

---

TOPICAL REVIEW

## Hybrid electric discharge plasma technologies for water decontamination: a short review

To cite this article: Kefeng SHANG *et al* 2019 *Plasma Sci. Technol.* **21** 043001

View the [article online](#) for updates and enhancements.

## Topical Review

# Hybrid electric discharge plasma technologies for water decontamination: a short review

Kefeng SHANG (商克峰)<sup>1</sup>, Jie LI (李杰)<sup>1</sup> and Rino MORENT<sup>2</sup>

<sup>1</sup>School of Electrical Engineering, Dalian University of Technology, Dalian 116024, People's Republic of China

<sup>2</sup>Department of Applied Physics, Ghent University, Sint-Pietersnieuwstraat 41 B4, 9000 Gent, Belgium

E-mail: [shangkf@dlut.edu.cn](mailto:shangkf@dlut.edu.cn)

Received 28 June 2018, revised 2 January 2019

Accepted for publication 3 January 2019

Published 25 February 2019



CrossMark

### Abstract

Electric discharge plasma (EDP) can efficiently degrade aqueous pollutants by its *in situ* generated strong oxidative species ( $\cdot\text{OH}$ ,  $\cdot\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , etc) and other physiochemical effects (UV irradiation, shockwaves, local high temperature, etc), but a high energy consumptions limit the application of EDP in water treatment. Some adsorbents, catalysts, and oxidants have been employed for enhancing the degradation of pollutants by discharge plasma. These hybrid plasma technologies offer improved water treatment performance compared to discharge plasma alone. This paper reviews the water decontamination performance and mechanisms of these hybrid plasma technologies, and some suggestions on future water treatment technologies based on discharge plasma are also proposed.

Keywords: discharge plasma, plasma/adsorbent, plasma/catalyst, plasma/oxidant, wastewater decontamination

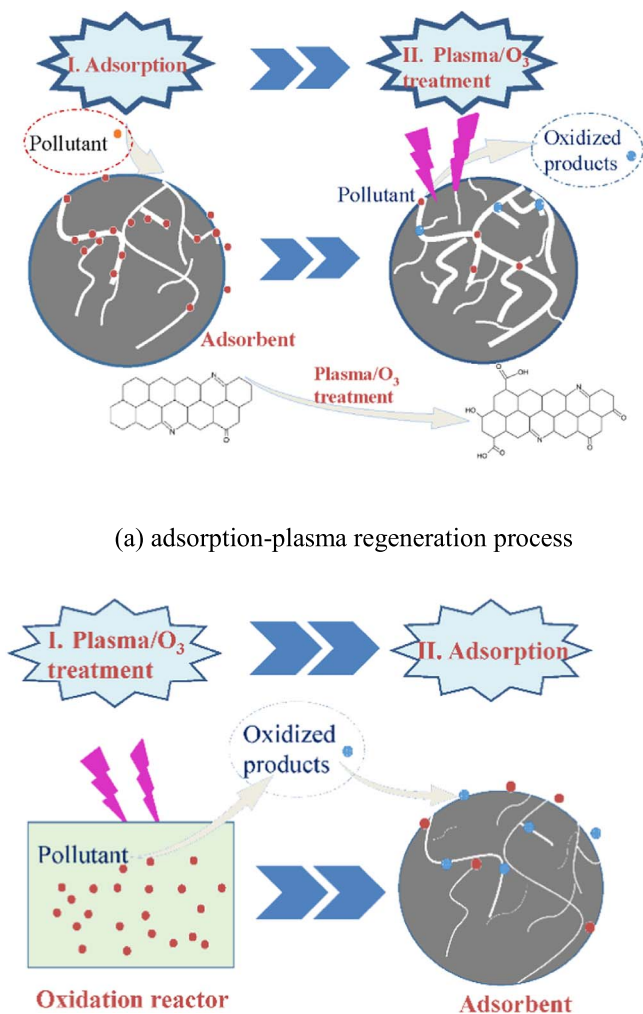
(Some figures may appear in colour only in the online journal)

## 1. Introduction

Synthetic chemicals such as dyes, pharmaceuticals, herbicides, and pesticides, invented for industrial and agricultural applications and human healthcare, have been found in trace amounts in drinking water sources and even in drinking water. These contaminants pose a potential threat to the ecological safety and the health of human beings, and one of the direct source of these contaminants is effluent from wastewater plants into rivers. Advanced oxidation processes (AOPs) including Fenton's reagent,  $\text{O}_3/\text{H}_2\text{O}_2$ , UV/ $\text{O}_3$ , and UV/ $\text{H}_2\text{O}_2$  have been developed to remove persistent organic pollutants from water and wastewater [1]. AOPs *in situ* generate powerful hydroxyl radical ( $\cdot\text{OH}$ ) which non-selectively oxidizes organic pollutants in water, but these AOPs usually consume a lot of chemical oxidants in realizing high mineralization of pollutants. Electric discharge in contact with water *in situ* generates many kinds of reactive species (e.g.

