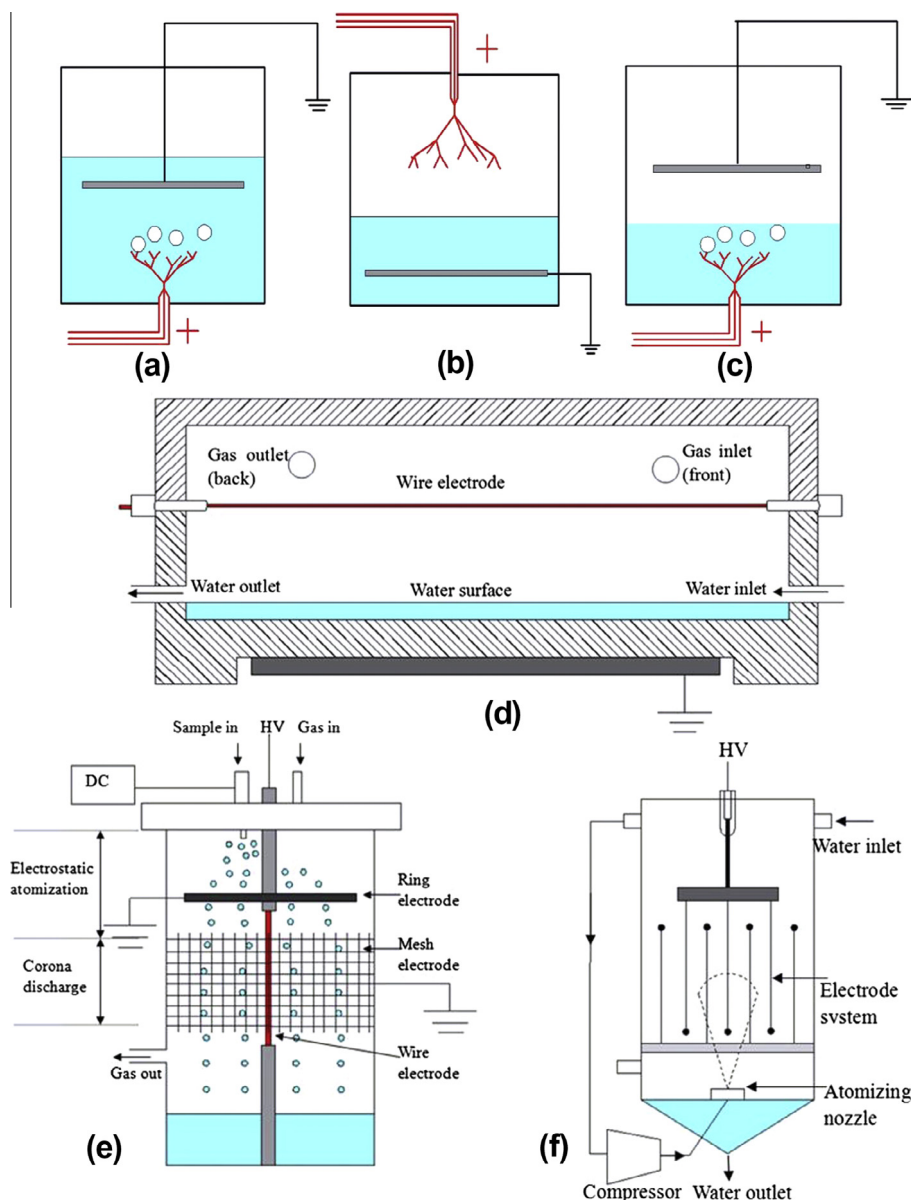


Fig. 1. Diagrammatic sketches of pulsed discharge plasma reactors: (a) liquid discharge reactor; (b) gas discharge reactor; (c) Hybrid gas-liquid discharge reactor; (d) wires-plate reactor [37]; (e) electrostatically atomized ring-mesh reactor [47]; (f) aerosol reactor [49].

The electrostatically atomized ring-mesh reactor (Fig. 1e) consisting of electrostatic atomization part and reaction part was developed by Sato et al. [47]. In electrostatic atomization part, DC voltage was applied to the nozzle for producing a large number of fine and droplets. In consideration of smaller-surface tension component tending to concentrate near the surface in mixtures of two liquids, these droplets enhance the pollutants concentrating in the surface region where plasma is generated [48]. Hence electrostatic atomization process increases the pollutant exposure to free radicals and hydrated electrons in the reaction part. In spite of this, the reactor length is too short to provide enough residence time for complete pollutant removal at one pass processing, posing as a major obstacle for industrial scale application.

Fortunately, a aerosol reactor of 120 L volume, as described in Fig. 1d was designed and its load can increase to 200 L h⁻¹ with installing four nozzles [46,49]. In treatment process, polluted water is introduced into the reactor through atomizing nozzles, is treated in the aerosol phase by electrical plasma and finally

condensates at the lower part of the vessel. Atomizing water significantly increases the air-liquid boundary surface area. In case of 10–100 μm droplets, the exposed water surface area reaches 10⁴–10⁵ cm² L⁻¹, which corresponds to approximately 10⁴ increase compared to bulk water. Thus the energy efficiency for phenol degradation can surprisingly reach approximately 13 g (kW h)⁻¹ as demonstrated in Table 1 posing great potential industrial application.

When scaling up the pulsed electrical plasma treatment system, development of reliable and inexpensive pulsed power supplies is one of the key technical obstacles, of which critical component is pulse-forming switch. In general, gas-filled spark-gap switch is more cost-effective for 1–10 kW plasma applications as compared with solid-state switch and magnetic compression switch. But, the pulse-forming switch has a limited service life for the electrode erosion in spark gaps. Besides, matching between a pulsed power source and a plasma reactor is also very important, which can not only affect the total energy efficiency but it can also affect

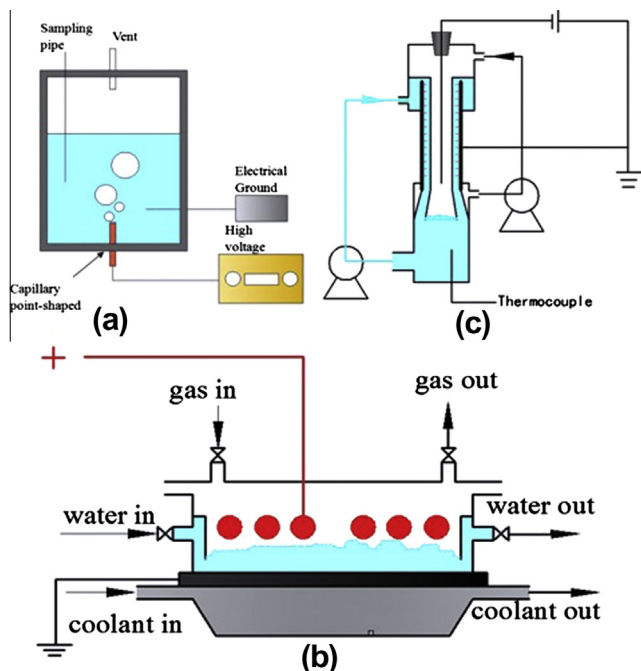


Fig. 2. Diagrammatic sketches of DC pulseless corona discharge reactors: (a) submerged capillary point electrode reactor [51]; (b) multiple wires-plate reactor [52]; (c) wire-cylinder wetted-wall reactor [55].

significantly the switch lifetime and investment and operational costs [50].

2.3.2. DC pulseless corona discharge

The pulseless corona system can obtain a high flux of electrons from DC electrical discharge in gases or liquids and therefore supplies active radical species for chemical oxidations. Contrary to pulsed electrical corona, the advantage of the DC corona is that it can continuously produce radical species. From another perspective, it consumes more energy because of the continuous operation and is also significantly affected by water conductivity.

An early submerged capillary point-shaped electrode discharge reactor (Fig. 2a) combines corona discharge with electrohydrodynamic spraying of oxygen through the capillary enhancing the interfacial area for mass transfer [51]. And emission spectra results suggested that the major radical species produced from such system were hydroxyl radicals, ozone and atomic hydrogen [51]. However, phenol degradation modeling results showed that only aqueous electrons and hydroxyl radicals are dominantly responsible for organic removal in pulseless corona discharge. Although pollutant phenol can be completely removed within 15 min under the conditions of input voltage of 5 kV and oxygen flow rate of 15 mL min^{-1} , it has a small discharge zone and is difficult to provide the great discharge zone for large volume solution treatment.

In another effort, a wire-plate type reactor as described in Fig. 2b was designed over the treated water by Sano et al. [52] displaying superior treatment performance by negative corona. Later, Sano et al. [53–55] proposed a wire-cylinder wetted-wall reactor (Fig. 2c), which can simultaneously treat phenol-containing wastewater and acetaldehyde-laden air by adding gas absorption effect to gas-phase reactions. When applying a high DC voltage onto the wire cathode, energetic electrons drifting along the electric field can induce dissociation and ionization of oxygen with O-based active species (O_3 , O radical and O^- , etc.) generation. These species initiate reactive OH radical production when reaching the interfacial water and dissolving into it. In view of this

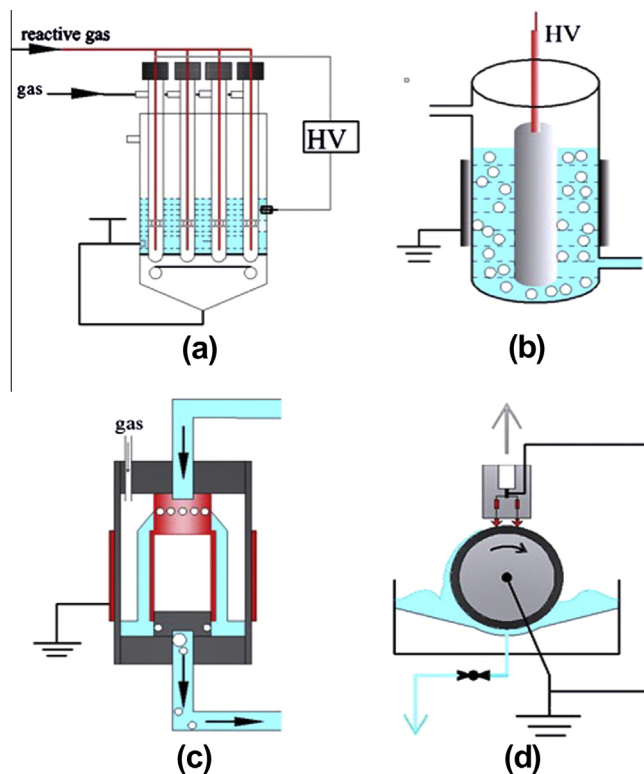


Fig. 3. Diagrammatic sketches of DBD reactors: (a) multiple tubes-liquid electrode reactor [60]; (b) rod-cylinder reactor [63]; (c) coaxial cylinder reactor [65]; (d) rotating drum reactor [73].

wire-cylinder arrangement of electrodes, a large volume of water or polluted gas can be exposed to electrical discharges. So this reactor configuration may be a candidate for continuous treatment of wastewater.