radical species of  $\cdot\text{OH}$ ,  $\cdot\text{O}$ ,  $\cdot\text{H}$ ,  $\text{HO}_2\cdot$ ,  $\text{NO}_2\cdot$ , and  $\text{NO}\cdot$ , and molecular species of  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , and  $\text{H}_2$ ), UV irradiation, and shockwaves, etc [2, 3], and studies have demonstrated that electric discharge plasma (EDP) can efficiently destroy recalcitrant organic compounds, mainly due to its efficient generation of the strongest electron radical oxidant  $\cdot\text{OH}$ .

Nonthermal atmospheric pressure streamer and dielectric barrier discharge (DBD) directly in water or in the gas phase are the most widely used electric discharge types for water decontamination. Direct streamer electric discharge in water with the discharge electrodes immersed in liquid water [4, 5] is conductivity dependent. High water conductivity is adverse for the buildup of local space charges, so a much higher applied electric field of  $\sim 1 \text{ MV cm}^{-1}$  is needed for the electric breakdown of water compared to an  $\sim 30 \text{ kV cm}^{-1}$  breakdown electric field in air at atmospheric pressure [6]. The smaller radius of the curvature of a high voltage electrode (e.g. point/needle electrode configuration) helps in the development of the intense electric



(a) adsorption-plasma regeneration process

(b) plasma/ozonation treatment-adsorption process

**Figure 1.** Schematic of the dual-step plasma-adsorption process.

field necessary for the ignition of electric discharges [7], and bubbling different gases in water also affects the plasma characteristics and plasma chemistry [6]. Streamer electric discharge over a water surface produces reactive species in the gas phase [8, 9], and the filamentary streamers which are initiated in the gas phase develop to and propagate along the water surface which behaves as a dielectric or resistive medium, according to the exposure time of water to an electric field and the specific value of water permittivity to the specific water conductivity [10]. During this process, the reactive species transfer into liquid water from the gas phase mainly through diffusion, so water decontamination efficiency is greatly dependent on the mass transfer efficiency of the reactive species. Instead, water spray type discharge plasma [11–13] has a higher mass transfer efficiency and more efficient gas–liquid interface reactions, and they are also less affected by water conductivity compared to direct electric discharge in high conductivity water. Inserting at least one insulating dielectric between the high voltage electrode and the ground electrode produces the so-called DBD, and the insulating dielectric can efficiently restrain the instability of the streamer discharge and

its transition to spark or arc breakdown, and covering a dielectric around electrodes helps to develop the electric field for ignition of electric discharges, so the treatment of high conductivity water often includes the use of DBD plasma. DBD plasma can be directly produced in contact with water [14–17] and is often also employed for the production of reactive species in the gas phase and then these species are injected into water for the degradation of aqueous pollutants [18, 19].

Although there is disagreement on the aqueous discharge plasma theory and some technological difficulties still exist for its successful application at industrial scales, aqueous discharge plasma technologies and their applications for water decontamination have achieved many valuable results during the past 30 years, and some papers and books have comprehensively reviewed and discussed the development of aqueous plasma chemistry, electric discharge mechanisms, and water treatment applications [3, 6, 7, 10, 20, 21]. EDP technologies show their feasibility for the degradation of various pollutants in water, but an enhancement of the energy efficiency of EDPs and the mineralization of pollutants are very important for the application of EDPs in wastewater treatment. In recent years some novel hybrid processes of discharge plasma coupled with adsorbents, catalysts, and oxidants have been developed to enhance the degradation of pollutants and improve its energy efficiency. This paper reviews the recent developments of these hybrid plasma processes and some suggestions on future water treatment technologies based on discharge plasma are also proposed.

## 2. Hybrid discharge plasma technologies for water decontamination

### 2.1. Plasma/adsorbent technology

Carbon materials, including granular activated carbon (GAC) [5, 22–24], activated carbon fiber (ACF) [25, 26], charcoal [27, 28] are popular adsorbents used in hybrid plasma/adsorbent technologies, and polyamide membrane [29] is also used as an adsorbent of organic compounds. Commercial carbon adsorbent is usually derived from natural coal and biomass through pyrolysis or the gasification process. During the thermal treatment process, the moisture and the volatile components of coal and biomass are removed, and the derivatives with very different porosity, surface area, pore structures, and chemical properties from their parent materials are produced through further activation process. These carbon materials of relatively low density usually possess  $sp^2$  hybridized carbon atoms with a strong cross-linking between them, developing a very good porous structure responsible for their good adsorptive capacity.