2.3.3. Dielectric barrier discharge

This discharge type is based on the use of at least one dielectric barrier (e.g., glass, quartz, ceramics, mica and alumina, etc.) in the discharge gap with time varying voltages applied to the electrodes, which prevents spark formation, eliminates electrode etching and corrosion and distributes the discharge almost uniformly over the entire electrode area.

Based on dielectric barrier discharge (DBD) technology, ozone has been industrially generated with oxygen or air feed, and applied for wastewater treatment. But this treatment technology requires separate ozone production systems, which are capital intensive in industry. Besides, a large number of radical species with very high oxidation potentials are produced in electrical discharge systems, which cannot be sufficiently utilized for pollutant treatment due to their short life spans, for example $3.7 \times 10^{-9} \text{ s}$ for OH^\cdot and quick decay before ozone enriched air/oxygen reaching the treated water solution.

Recently, some compact built-in tube surface DBD plasma reactors were developed inducing ex situ plasma oxidation processes [56–59]. In these reactors, the wastewater acts as the ground electrode and gas plasma is generated in the tube directly connected to the water reservoir which can be immediately sparged throughout the wastewater to degrade the organic contaminant. This configuration can simplify the operation system and reduce operation cost. An example is that Chen et al. [60] developed a water treatment system with four built-in plasma generating tubes as depicted in Fig. 3a. When methyl violet 5BN (22.4 mg L^{-1}) was selected as a target, almost complete

decoloration was obtained within a treatment time of 360 s at an oxygen gas velocity of $0.3 \text{ m}^3 \text{ h}^{-1}$ and a discharge power of 40 W.

Brunet [61] compared the treatment performance between ex situ plasma technology and in situ electrical discharges in or above water and reported that the average rates of ozone accumulation in water and methylene blue degradation in the case of parallel plate DBD are approximately two and three, respectively times larger than those with external ozonation. There are several potential additional mechanisms: formations of massive active species in water or near water level, which can in situ attack the aqueous organic pollutant; UV radiation enhancing the production of hydroxyl radicals from ozone; formation of Taylor cones due to the application of electrical field to the water surface allowing greater mass transfer across the interface.

Besides the traditional parallel plate reactor [61] and wire-plate reactor [62], an in situ electrical discharge reactor with rod-cylinder electrode was also presented (Fig. 3b), and its treatment efficiency was demonstrated preferable due to full utilization of reactive species with both electrodes submerged in liquid phase [63,64]. In the case of crystal violet decoloration [63], it was observed that both decoloration efficiency and TOC reduction increased with increasing the input energy and the highest decoloration yield up to $86.3 \text{ g (kW h)}^{-1}$ can be achieved (voltage 14 kV, frequency 50 Hz, initial concentration: 50 mg L^{-1} , solution volume 100 mL, air flow rate 200 mL min^{-1}).

Recently, Magureanu and Rybkin et al. presented a novel coaxial cylinder reactor with water falling film in Fig. 3c [65–69], which can increase the effective interfacial area for oxidation reaction. Ognier et al. [70] estimated the thickness of the liquid film of approximately 0.14 mm by the correlation for a smooth laminar flow at a liquid flow rate of 6 mL min^{-1} in this configuration. When electrical discharge occurs in gas or gas–liquid interface, some formed highly reactive species are instantaneously consumed in liquid film with diffusion distances no further than 6–2000 nm due to their short life-spans, e.g. $3.7 \times 10^{-9} \text{ s}$ for OH^\bullet ; $1.2 \times 10^{-6} \text{ s}$ for H^\bullet and $1.0 \times 10^{-6} \text{ s}$ for aqueous electrons [21]. As for relatively stable species such as ozone, it may be depleted in liquid film or diffuse through liquid film into liquid phase with molecular diffusion in liquid phase, which is greatly depended on reaction rate constant, ozone concentration and pollutant concentration, etc. Thus the reasonably thin solution falling layer is propitious to oxidizing species penetrating the solution and pollutant removal. Additionally, the active species, which are not consumed inside the discharge reactor, can be bubbled through the solution in the

reservoir. As a result, a highlighted treatment performance for methylene blue removal was obtained using this water falling film reactor, achieving 57 g (kW h)^{-1} at 95% conversion with pulsed power input of 0.46 W in oxygen atmosphere with liquid flow rate of 30 mL min^{-1} [67]. Theoretically, this DBD reactor configuration is scalable and flexible. And for industrial application, the scale of reactor must be designed as large as possible. Otherwise, large liquid flow inevitably leads to thick water falling film, which thereby reduces the final treatment performance.

Dojčinović et al. [71,72] developed an upgraded reactor of three parallel coaxial units with AC voltage input at laboratory level. And after 6 min plasma treatment, the removals of 2-chlorophenol, 4-chlorophenol and 2,6-dichlorophenol were 90.7%, 85.4% and 64.6%, respectively in bidistilled water (conditions: input power 115 W, water flow rate 150 mL min^{-1} , initial concentration 20 mg L^{-1} , volume 5 L) [72].

Besides these common reactors, some novel reactors were designed from the traditional reactors in recent years such as rotating drum type (Fig. 3d) [73]. In operating process, with the drum rolls past the reservoir, a water film of 0.2 mm was clung to the drum surface and then exposure to the plasma generated from the two ceramic barrier electrodes above the rotating drum. In this report, preferable results of persistent pharmaceuticals removal can be achieved under the optimal conditions. However, in consideration of its high operating cost and energy consumption, this reactor would be appreciable for the treatment of concentrated solutions such as hospital or industrial effluents.

In general, the advantage of DBD over other discharges lies in a comparatively straightforward scale-up to large dimensions. But there are still lots of problems to be solved for applying this technology in industrial effluent treatment.

2.3.4. Gliding arc discharge

The gliding arc discharge (GAD) is considered as an innovative technology exhibiting a dual character of thermal and non-thermal plasma and a typical reactor, as shown in Fig. 4a, consists of insulating cover, “knife-edge” divergent electrodes, high voltage power supply, the nozzle and impedance [74]. In gliding arc discharge processes, high voltage is introduced between two or more thin “knife-edge” divergent electrodes and the narrowest point is electrical breakdown resulting in arc discharge when the electric field reaches approximately 3 kV mm^{-1} in air. As a high velocity gas flows through the nozzle, the length of the arc (actually a thermal plasma) increases and the temperature of the ionized gas

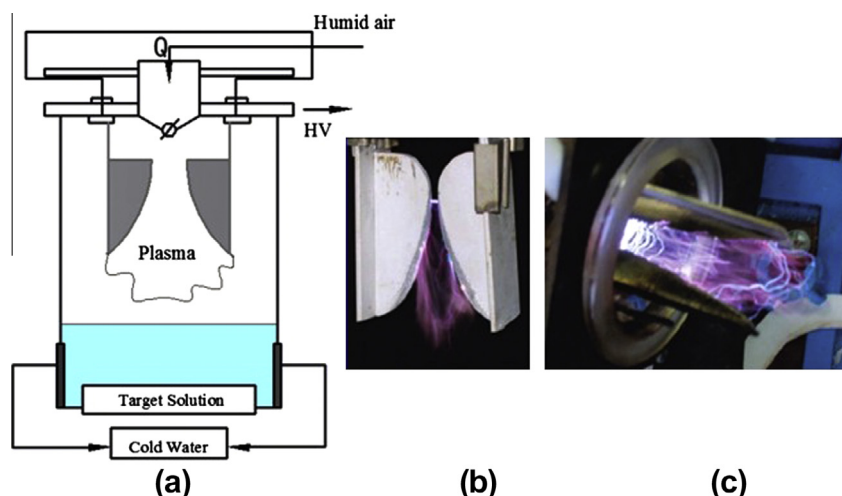


Fig. 4. (a) Diagrammatic sketch of gliding arc discharge reactor [76]; (b) photographs of electrical discharge in gliding arc reactor (adapted from Ref. [75] with permission from ACS).

decreases, so that it becomes a non-thermal quenched plasma upon breaking into a plasma plume, as illustrated in Fig. 4b and c. After the decay of the plasma plumes, the evolution repeats from the initial break-down. Unlike the pulsed corona discharges, this technique allows high electrical power introduction and consequently results in the larger yields of short-lived active species.

A gas gliding arc discharge reactor was manufactured and widely utilized for different wastewater remediation [75–81]. Generally a humid gas is injected into the gap between the electrodes. And it was reported that hydrogen peroxide and ozone were not detected for any working gas in the solution in this reactor. The reasons may be that the presence of water vapor strongly suppresses ozone formation and the hydroxyl radicals generated in the plasma do not recombine to produce measurable levels of hydrogen peroxide [82]. As the plasma gas of high velocity blows towards the liquid surface from discharge zone, it can lick the surface of liquid inducing series of reactions and, together with the action of magnetic stirring at the bottom of reactor, make good gas and liquid phase mixing. Accordingly, short-lived active species can favorably react with aqueous targets, while stable species can successfully dissolve in the liquid.

Based on electrohydraulic effect and the properties of gliding arc discharge, Liu and Yan et al. [83,84] utilized a gas–liquid gliding arc discharge reactor for water remediation. The disparity between these two main configurations is that only humid gas is compressed into the gas discharge reactor while the latter requires gas and liquid to be treated simultaneously injecting into discharge ozone through the nozzle. In such process, high power arc discharges is sufficient to partially vaporize the water droplets and can enhance the plasma chemical conversion. And in contrast to the discharge over water cases, with oxygen as a carrier gas, significant amounts of hydrogen peroxide are formed and can be collected by the liquid droplet [85]. With the virtues of atomization

of wastewater, full contact between plasma and wastewater, full use of input energy, continuous-flow mode, etc., this reactor compensates the drawbacks of the above gas discharge reactor and thus enhances the overall treatment efficiency for aqueous pollutants removal, especially for high concentration organic wastewater. One example in Table 1 is an application of this reactor for concentrated phenol solution treatment with initial COD of $1878 \text{ mg O}_2 \text{ L}^{-1}$ [74]. The COD was 91.8% abatement after 38 min treatment by the gas–liquid gliding arc discharge reactor, while only 44.6% abatement by the gas gliding arc discharge reactor.

However, a problem that cannot be ignored in this configuration is that the radius of outlet nozzle is very small in this reactor, e.g., 0.15 mm [86] and 1 mm [87]. So a severe issue must be taken into consideration that the phase of wastewater should not contain any insoluble matter which can easily plug the nozzle. Consequently, some pre-treatment methods (e.g., filtration and coagulation) should be necessary for this gas–liquid gliding arc discharge process.

2.3.5. DC glow discharge

A variety of different types of DC glow discharge reactors have been studied for water treatment. According to the positions of both electrodes, glow discharges can be classified into contact glow discharge reactor and submersed glow discharge reactor.

Contact glow discharge reactor is explored as an effective reactor for water purification and the most commonly used configuration as portrayed in Fig. 5a, which sustains plasma between the electrode and the surrounding electrolyte [88–92]. Since contact glow discharge electrolysis (CGDE) is more stable when developed at an anode than at cathode, most studies concentrated on an anodic CGDE [93]. In this case, there is a critical voltage for the onset of full CGDE, called mid-point voltage 420 V for the anode independent of external variables. Normally, to avoid complications from oxidation-reduction of electrolyte constituents, inert-type electrolytes were employed. In electrical discharge process, a thin wire anode is in contact with the surface of the electrolyte and the DC glow discharge is initiated in a thin sheath film of vapor covering the electrode surface, where vapor phase water molecules are electrolytically dissociated at a high temperature with generations of active species such as OH^\cdot , H^\cdot and HO_2^\cdot . Furthermore, $\text{H}_2\text{O}_{\text{gas}}^+$ ions produced from vapor H_2O molecules in the gas phase bombard the gas–liquid interface under the influence of the large electric field driving force and subsequently react with liquid H_2O molecules to form additional OH^\cdot and H^\cdot radicals [93]. In efforts to improve the treatment efficiency of CGDE, multiple anodes can be used to generate large volume plasma, which performed better than single anode for dye decoloration [94]. Jin et al. [94] stated that discoloration rates of Acid Orange 7 (volume: 300 mL; concentration: 25 mg L^{-1}) with six stainless steel anodes and six platinum wire anodes are 13.7 and 6.7 times, respectively faster than with single anode under input voltage of 515 V.

A remarkable feature of CGDE is its highly non-Faradaic chemical effect and this effect of CGDE originates in two reaction zones: the plasma around the electrode and the solution near the plasma–electrolyte interface. To validate this two-reaction zone mechanism, Sengupta et al. developed “H” type reactor with two equal volume compartments equipped with the necessary facilities for collecting both electrode gases and electrolyzed solutions from each electrode chamber (presented in Fig. 5b) [95]. Afterwards, Gao et al. further applied this type reactor for pollutant removal [96,97] and demonstrated that this reactor was preferable for organic abatement with large volume.

Gao et al. [98–100] also focused on the ways to investigate the possibility to use submersed glow discharge electrolysis technologies with two electrodes both placed in liquid as shown in Fig. 5c for dyes and phenolic compounds degradation. Given that the

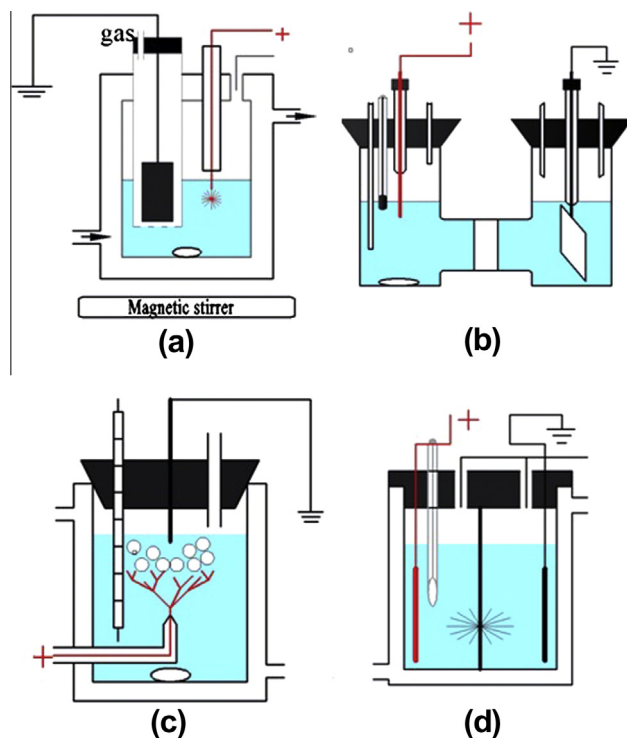


Fig. 5. Diagrammatic sketches of glow discharge reactors: (a) contact glow discharge reactor [88]; (b) contact glow discharge reactor with two cells [96]; (c) submersed glow discharge reactor [98]; (d) DC diaphragm glow discharge reactor [102].

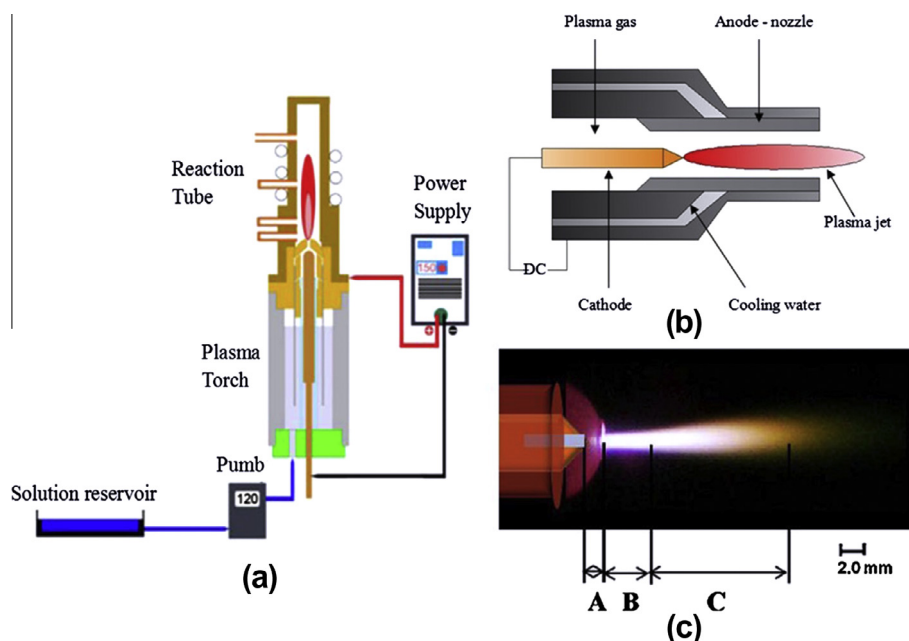


Fig. 6. (a) Diagrammatic sketch of DC arc discharge reactor (adapted from Refs. [107] with permission from Elsevier); (b) diagrammatic sketch of a torch [15]; (c) DC arc water plasma is estimated for different regions according to the plasma temperature distribution along the plasma jet; "A", "B", and "C" are displayed arc region, plasma flame region, and downstream region, respectively (adapted from Ref. [107] with permission from Elsevier).

power dissipation in the vicinity of the electrode is large enough to evaporate the liquid, the glow plasma is generated in the vapor layer and covers the metal electrode. They conducted lab-scale experiments with this reactor for dyes degradation, indicating that 10 min of plasma degradation (voltage 600 V, current 120–150 mA, electrolyte Na_2SO_4 2 g L^{-1} , pH 6.72, initial concentration: 30 mg L^{-1} , solution volume 250 mL) resulted in 95% decoloration of Brilliant Green and almost complete mineralization (100% of COD) [98].

In CGDE, compared with stainless steel [94], aluminum and titanium [101], etc., platinum is more suitable as the working anode due to its properties of corrosion resistance, high melting points and service life. However, platinum utilization greatly limits economical feasibility of glow discharge processes for industrial applications. In view of this obstacle, a diaphragm glow discharge reactor was proposed which was separated by a diaphragm with a small hole into two compartments as shown in Fig. 5d [102–104]. When applying a high voltage into each compartment, a considerable current is generated in the system and will constrict in the diaphragm causing strong Joule heating and eventually evaporation. The high voltage across the reservoirs will stand in good approximation across the vapor phase which fills the diaphragm hole and plasma will be formed in the vapor. This means that plasma streamer propagating from the small hole towards electrodes do not contact with electrode surface. Thus electrode erosion is avoided and electrode lifetime is prolonged.

The most obvious advantage of glow discharge technology over pulsed corona discharge is that it can be operated under high-salt-containing water, because the aqueous solution itself serves as the cathode in glow discharge processes [104].

2.3.6. DC arc discharge

Recently, thermal plasma has also been applied for contaminated solution treatment due to its high energy densities and temperatures, oxidation or reduction atmosphere and rapid quenching rate (10^5 – 10^6 K s^{-1}), which can produce non-equilibrium chemical compositions [15,105].

The widely utilized thermal plasma generation reactor is a torch configuration as shown in Fig. 6a and b. The contaminated solution is usually directly introduced into torch as plasma forming gas. When the arc is ignited, the aqueous solution can be evaporated spontaneously to provide the generation of 100%-water plasma due to enormous heat from an anode. Simultaneously, the anode is cooled by the water evaporation, therefore no cooling-controlled units are required [106]. In the highly reactive plasma zone, there is a large fraction of electrons, ions and excited molecules together with the high temperatures. On the basis of temperature distribution along the plasma jet the arc plasma can be divided into three thermal regions, namely, arc region (over 10,000 K), plasma flame region (about 6000 K), and downstream region (lower than 1000 K) as illustrated in Fig. 6c at arc current of 7 A. Thus, when wastewaters are injected into arc discharge plasma zone, they are heated very rapidly by the plasma. And the volatile matter is released and cracked giving rise to hydrogen and light hydrocarbons such as methane and acetylene via thermal plasma pyrolysis process [107].