Hybrid plasma/adsorbent technologies can be classified into the dual-step and one-step types. The dual-step process separately completes the adsorption procedure of pollutants by adsorbent and the regeneration of adsorbent by discharge plasma (namely, degradation of the pollutants adsorbed on the adsorbent). In general, the adsorption of pollutants on an adsorbent is the first step, followed by an adsorbent regeneration procedure (figure 1(a): adsorption-plasma/ $O_3$  regeneration process) [23, 26]. Some researchers have also studied

**Table 1.** Degradation performance of pollutant by *in situ* plasma/adsorbent.

Pollutants	Plasma	Adsorbent	pH <sub>0</sub>	C <sub>0</sub> (μS cm <sup>-1</sup> )	k (min <sup>-1</sup> )	DE (%)	EY(g kWh <sup>-1</sup> )	Ref.
Acid orange: 20 mg L <sup>-1</sup> , 250 mL	Multi-needle to plate pulsed discharge; 20 kV, 50 Hz	No adsorbent	6.9	12	—	76.7%, 120 min	—	[5]
		GAC 4 g	6.9	12	—	96.1%, 120 min	—	
Atrazine: 30 μg L <sup>-1</sup> , 500 ml	Cylindrical DBD, quartz dielectric; 21 W, 47.8 kHz	AC membrane	5.06	350	0.121	50%, —	3.7 × 10 <sup>-3</sup> (G <sub>50</sub> )	[22]
Triclosan: 10 mg L <sup>-1</sup> , 120 ml	Plate-plate DBD, quartz dielectric; 80 W	No adsorbent	—	—	—	85.1%, 18 min	4.3	[25]
		ACF 1 mm thick	—	—	—	93.2%, 18 min	4.7	
		ACF 2 mm thick	—	—	—	97%, 18 min	—	
Methyl orange: 30 mg L <sup>-1</sup> , 250 ml	Multi-needle to plate pulsed discharge; 20 kV, 60 Hz	No adsorbent	—	—	—	29.2%, 7.5 min	—	[27]
		Charcoal 0.1 g L <sup>-1</sup>	—	—	—	~100%, 7.5 min	—	
		Charcoal 0.3 g L <sup>-1</sup>	—	—	—	69.8%, 7.5 min	—	
		Charcoal 0.5 g L <sup>-1</sup>	—	—	—	~40%, 7.5 min	—	
Atrazine: 30 μg L <sup>-1</sup> , 100 ml	Plate-plate pulsed DBD; 23 kV, 300 Hz, 1.7 W	No adsorbent	5.06	350	2.1 × 10 <sup>-2</sup>	61%, 45 min	3.5 × 10 <sup>-4</sup> (G <sub>50</sub> )	[29]
		Nanofiber membrane polyamide	5.06	350	4.14 × 10 <sup>-2</sup>	84.7%, 45 min	1.4 × 10 <sup>-3</sup> (G <sub>50</sub> )	

**Note:** pH<sub>0</sub>: Initial pH value of solution; C<sub>0</sub>: Initial solution conductivity; k: Kinetic constant; DE: Degradation efficiency; EY: Energy yield at any degradation efficiency; G<sub>50</sub>: Energy yield at 50% degradation efficiency; AC: Activated carbon.

degrading aqueous micropollutants by ozonation and then adsorbing the residue pollutants with GAC filters (figure 1(b): plasma/ozonation treatment-adsorption process), but GAC filters cannot eliminate certain micropollutants and their transformation products completely [30], so the pollutants adsorbed on GAC filters should also be considered for further treatment in order to eliminate secondary pollution. Compared to the degradation of aqueous pollutant by direct electric discharge in water, the adsorption-plasma regeneration process has some merits: (1) the enrichment of aqueous pollutants of low concentrations on an adsorbent enhances the treatment efficacy of pollutants by discharge plasma; (2) the catalytic and interfacial reactions on some adsorbents promote the degradation of pollutants; (3) the influence of water conductivity on the formation of discharge plasma can be avoided. However, the textural and chemical characteristics of carbon materials can be modified during the regeneration process by DBD plasma [23, 24] or O<sub>3</sub> [26]. Although the functional groups (e.g. -OOH, -OH, etc) on carbon materials can be increased during the regeneration process, and the increase of these functional groups benefits the production of ·OH through the catalysis of H<sub>2</sub>O<sub>2</sub>, the textural changes such

as a reduction in microspore diameter and specific surface area may decrease the adsorption capacity of regenerated carbon materials.