Furthermore, the optical emission spectrum indicates that arc discharge can dissociate the water molecules at high temperatures into OH, H, and O radicals [108]. These active species are directly or indirectly beneficial for the oxidation of target pollutant.

Therefore, this process provides an alternative method for pollutant treatment by plasma technology. In the case of phenol solution with high COD, the results show that 1 mol% phenol was drastically decomposed by DC water plasma torch [107]. The value of COD was reduced from 52.8 g L^{-1} down to $1.0 \times 10^{-5} \text{ g L}^{-1}$ over a short retention time at an arc current of 8 A with the energy yield of $8.12 \text{ g (kW h)}^{-1}$. The major disadvantage of this plasma process is the use of high electrical energy. However, it may be economically viable for refractory and high concentration toxic organic wastewater treatment.

Table 1 provides the information on these electrical discharges and their applications for phenolic compounds destruction. In plasma generation technologies, power source is one of the primary determinants and various types including AC, DC and pulse are introduced into a wide range of electrode configurations.

Table 2
Summary of the typical studies of plasma technologies for organics removal with various catalyst additions.

No./refs.	Type of catalyst	Plasma properties	Target properties	Removal efficiency; energy efficiency	Notes
1 [115]	AC	Pulsed liquid discharge, V: 57 kV, F: 60 Hz, t: 15 min	Phenol, Vo: 1 L, C: 100 ppm, m: 1 g L ⁻¹	Without catalyst 40%; 0.57 g (kW h) ⁻¹ With catalyst 89%; 1.26 g (kW h) ⁻¹	Surface reaction rate constant is 0.0011 s ⁻¹
2 [116]	AC (coal/coconut shell/coconut shell)	Pulsed gas–liquid discharge, V: 46 kV, F: 100 Hz, air Q: 120 L h ⁻¹ , t: 21 min	Methyl orange, Vo: 0.2 L, C: 60 ppm, m: 5 g L ⁻¹	Without catalyst 84%; 4.1 g (kW h) ⁻¹ With catalyst 96.3%/92%/95.4%; 4.7/4.5/4.6 g (kW h) ⁻¹	Physical properties of the used AC altered slightly, while strongly for the chemistry properties
3 [117]	AC _{original} AC _{HN} AC _{HT}	Pulsed liquid discharge, V: 14 kV, F: 150 Hz, O ₂ Q: 100 L h ⁻¹ , t: 12 min	Parachlorophenol, Vo: 0.1 L, C: 100 ppm, m: 0.5 g L ⁻¹	Without catalyst 69%; 0.29 g (kW h) ⁻¹ With catalyst 73.4%/77.7%/87.6%; 0.31/0.32/0.36 g (kW h) ⁻¹	AC with strong adsorption capacity and highly catalytic activity is preferable
4 [118]	AC	Pulsed liquid discharge, V: 23.6 kV, F: 40 Hz, O ₂ Q: 360 L h ⁻¹ , t: 60 min	Phenol, Vo: 0.25 L, C: 100 ppm, Q _L : 100 mL min ⁻¹ , m: 4 g L ⁻¹	Without catalyst 28%; 0.19 g (kW h) ⁻¹ With catalyst 88%; 0.60 g (kW h) ⁻¹	Phenol is degraded to hydroxylated intermediates and organic acids by OH radicals, H ₂ O ₂ and O ₃
5 [121]	AC	Dielectric barrier discharge, V: 20.4 kV, F: 50 Hz, t: 60 min	Pentachlorophenol, Vo: 0.4 L, C: 2000 ppm, m: 2 g L ⁻¹	–	Relatively high level regeneration. Obtaining larger micropore and more total acid after DBD treatment
6 [124]	ACF-0 ACF-H ACF-N	Pulsed gas–liquid discharge, V: 46 kV, F: 100 Hz, O ₂ Q: 60 L h ⁻¹ , t: 21 min	Methyl orange, Vo: 0.2 L, C: 80 ppm, ACF 1.25 g L ⁻¹	Without catalyst 81%; 3.9 g (kW h) ⁻¹ With catalyst 89%/97%/98%; 4.3/4.7/4.7 g (kW h) ⁻¹	A synergistic effect appeared in the combined treatment due to AC acting as a adsorbent and a catalyst
7 [125]	ACF ₀ ACF/H ₂ O ₂ ACF/Fe(NO ₃) ₃ ACF/steam	Pulsed gas–liquid discharge, V: 40 kV, F: 100 Hz, O ₂ Q: 80 L h ⁻¹ , t: 30 min	Methyl orange, Vo: 0.2 L, C: 60 ppm, ACF 1.75 g L ⁻¹	Without catalyst 86%; 3.8 g (kW h) ⁻¹ With catalyst 96.5%/95.3%/99.4%/99.5%; 4.3/4.2/4.5/4.5 g (kW h) ⁻¹	ACF adsorption contributed little for MO removal and was well regenerated in plasma process
8 [38]	TiO ₂ supported beads	Pulsed liquid discharge, V: 21 kV, F: 50 Hz, O ₂ Q: 300 L h ⁻¹ , t: 40 min	Phenol, Vo: 0.25 L, C: 100 ppm, 100 TiO ₂ supported beads	Without catalyst 60%; 0.84 g (kW h) ⁻¹ With catalyst 91.4%; 1.27 g (kW h) ⁻¹	Observing a more radicals in the plasma/TiO ₂ system than in the plasma alone system
9 [76]	TiO ₂	Gliding arc discharge, V: 9 kV, I: 100 mA, t: 60 min	Dye wastewater, Vo: 0.3 L, COD: 147.8 mg O ₂ L ⁻¹ , m: 3 g L ⁻¹	Without catalyst 86%; 0.04 g (kW h) ⁻¹ With catalyst 96.4%; 0.041 g (kW h) ⁻¹	Improving wastewater biodegradability within short treatment times
10 [77]	TiO ₂	Gliding arc discharge, V: 9 kV, I: 100 mA, t: 15 min, air Q: 800 L h ⁻¹	Anthraquinonic acid green 25, Vo: 0.18 L, C: 50 ppm, m: 2 g L ⁻¹	Without catalyst 51%; 0.02 g (kW h) ⁻¹ With catalyst 100%; 0.04 g (kW h) ⁻¹	The plasma processes followed pseudo-first order kinetics
11 [101]	TiO ₂ /TiO ₂ film	Contact glow discharge electrolysis, V: 550 V, t: 40 min	Brilliant red B, Vo: 0.1 L, C: 20 ppm, Na ₂ SO ₄ 5 g L ⁻¹	Without Ti electrode: 97.8%; – With Mo electrode: 71%; –	The performance with Ti electrode was much better than those with Mo and Al electrodes due to additional photocatalysis process
12 [129]	TiO ₂ film	Pulsed liquid discharge, V: 24 kV, F: 50 Hz, Q: 80 L h ⁻¹ , t: 60 min	Phenol, Vo: 0.25 L, C: 100 ppm, 4 films	Without catalyst 53%; 0.23 g (kW h) ⁻¹ With catalyst 78%; 0.34 g (kW h) ⁻¹	Maintaining preferred catalytic activity even after five cycles
13 [132]	TiO ₂	Gliding arc discharge, V: 10 kV, I: 100 mA, air Q: 700 L h ⁻¹ , t: 30 min	Perfluorinated surfactant, Vo: 0.18 L, C: 200 ppm, m: 0.2 g L ⁻¹	Without catalyst 75.3%; 0.54 g (kW h) ⁻¹ With catalyst 80.7%; 0.58 g (kW h) ⁻¹	Anatase TiO ₂ expressed efficient than rutile TiO ₂ in plasma system
14 [133]	TiO ₂ film	Coaxial cylinder DBD, V: 16 kV, F: 50 Hz, O ₂ Q: 3.54 cm ³ s ⁻¹ , residence time 45 s	Phenol, C: 50 ppm	Without catalyst 85.5%; – With catalyst 94%; –	Compared with NiO catalyst, TiO ₂ provided higher yields of CO ₂
15 [134]	TiO ₂	Coaxial cylinder DBD, P: 220 kJ L ⁻¹	Yellow Tartrazine, Vo: 0.25 L, C: 54 ppm, Q _L : 6 mL min ⁻¹ , m: 4 g L ⁻¹	Without catalyst 11%; 0.1 g (kW h) ⁻¹ With catalyst 96%; 0.85 g (kW h) ⁻¹	The plasma-catalytic degradation mechanism is: (i) dye molecules adsorption, (ii) degradation on the surface and finally, (iii) desorption as intermediate products
16 [135]	TiO ₂	Pulsed liquid discharge, V: 14 kV, F: 150 Hz, O ₂ Q: 100 L h ⁻¹ , t: 18 min	4-Chlorophenol, Vo: 0.1 L, C: 100 ppm, m: 0.05 g L ⁻¹	Without catalyst 74%; 0.42 g (kW h) ⁻¹ With catalyst 90%; 0.51 g (kW h) ⁻¹	Electrical discharge process had no influence on the crystal structure of TiO ₂
17 [41]	Fe ²⁺	Pulsed hybrid gas–liquid discharge, V: 45 kV, O ₂ Q: 24 L h ⁻¹ , t: 20 min	2-Chloroethyl phenyl sulfide, Vo: 0.55 L, C: 100 ppm, m: 27 ppm	Without catalyst 53%; 0.24 g (kW h) ⁻¹ With catalyst 88.6%; 0.41 g (kW h) ⁻¹	With mathematical model–data comparison, simulant removal was complete
18 [63]	Fe ²⁺	Rod-cylinder DBD, V: 14 kV, F: 50 Hz, air Q: 6 L h ⁻¹ , t: 25 min	Crystal violet, V: 0.1 L, C: 100 ppm, m: 0.2 g L ⁻¹	Without catalyst 89%; 17.8 g (kW h) ⁻¹ With catalyst 93.7%; 18.7 g (kW h) ⁻¹	‘OH attack Fenton-type reactions acted as an additional ‘OH source
19 [71]	Fe ²⁺	Coaxial cylinder DBD, V: 17 kV, F: 200 Hz	Reactive Black 5, Vo: 2 L, C: 40 ppm, Q _L : 210 mL min ⁻¹ , m: 5 ppm	Without catalyst 74%; 0.79 g (kW h) ⁻¹ With catalyst 83%; 0.89 g (kW h) ⁻¹	Long lived active species led to complete decolorization after 24 h residence time with adding Fe ²⁺
20 [83]	Fe ²⁺	Gas/liquid gliding arc discharge, P: 230 W, air Q: 204 L h ⁻¹ , t: 76 min	4-Chlorophenol, Vo: 0.2 L, COD: 1679.2 mg O ₂ L ⁻¹ , Q _L : 10.5 mL min ⁻¹ , m: 40 ppm	Without catalyst 89%; 1.02 g (kW h) ⁻¹ With catalyst 94.6%; 1.09 g (kW h) ⁻¹	With iron, H ₂ O ₂ were catalytically transformed into ‘OH resulting in complete pollutant degradation
21 [99]	Fe ²⁺	Submersed glow discharge electrolysis, V: 600 V, I: 137 mA, t: 10 min	Alizarin red S, Vo: 0.25 L, C: 30 ppm, m(Na ₂ SO ₄): 2 g L ⁻¹	Without catalyst 14%; 0.08 g (kW h) ⁻¹ With catalyst 100%; 0.547 g (kW h) ⁻¹	Phthalic acid and carboxylic acids were produced in the decoloration process
22 [104]	Fe ³⁺	Diaphragm glow discharge, V: 900 V, I: 110 mA, t: 30 min	Phenol, Vo: 0.25 L, C: 300 ppm, m: 60 ppm, Na ₂ SO ₄ 4 g L ⁻¹	Without catalyst 70%; 1.06 g (kW h) ⁻¹ With catalyst 95%; 1.45 g (kW h) ⁻¹	Fe ³⁺ showed a better catalytic effect than Fe ²⁺ because of Fe ³⁺ oxidizing the phenol intermediates
23 [141]	Cast iron scrap	Pulsed liquid discharge, V: 25 kV, F: 140 Hz, O ₂ bubbling, t: 36 min	4-Chlorophenol, Vo: 0.5 L, C: 100 ppm, m: 15 g	Without catalyst 70%; 1.1 g (kW h) ⁻¹ With catalyst 90.5%; 1.4 g (kW h) ⁻¹	Micro-cells were formed in negative electrode inducing Fenton reactions

Table 2 (continued)

No./refs.	Type of catalyst	Plasma properties	Target properties	Removal efficiency; energy efficiency	Notes
24 [142]	Fe ²⁺	DBD, P: 120 W, t: 0.5 min	Diuron, Vo: 0.01 L, C: 23 ppm, m: 30 ppm	Without catalyst 70%; 0.16 g (kW h) ⁻¹ With catalyst 97%; 0.22 g (kW h) ⁻¹	The input power intensity, initial pH value and loadings of H ₂ O ₂ and Fe ²⁺ all strongly affected the diuron degradation efficiency
25 [148]	Fe ²⁺ /Fe ³⁺	Contact glow discharge electrolysis, V: 500 V, I: 100 mA, t: 4 min	Bisphenol A, Vo: 0.15 L, C: 100 ppm, m: 74 ppm/18 ppm	Without catalyst 6%; 0.27 g (kW h) ⁻¹ With catalyst 52%/95%; 2.3/4.3 g (kW h) ⁻¹	Fe ³⁺ exhibits a better catalytic effect than Fe ²⁺ for dye decoloration
26 [149]	Fe ²⁺	Pulsed liquid discharge, V: 25 kV, F: 60 Hz, t: 70 min	Phenol, Vo: 0.1 L, C: 50 ppm, m: 45 ppm	Without catalyst 59%; 0.05 g (kW h) ⁻¹ With catalyst 87.4%; 0.077 g (kW h) ⁻¹	Gas and catalyst have great influence on intermediate products and degradation mechanism

(1) V: input voltage; F: input frequency; I: electric current; P: input power; Q: gas flow rate; Q_L: liquid flow rate; t: treatment time; Vo: liquid volume; C: concentration; m: amount of addition.

(2) The energy yield of the degradation was calculated from: $Y(g(kW h)^{-1}) = \frac{C_0(L^{-1}) \times V(L) \times \eta_{removal}}{P(kW) \times t(h)}$, where $P(kW)$ is the input power.

For example, pulsed electrical power can be applied for several discharge types such as corona discharge, DBD and gliding arc discharge, due to its high ionization efficiency and low energy consumption [109–111]. And the electrical generators are normally DC rather than AC for arc water plasma discharge because of its less flicker generation and noise, a more stable operation and a minimum of two electrodes etc. [15].

For given solutions to be treated, it required great intelligence to choose the most suitable plasma technology. It is advisable to apply lower-energy corona and glow discharge processes for treating organic contaminating with low concentrations. For high concentrations of organic compounds in the liquid phase, DC arc plasma or gliding arc plasma may be more effective [84,107]. Hybrid gas–liquid reactor and aerosol reactor are especially effective for degrading gas and liquid phase pollutants simultaneously [49,54]. As for pulsed or DC pulseless corona discharge, they can readily be applied to treat the water of the low electrical conductivity because of a higher efficiency of radical formation. While DC glow discharge maybe the first-rank option for high conductivity water remediation.

3. Plasma for wastewater remediation

3.1. Combined with catalysts

As discussed above, plasma technology is an efficient alternative for wastewater remediation with in situ generation of active species, especially hydroxyl radicals. For example, when hydroxyl radicals are present for pollutant abatement, all other slower oxidation routes (e.g., O₃ and H₂O₂) are 'shunted' or even by-passed. Thus, many efforts have been devoted to improve energy efficiency in plasma degradation processes. Table 2 summarizes many typical studies of plasma technology for organic removal with various catalyst additions.

3.1.1. Carbon materials

Due to their excellent adsorption and specific catalytic properties, carbon materials have been widely used as adsorbents and can give rise to the possibility of catalytic oxidation reactions in the oxidizing environment [112,113].

It is widely known that electrical discharge plasma produced oxidizing environment containing H₂O₂, O₃ and other species in reactor, which is desirable for heterogeneous catalytic reaction of activated carbon (AC). Grymonpré [114,115] initially introduced activated carbon into pulsed streamer-like plasma degradation system for phenol oxidation leading to enhancement of the overall removal of organic as compared with the electrical discharge alone as provided in Table 2. With considering the balance of total carbon in these proceeds, it can be inferred that catalytic reactions occurred on the surface of the carbon and activated carbon particles acted as the concentrated centers of pollutant providing more choice for pollutant abatement.

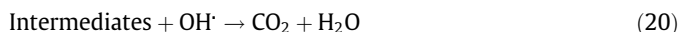
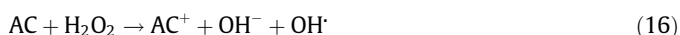
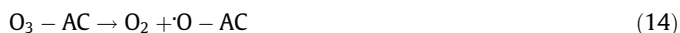
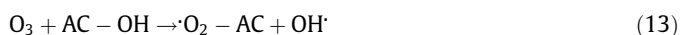
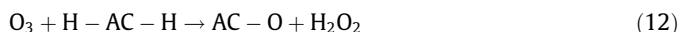
Afterwards, many groups coupled activated carbon materials with pulsed electrical discharge technologies and intensively investigated the synergistic behavior of these processes for organic removal [116–118]. In previous study [116], we know that activated carbon source pose effect on organic removal in plasma reactor. And coal-based activated carbon expressed superior enhancement performance with decoloration efficiency of 96.3% and COD reduction of 91.3% by comparison with coconut shell-based granular activated carbons.

Besides, physical or chemical surface modifications for activated carbon also play important roles on its catalytic effect coupling with plasma degradation. Hao et al. [117] used HNO₃ oxidation and N₂-thermal treatments to adjust the textural and

surface chemistry properties of activated carbon sample. And it was reported that N₂-heated activated carbon had high adsorption capacity of parachlorophenol and high catalytic activities for H₂O₂ and O₃ decompositions resulting in more amount of organic abatement.

In these combined processes, activated carbon samples can physically and chemically adsorb both organic compounds and oxidizing molecules (O₃ and H₂O₂) due to its high surface area and abundant surface functional groups. The activated carbon can be regarded to function as an electron-transfer catalyst just like the Haber–Weiss mechanism involving the reduced and oxidized catalyst states, which can catalytically react with H₂O₂ molecules for hydroxyl radicals generations [119]. When reacting with O₃ in aqueous solution, electrons of the graphenic layers (basal plane electrons) and basic surface groups of activated carbon can also accelerate ozone decomposition resulting in the formation of hydroxyl radicals [120]. As a result, produced OH[•] attacked the accumulated organic into intermediates and finally into harmless products such as H₂O and CO₂.

Above, the possible mechanisms of heterogeneous degradation are proposed in reactions (12)–(20) (M is an organic molecule) [117,119,120].



These surface reactions imply that the combination of electrical discharge plasma and activated carbon would result in a self-regenerating process. And it has been proved that DBD plasma was an applicable alternative for simultaneous organic degradation adsorbed on activated carbon and exhausted saturated activated carbon [121–123].

As a novel porous activated carbon, activated carbon fibers (ACFs) were also applied in plasma systems, the similar conclusions were drawn with activated carbon and more advantages are visualized in combined processes, which were justified in previous studies [124,125].

In addition to activated carbon materials utilized as catalytic-adsorbents in above plasma technologies, some other carbon materials, e.g., multiwalled carbon nanotubes and mesoporous carbon gels, were also applied in DC pulseless corona discharge processes [55,126]. For example, Sano et al. [55] manufactured a cylindrical anode (Fig. 2b) consisting of multiwalled carbon nanotubes with a surface area approximately 332 times larger than that of the bare stainless steel anode. When cobalt nanoparticles were loaded onto these MWCNTs, the performance of a corona discharge reactor was significantly improved due to catalytically generating more OH radicals.

Above, activated carbon addition can favor adsorption removal and catalytic degradation of pollutant in plasma systems. However, much more researches are required on the interactions of activated carbon with the contaminant with various hydrophobic or

hydrophilic nature, molecular polarity and size, etc. in plasma systems and the influence of electrical discharge on the properties of activated carbon. Besides, in view of the lowest expenditure for these processes, these materials as powder or granule should be separated immediately after water treatment and recycled sequentially. Therefore, some auxiliary facilities need to be designed to match the plasma reactors from the aspects of industrial requirements.

3.1.2. Metal oxide

Nano TiO₂ is the most common semiconductor due to its availability, low cost, high chemical stability, and zero toxicity [127]. The high voltage discharge zone can play as the lamp-house to induce the photocatalysis of TiO₂. For example, Ching et al. [128] estimated the UV light intensity generated by the pulsed electrohydraulic discharges of the order 10⁶ W cm^{−2} with the input energy per pulse of 2 kJ and determined the UV radiation as the dominant agent in *Escherichia coli* disinfection. Many reports concerning plasma-photocatalytic processes have addressed that TiO₂ poses greatly favorable effect for the decomposition of organic pollutants in liquid media in detail [38,76,77,101,129–136].

In plasma-photocatalysis process, the high electric field is thought to be able to prevent recombination of electrons with holes on the surface of TiO₂, which could improve the quantum effect of photocatalysis [130]. Furthermore, ultrasound and shock-wave generated in electrical discharge process can clean and sweep of the TiO₂ surface and enhance the mass transport of the reactants to the solid surface allowing for more active catalyst sites participating in the heterogeneous catalytic reactions. Accordingly, the combination of plasma technologies and photocatalysis may synergize the advantages of their treatment performance, while overcome their respective limitations.

Particularly strong UV emission can be produced by arc discharges, and spark, gliding arc and dielectric barrier discharges can also generate available UV light in plasma-catalytic processes [12]. As shown in Table 2, more efficient removals of organic compounds from aqueous solutions treated by pulsed discharge, gliding arc discharge and DBD has been demonstrated with the presence of TiO₂ compared to the cases without TiO₂ in the solution. The contribution of TiO₂ for pollutant removal in the electrical discharge system can be validated with measuring the concentrations of reactive species such as OH, O radicals and H₂O₂ [38,136]. For instance, the relative emission intensities of OH (313 nm) and O (777 nm) radicals in distilled water with the presence of TiO₂ were 1.7 and 3.8, respectively times as great as those of TiO₂ absence, indicating that plasma-photocatalysis system produced much more active species as compared with plasma alone system [38]. And with analysis of pollutant intermediates, it was inferred that the oxidation by OH radical was the dominant process in the liquid-phase plasma systems combined with the TiO₂ catalyst [135,136].

In plasma-catalytic processes, bubbling O₂-containing gas into plasma-catalysis systems is necessary. Because dissolved O₂ as electron acceptors can react with e[−] so that produces superoxide radical (·O₂[−]), which can further undergo successive one-electron reduction to produce desirable OH[•] for nonselective oxidations and then additional H₂O₂. The photocatalytic redox reactions are delineated as the following:





A positive dependency of degradation efficiency enhancement on the concentration of slurry TiO_2 holds within a certain extent. While excessive amounts of TiO_2 particles (leading to a high turbidity state) create screening effects which will not only block the organic molecules from receiving the ultraviolet light generated from discharge zone but also reduce the light photon absorption efficiency for TiO_2 . In addition, slurry TiO_2 plays the part of a barrier for the initiation and propagation of the electrical discharge in the cases of electrical discharge occurring in liquid phase. The optimum concentration of slurry TiO_2 used in plasma degradation system is determined by many factors such as the working conditions (e.g., input energy intensity, reactor geometry), characteristic of catalyst (e.g., catalyst size distribution) and target organic characteristic (e.g., properties and concentration of the pollutant) as well as gas/water hydrodynamics. For instance, optimum amount of 2 g L^{-1} TiO_2 was necessary for maximum decoloration of anthraquinonic acid green 25 in gliding arc discharge reactor after 60 min [77]. While for the decoloration of acid Orange 7, the optimum amount was 0.6 g L^{-1} and almost 100% dye decoloration efficiency was obtained in corona-steamer type reactor at the parameters of 27 kV peak pulse voltage, 70 Hz repetitive frequency, and 45 min treatment time [130].

In the technical perspective, direct utilization of suspended TiO_2 powder in plasma reactor may be problematic owing to the difficulties of recovery and separation of the nano particles. To overcome this problem, a thin film of photocatalyst can be deposited on a support inside the reactor, which will be in direct contact with effluent stream and indirectly irradiated by the ultraviolet light generated from discharge zone.

Zhang et al. [137] applied TiO_2 nanotube film in a streamer discharge system to evaluate the performance of synergistic plasma/photocatalysis action for phenol degradation. The results presented that the rate constant of phenol degradation for pulsed discharge/ TiO_2 system was 2.5 times larger than that in the pulsed discharge alone system with 20 kV voltage input. At the same time, the efficiency was still at high level even after 6 cycles and therefore the technical barrier of post-recovery of the catalyst particles was compensated.

Recently, TiO_2 film can be novelty in situ generated on Ti anode via micro-arc discharge in glow discharge electrolysis [101]. When electrical discharge enters the non-Faradaic area, the insulating TiO_2 film is broken into the bulk solution realizing the process of electrode catalysis and electrolyte catalysis. Thus, glow discharge electrolysis combined with this photocatalysis system creates a mutually coupling and self-exciting system showed the synergic effects for pollutant removal as shown in Table 2, which is a promising alternative for practical application.

However, for wastewater remediation, it is necessary to develop continuous reactors rather than batch reactors because of large quantities of effluents to be treated. The plasma- TiO_2 film catalyst hybrid process in a falling film DBD reactor has been applied for continuous solutions treatment of pollutant phenol, oil hydrocarbons and synthetic surfactants [69,133]. The experiment results showed that decomposition efficiency for 0.533 mM phenol solution can reach up to 95% at input power of approximately 9 W and resistance time of 120 s [133]. This process provided not only a high level of phenol, resorcin, pyrocatechol and hydroquinone decomposition but also a high degree of their conversion into small toxic and non-toxic products such as carboxylic acids and carbon dioxide.

In consideration of catalytic enhancement efficiency of TiO_2 in plasma system, TiO_2 mounted on activated carbon can significantly improve the decomposition of phenol adsorbed on activated carbon and the simultaneous regeneration of the saturated activated carbon [138].

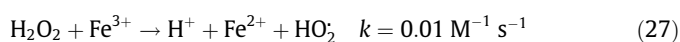
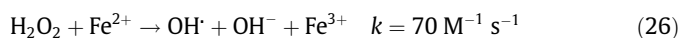
In many literatures [139,140], some other oxides, e.g., Fe_3O_4 , NiO and Ag_2O were also applied for assessing the synergistic effect for organic abatement in plasma system. Although these powder catalyst can also pose positive effects for organic substances decomposition than that of plasma alone treatment, they gain little attention due to their less popularity in water treatment than photocatalyst TiO_2 .

3.1.3. Metal ions

For electrical discharge, a large number of the short-lived active species such as OH^\cdot , H^\cdot , and O^\cdot radicals, and strong UV emission are primary confined in the discharge zone by liquid–gas boundary [5]. As we know, the intermediates of the plasma oxidation are primary hydrophilic acids [141,142], which are limited with direct diffusion into the highly hydrophobic zone of the gas–liquid interface where highly reactive species are dominant [143]. In efforts to improve the efficiency of plasma oxidations, addition of ferrous salt in plasma system is an attractive alternative arising from the fact that adding iron salts can catalytically transform formed H_2O_2 into hydroxyl radicals via Fenton reactions [144]. In addition, the Fenton reaction in plasma system can be activated by self generated “white light” containing wavelengths from 200 nm in the UV range to 1000 nm in the infrared range.

Since pioneering work was published by Sharma et al. [145], who first reported the enhanced phenol degradation by adding iron in pulsed liquid corona discharge due to Fenton’s process. The combined processes of electrical plasma and Fenton reaction based on the plasma generation of H_2O_2 are being comprehensively studied for the treatment of acidic wastewater containing organic [41,43,63,71,74,79,98,114,146–151]. As summarized in Table 2, when introducing Fenton reagents into the various electrical discharge systems, Fenton reactions happen in plasma system and thereby enhance the efficiency of the plasma chemical removal of organic compounds from water. And it is obvious that compared with other plasma systems, DC glow discharge systems provide a much more desirable conditions for Fenton reactions due to its larger yields of H_2O_2 , which lead to a significant enhancement for pollutant abatement [99,104,148].

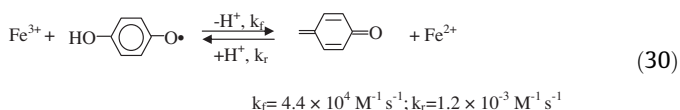
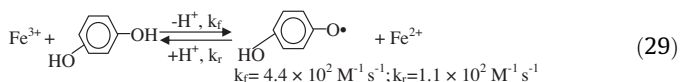
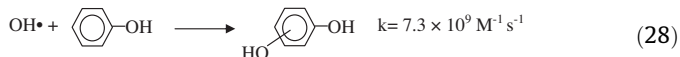
Fenton reactions involve the transformation reactions between Fe^{2+} and Fe^{3+} , therefore they both may express remarkable catalytic effects on organic removal coupled with plasma technology [144]. When Fe^{2+} was added into the plasma system for organic oxidation, Fe^{2+} can directly involve in the catalytic composition of hydrogen peroxide into hydroxyl radicals in Eq. (26). Whereas Fe^{3+} as Fenton reagent source initially was transformed into Fe^{2+} consuming massive plasma-generating hydrogen peroxide as Eq. (27) [92].



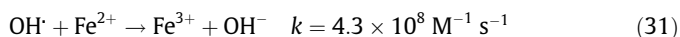
Consequently, less additional hydroxyl radicals can be generated through Fenton reactions leading to inferior treatment performance of Fe^{3+} to that of Fe^{2+} [146,151,152].

However, a contradictory result was observed that the efficiency of Fe^{3+} expected for catalysis was much better than that of Fe^{2+} for aromatic organic substrate abatement in glow discharge plasma system [88,92,148,153–156]. For example, phenol removal increases from approximately 15% for plasma alone to 55% with the presence of 186 mg L^{-1} Fe^{2+} within 10 min. While 90% phenol removal can be achieved within the same time in the presence of 186 mg L^{-1} Fe^{3+} [92]. It can be interpreted that the hydroxycyclohexadienyl-like radicals produced from the attack of hydroxyl radicals to phenol (Eq. (28)) may reduce Fe^{3+} indirectly through the catalytic mediation of hydroquinones and semiquinones

(Eqs. (29), (30)) [151,157]. These reaction rates present much faster reduction of Fe^{3+} than a slow rate-limiting reduction of Fe^{3+} by H_2O_2 (rate constant $0.01 \text{ M}^{-1} \text{ s}^{-1}$), which intensify Fenton reactions with Fe^{3+} as original additives. Besides, quinone intermediates shuttle electrons from the hydroxyl radical adduct of the starting aromatic compound to Fe^{3+} , thus facilitating the degradation of the starting aromatic compound [157].



In Fenton reaction system, excessive Fe^{2+} can act as hydroxyl radical scavengers via the reaction with rate constant of $4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ as below:



As a result, the optimum of Fe ions addition should be determined and is an essential parameter for synergistic effect of combined processes [71,146].

Afterwards, Bian et al. [141] applied cast iron scrap as high voltage electrode materials which contains about 2–4.5% carbons and can produce iron–carbon internal electrolysis in pulsed electrical plasma system. In the combined system of plasma and internal electrolysis, it was found that the internal electrolysis reactions can be strengthened in acid solution due to the enhancement of Fenton reaction. And reactions mechanism of the internal electrolysis system is depicting as follows [141]:

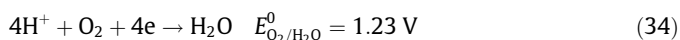
At anode:



At cathode: in the absence of oxygen:



in the presence of oxygen:



Although additional Fenton reactions offer a cost-effective source of hydroxyl radicals in plasma systems, there are still some confines that limit the wide application of this combined technology: (i) being efficient only for acid water ($\text{pH} < 5$), (ii) the auxiliary equipments for recovery of iron ions are necessary after treatment.

3.1.4. Other catalysts

Apart from above catalyst additions, some other substances such as powdered oyster shells, silica gel beads, zeolites and pyrite, were also applied in plasma systems [40,80,158–162]. For example, the powdered oyster shells acting as a catalyst and an acidity control agent can be incorporated into plasma treatment processes for pollution control of surface waters [80,160]. The coupled processes induced large COD and BOD abatements, which may be attributed to the limited decreasing pH and associated to buffer effects which accounted for the acid-base reaction between the treated liquid sample and the incorporated basic solid and to its adsorption properties which enables concentration of the pollutants.

3.2. Factors affecting plasma efficiency

The plasma technologies are intricate involving in many different electrical discharge processes, which own their specific physical or chemical characteristics. Thereby, some factors in question below may behavior different to some extent in various electrical discharge processes. For instance, as for solution conductivity, it may pose less impact on plasma chemistry in gas gliding arc discharge or DC arc water discharge. Consequently, specific behaviors of these factors need specific analysis in various plasma cases. To intensively illustrate the effects of these factors on pollutant removal, pulsed electrical discharge technologies are provided as a typical case to be discussed in this part.

3.2.1. Reactor system

Usually reactor geometry design should be such that as much as possible energy utilization and contact surface of plasma and water are obtained at a given energy input.

The pulsed electrical plasma reactors are usually made-up of glass/Perspex as rectangular parallelepiped [37,163], vessel [40,44,115,137,141] or reaction column type reactor [43], which are operated in batch [141,150], circulating [35,37,43] or continuous-flow mode [43,46,163]. Batch mode vessel reactors are representative types for lab study due to their high operational stability. As compared with batch mode, circulating and continuous-flow mode reactors can provide large reaction surface for plasma species and liquid displaying superiority in large scale application. Especially for the continuous flow mode reactors, multiple units can be combined in a sequential manner, which increases residence time and thereby enhances the treatment efficiency after one pass.

Additionally, water inletting method has a big impact on the surface-to-volume ratio of water with air, a parameter that has a significant impact on the mass transfer coefficient and thereby energy efficiency. For example, compared with batch reactor with gas corona discharge, a rectangular shape reactor with water flowing as a much thinner layer has roughly an order of magnitude larger surface-to-volume ratio [34,37]. What is more, spraying the water into the aerosol reactor further increases the surface-to-volume ratio by roughly three orders of magnitude in comparison with the above rectangular shape reactor, leading to even shorter treatment time and higher conversion, as had been expected [46]. It is illustrated in Table 1 that the corresponding energy efficiencies of above three reactors are 0.13, 2.97 and 13 g (kW h)^{-1} , respectively.

In electrical discharge processes, vent gas from the reactor contains much unused active species. Thus installing a gas re-circulation or reutilization system can favor the increase of energy efficiency [35,46]. For example, incorporation of gas re-circulation leads to an increase in phenol removal from 15% up to 42% for a corona operated in ambient air with electrical power of 20 W using the aerosol reactor [46].

3.2.2. Electrode

During the electrode design process the main goals, which had to be considered, are large electrical discharge zone and good matching with reactor.

Normally, two asymmetric conductive materials are applied for electrodes in pulsed discharge system, and the high curvature electrodes basically determine the plasma formation. In the industrial perspective, one-dimensional electrodes (e.g., wire) can create larger and more uniform distribution plasma zone than zero-dimensional electrodes (e.g., needle and pin) as demonstrated in Table 1. In addition, it has been demonstrated that multiple electrodes display superior treatment performance [164]. As for the applied number of electrodes, it is mainly dependent on power input, reactor configuration and processing load.

It should also be noted that the gap distance between the electrodes is significant for plasma generation. The discharge inception voltage can be reduced with narrowing the gap dimension of electrodes due to an increasing electric field. But too narrow gap distance certainly will diminish the volume of plasma generation zone. Therefore, there is an optimum gap distance for electrical plasma formation at a given voltage input in the decomposition of the target pollutants [52,73,164].

Moreover, electrode materials are demonstrated to have significant effects on plasma chemical processes in water via substance sputtering from electrodes into the water. For instance, platinum and tungsten as high-voltage electrodes decreased the yield of H_2O_2 produced by a pulsed corona discharge in water [165,166]. At the same time, these materials, when used as high-voltage electrodes, increased the efficiency of plasma chemical removal of organic compounds from water due to their catalytic effects [14,147,166].

When the electrode is coated with a thin ceramic layer, the electric field strength on the electrode surface may be enhanced by concentration of the pre-discharge current in small open pores [167,168]. As a result of the inhomogeneous nature of the ceramic layer, the electric field may be higher and easier to initiate streamers from some spots than that expected. Such a system can be simply scale-up and the porous ceramic material may also be promoted with its catalytic activity or designed as a support for a suitable catalyst of the plasma chemical reactions.

3.2.3. Energy input

The nature of the plasma oxidation has outlined the dependency of the overall organic degradation rate on the energy input in a specific range [35,150,164]. To satisfy various needs of experiments, energy input can be varied either by changing the voltage or the frequency introduced into the discharge system. Normally the higher the electron density, the more densities of OH^\cdot , O^\cdot , HO_2^\cdot , H_2O_2 and O_3 are produced [3,11,169]. Besides, higher energy input favors more intense physical effect, which is greatly favorable for pollutant removal. For example, Lukes et al. [170] quantitatively obtained the relationship between photon flux ($J_{190-280}$) and discharge pulse mean power (P_p) in pulsed corona discharge in water with needle-plate electrode geometry as follows:

$$J_{190-280} = 44.33P_p^{2.11} \quad (35)$$

Normally, you can obtain the best pollutant degradation efficiency or highest energy yield, but not both [35,110,130,163,164,171]. Thus, according to the different treatment requirements of the contaminated water, it is required to weigh the above two indexes, degradation efficiency and energy yield.

3.2.4. Solution pH

The solution pH significantly affected the plasma chemistry properties during the electrical discharge process. Analysis of optical emission spectra indicates that the OH^\cdot emission intensity generated by the pulsed streamer discharge is pH-dependent and increases when neutral and alkaline conditions are used [169]. Thagard et al. [172] also reported that the formation of hydrogen peroxide in either gas phase or liquid phase depends on solution pH.

Besides, there are acid base equilibriums between various plasma species, which finally impact degradation reactions of aqueous pollutant. Hydroxyl radicals, as one of the most oxygen-based oxidizers, can be rapidly converted to O^- in strongly alkaline solution, which exhibits substantially different chemical reactivity from OH^\cdot . And in reaction with organic molecules, OH^\cdot acts as an electrophile, while O^- is a nucleophile, leading different intermediates and thus distinct reaction pathway [11].

Furthermore, the acid–base equilibrium of organic molecules dependent on pH also influences significant on degradation potential of organic molecules. In the cases of phenol degradation, the basic form of phenol is more reactive than the associated acidic form because the electron liability of the π bonds in the phenol aromatic ring is enhanced. It has been justified by Li et al. who reported that superior phenol removal efficiency was achieved at pH 10.2 using a gas–liquid phase pulsed discharge plasma reactor [171]. This viewpoint can be used to explain the fact that quite different optimal pH required for various pollutant treatment using plasma technologies [99,150].

3.2.5. Temperature

Chen et al. [173] studied the phenol decomposition in a batch electrical liquid discharge reactor with oxygen bubbling and reported that a lower water temperature tended to significantly increase the degradation rate. And our previous research also illuminated that preferable decoloration of methyl orange can be attained at low temperature using gas discharge plasma technology [35].

In plasma oxidation processes, hydroxyl radical is the prominent agent. So it was proposed that the concentration and the live time of radicals are two main factors influencing the decoloration efficiency [97]. According to Arrhenius equation, higher temperature leads to larger rate constant. Thus hydroxyl radical can be quickly quenched by ambient substances, such as H_2O molecules due to its higher concentration than pollutant target. In view of this, increasing temperature finally causes a decreasing degradation rate.

When it comes to the plasma oxidation processes with ozone generation, the ozonation efficiency may be also temperature dependent. Henry constants (gaseous pressure to aqueous mole-fraction) of ozone vary at different temperatures, for example, 3550, 3930, and 4530 atm^{-1} for 15, 20, and 25 $^\circ\text{C}$, respectively [55]. As a result, lowering the water temperature in the observed range can lead to enhanced absorption of ozone into water favorable for organic abatement.

3.2.6. Gas input

In a pulsed discharge system, O_2 -containing gas injection would induce the production of O_3 and other O-based active species that can boost OH^\cdot production and together with OH^\cdot significantly enhance degradation rate of organic compounds. With efficiency comparisons among various feeding gases, it has been widely demonstrated that the first-rank treatment performance was assigned to oxygen as the feeding gas, in turn followed by air and argon, and the least for nitrogen [39,47,149,169,173,174].

One should be noticed that, when nitrogen-containing gases are exposure to electrical discharge, electrical discharge can give enough energy to dissociate nitrogen molecules into nitrogen radicals [175]. With the presence of oxygen in this process, reactive atoms or radicals such as N^\cdot , O^\cdot , H^\cdot and OH^\cdot would be formed and recombine either among themselves or with initial molecules (N_2 , O_2 , H_2O , etc.) inducing new products, such NO_2 , HNO_2 and HNO_3 . These nitrate and nitric products dissolving in water can induce a steep pH lowering of the solution and an increasing of conductivity as well as participate in various reactions. Kornev et al. [176] found that only nitrates with concentrations from 0.4 to 0.8 mg L^{-1} were detected when potable water treatment was treated with pulsed corona discharge at given energy inputs of about 50 to 100 W h m^{-3} in air atmosphere. This value was substantially lower than maximum permissible concentration (MPC) for nitrates in potable water.

In some liquid electrical discharge processes, external gases injected into the reactor are bubbling through the discharge zones, which thereby transform liquid discharge into discharge in bubbles. The gas bubbles in discharge region can facilitate higher-energy electron production resulting in creating more radicals

and affect the generations of UV light and hydrogen peroxide [24]. In the cases of bubbling oxygen or air through the electrode needles at high potential, the ozone formed in bubbles can directly transfer into the liquid enhancing oxidation reactions. Additionally, bubbling gas can create turbulent flow in reactor resulting in homogeneous pollutant distribution and alleviating mass transfer resistance.

3.2.7. Conductivity

Liquid conductivity is one of the important parameters to influence the discharge characteristics and therefore production of active species in plasma [169].

In pulsed liquid discharge processes, the discharge mode changes from spark discharge to spark-streamer, and then from spark-streamer to corona discharge with increasing conductivity [177]. Decreasing the conductivity of the solution can cause an increase in streamer length and upon streamers reaching the counter electrode a spark discharge is induced. A spark discharge can provide a more reactive environment than a streamer corona discharge because high-energy particles, UV radiation, shockwaves and supercritical water simultaneously cause pyrolytic and free radical reactions in and around the plasma channel. As the conductivity rises, the discharge gradually becomes stronger and in turn the OH[•] intensity increases with a maximum at conductivities between 10 and 80 $\mu\text{S cm}^{-1}$ [169]. But higher conductivity results in larger discharge current, more intensive UV light and higher plasma temperature, unfortunately, leads to lower rates of formation of active species [5]. With weighting the contributions of plasma chemistry and physic for pollutant removal, it can be gotten that high conductivity is not desirable for applying pulsed electrical discharge technology for water treatment [35].

In the case of electrical discharge directly over the water surface, solution conductivity has an important role in the nature of the discharge channel propagation along the surface, the channel length and current. As the conductivity increases, with fixed gap discharge, brushlike discharge channels propagating along the surface of the liquid become thicker, brighter, and shorter [178]. The values of emission spectra intensity for H, OH and O radicals indicate that formations of plasma species are quantitatively influenced by the conductivity and electrolyte. For the H_3PO_4 electrolyte, OH radical intensity goes through a maximum, after which, with a further increase in conductivity, starts to decay. On the other hand, intensities of H radical and O radical show a continuous increase in intensity with an increase in conductivity [172].

One obvious action by some chemical inorganic ions, e.g., CO_3^{2-} , HCO_3^- , PO_4^{3-} , NO_2^- and Cl^- , is control of the solution conductivity. One must also consider that these ions are well known scavengers to quench OH radicals [131,179,180]. These ions can react with OH[•] rapidly to form certain non active products and terminate the whole radicals reaction course.

For example, it can be seen in literature [131] that energy efficiencies for phenol removal reduce dramatically with the increase of Na_2CO_3 concentrations in both plasma alone and plasma-photocatalysis process. From this perspective, in plasma treatment process with free-radical attack as the controlling mechanism, pretreatment with the aim of removing these scavengers may be prerequisite for high treatment efficiency.

3.3. Target compounds

With the aim of preserving the aquatic environment, plasma technologies of bench-scale or pilot-plant have been developed for organic wastewater remediation. Most of studies placed emphasis on simulant organics destruction such as pesticides, dyes, pharmaceuticals and phenolic compounds, and demonstrating the viability of plasma for wastewater treatment.

For industrial application, many literatures have also paid attention to the viability of electrical plasma technology for the treatment of real wastewaters, e.g., city rain sewage [69], textile wastewaters [76,78], surface waters [80], brewery effluents [181], coke-oven wastewater [182]. Some peculiarities of these wastewaters are the high level of COD and complex mixture of a large variety of constituents. For example, stream from industrial centre is released with a pH 4.2–4.9, COD as high as 1195 mg L^{-1} and BOD_5 up to 928 mg L^{-1} at a turbidity of 245.4 mg L^{-1} SiO_2 , containing up to 480 g L^{-1} of total dissolved solids and 740 g L^{-1} of suspended solids [181]. Thus the treatment of such complicated wastewater is a troublesome task and relies on a strategy of coupling various methods to obtain preferable efficiency for its use at an industrial scale.

4. Further researches

The work associated with electrical plasma technology for wastewater remediation can be split into two broad areas, namely, theoretical analysis and experimental studies to explore pathways for transferring the theoretical knowledge into practice. A number of experiment results can be seen in the literatures regarding utilize of electrical plasma for water treatment, few of which on plasma industrial applications are available. So far, the application of such plasma technology for industrial water treatment is still experiencing a series of technical challenges.

(1) Fundamental research of plasma in wastewater treatment.

The plasma reactivity intricately depends on input energy, excitation source (DC, AC and pulse DC, etc.), the gas (where and which gas is used), and the liquid properties (e.g., conductivity, pH, and additives such as salts, ions, particles from the electrodes and catalysts). Thus the generations and evolutions of active species and physical effects in the degradation process need to be further explored to theoretically optimize the plasma treatment processes and systematically explain the plasma oxidation mechanisms.

Additionally, a deeper inspection is required for understanding how electrical plasma interacts with parent pollutant molecules. Usually experiment results available in the literatures are based on the simulated effluents or single-constituent solutions, whereas in the real wastewaters, besides the hazardous organic pollutants, an abundance of impurities are present. With this regard, some doubts are raised that whether plasma oxidation will produce the same destructive efficiencies for the real wastewaters and whether a variety of unexpected intermediates are generated as reported in academic studies.

Furthermore, the researches on the effects of targets properties including solubility, volatility, hydrophobic/hydrophilic nature, thermal stability and diffusivity, etc., should be performed. For instance, it was stated that as for the degradation of volatile target in aqueous solution using the gas–liquid electrical discharge system, the main mechanism would not be a transfer of radicals or ozone from the gas phase to the liquid phase as generally stated but a transfer of the pollutants from the liquid phase to the gas phase where they can react with the active species, especially radicals [70].

(2) Large scale plasma reactor design

Plasma reactor design to satisfy industrial wastewater treatment requirement is considerably complex and difficult. And it should be noted that theoretical information for efficient scale-up of plasma reactor design is also required from diverse fields,

e.g., chemical engineering (gas/liquid hydrodynamics and mass transfer kinetics), materialogy (for construction of electrodes efficiently operating at conditions of high frequency and high voltage input) and electricity (electrical discharge in various reactor configurations).

To improve its commercial availability for full-scale wastewater treatment, plasma technology should undergo a long-term reliability test about its preferable efficiency sustainability and normal working lifetime as well as operation safety.

(3) Combination with other economical technology

The main routes for destroying toxic compounds in wastewater are biodegradation, chemical oxidation and advanced oxidation processes. Biological degradation refers to the elimination of the pollutant by the metabolic activity of living organisms and with its wide applicability for suitable BOD₅/COD (>0.3) economically utilized for industrial wastewater treatment. However, when it comes to biological undegradable effluents, biological degradation unfortunately loses its superiority of efficient and economical water treatment. Plasma technologies as advanced oxidation processes are efficient for mineralization due to the fact that they can continuously generate hydroxyl radicals but generally expensive because of consuming electrical energy.

In light of respective advantages of AOPs and conventional biological process in wastewater remediation, applications of AOPs/biological treatments are gaining popularity since Ollis et al. firstly proposed this integrated technologies [183]. An attractive alternative is to apply plasma processes in a pre-treatment to convert the initially persistent organic compounds into more biodegradable intermediates, which would then be treated in a biological oxidation process with a considerably lower cost. The key issue is to design the process for the best overall economic and ecological performance with weigh each treatment step time for minimizing AOP treatment and maximizing the biological stage as much as possible. Accordingly, some significant issues must be taken into consideration in system design on the wastewater treatment technologies as follows:

- (a) The properties of the wastewater and the target constituents.
- (b) The suitable discharge type and plasma reactors applied.
- (c) Toxicity tests and biodegradability tests of plasma-generated intermediates
- (d) Selection of the efficient biological technology.
- (e) Application of some auxiliary facilities (For example, it is necessary to eliminate the adverse effect of high concentrations of hydrogen peroxide on the microorganisms.
- (f) Assessment of environmental compatibility of the combination technologies.
- (g) Economic estimation.

Generally, it is required to conduct a large number of bench-scale and pilot-plant studies for developing the technologies and generating information on new industrial wastewater treatment processes.

5. Summary

In recent decades, interest in the application of electrical plasma technology for aqueous pollutants abatement has significantly increased. In present review, commonly used atmospheric plasma reactors have been extensively presented and demonstrated effective for decomposing a range of pollutants. When plasma technologies are combined with catalysts, synergetic pollution abatement

results may be achieved and the mechanisms were also discussed. Besides, several factors including reactor system, electrode, input energy, solution pH, gas input, temperature and solution conductivity can influence the performance of plasma systems. Plasma technologies coupled biological treatments seem to be feasible, economic, efficient and prospective methods for the aqueous pollutants removal in industrial scale. But, looking ahead, still many obstacles remain to be surmounted for further research and development in order to meet the industrial demand.

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