Many studies have also focused on the degradation efficiency and mechanism of aqueous pollutants by the one-step plasma/adsorption process [5, 22, 25, 27, 29, 31]. Table 1 shows that adsorbent obviously promotes the degradation efficiency of pollutants [5, 25, 27, 29] and the energy efficiency [25, 29] compared to plasma treatment alone, possibly due to the enhanced interfacial reactions, the enrichment of pollutants in the plasma zone, and the production of stronger reactive species; moreover, the added dosage of adsorbent affects the degradation of pollutants, and an overdosage of adsorbent is not definitely helpful for enhancing the treatment efficiency of the pollutant. The result may be partly due to the effect of the adsorbent dosage on the production of reactive species because Wang *et al* found that an GAC dosage of 2–4 g L<sup>-1</sup> promotes H<sub>2</sub>O<sub>2</sub> production but H<sub>2</sub>O<sub>2</sub> concentration decreases at a dosage of 5 g L<sup>-1</sup> [5]. Electric discharge in water is initiated in the gas–liquid interface of the bubbles. During the process, O<sub>3</sub> and ·OH can be produced through the dissociation of O<sub>2</sub> and H<sub>2</sub>O and the

subsequent radical reactions, and  $\cdot\text{OH}$  also recombines into  $\text{H}_2\text{O}_2$ . On the one hand, adsorbent may enhance the recombination of  $\cdot\text{OH}$  through enhancing their reaction probability on the adsorbent surface; on the other hand, carbon materials also present some catalytic activities for  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  into  $\cdot\text{OH}$  [5, 27, 31]. The above-mentioned facts lead to a different rule of  $\text{H}_2\text{O}_2$  formation at different carbon adsorbent dosages.

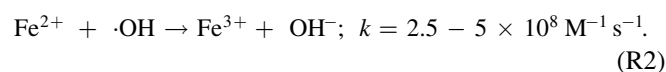
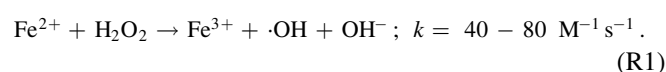
Moreover, the pH value of the solution may also affect the degradation of pollutant in hybrid plasma/adsorbent technologies through the interfacial adsorption and reaction pathways because solution pH values have an important influence on the enrichment of pollutants on adsorbent. When the pH value of the solution is higher than the  $\text{pH}_{\text{pzc}}$  (point of zero charge) of the adsorbent, the negative surface charges on the adsorbent benefit the adsorption of pollutants of positive polarity; instead, an adsorbent prefers to adsorb the pollutants of negative polarity at a solution pH lower than  $\text{pH}_{\text{pzc}}$ , so the selection of a suitable adsorbent is very important for the enrichment and degradation of aqueous pollutants.

## 2.2. Plasma/catalyst technologies

Besides reactive radical species ( $\cdot\text{O}$ ,  $\cdot\text{OH}$ ,  $\cdot\text{H}$ , etc), molecular species of  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , ultraviolet–visible (UV–vis) irradiation, local high temperature, and shockwaves are also produced during electric discharge in contact with water.  $\text{O}_3$  ( $E = 2.07\text{ V}$ ) and  $\text{H}_2\text{O}_2$  ( $E = 1.78\text{ V}$ ) are two strong chemical oxidants which are produced by EDPs in water; however, compared to  $\cdot\text{OH}$ , the strongest electron radical which unselectively reacts with most organic molecules through electron transfer, hydrogen abstraction, or radical addition at rate constants of  $10^6\text{--}10^9\text{ M}^{-1}\text{ s}^{-1}$  [32],  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  selectively oxidize pollutants in water. Various homogeneous and heterogeneous catalysts are employed for the catalysis of  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  or cooperate with the UV effect for enhancing the degradation of pollutants in water. Table 2 shows that homogeneous (e.g.  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) and heterogeneous (e.g. doped/undoped metal oxides) catalysts obviously enhance the degradation of pollutants compared to plasma alone, regardless of the discharge plasma types, mainly due to the generation of the strongest one-electron oxidant  $\cdot\text{OH}$  by plasma Fenton/Fenton-like reactions and catalytic ozonation, more efficient interface reactions of catalysts, photocatalysis effect, etc.

Fe-based ions and compounds such as  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  [33], Fe/AC [34], pyrite ( $\text{FeS}_2$ ) [35], maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) [36], magnetite ( $\text{Fe}_3\text{O}_4$ ) [37], and so on are the most frequently used catalysts in plasma Fenton-like reactions. Figure 2 shows the pathways of homogeneous or heterogeneous catalysis of  $\text{H}_2\text{O}_2$  into  $\cdot\text{OH}$  by Fe-based catalysts (R1), different from the homogeneous catalysis process, the interfacial reactions are very important for the decomposition of  $\text{H}_2\text{O}_2$  into their reactive species ( $\cdot\text{OH}$ ,  $\text{HO}_2\cdot$ , etc) and the degradation of pollutant on the surface of heterogeneous Fe-based catalysts. Although homogeneous catalysis of  $\text{H}_2\text{O}_2$  by  $\text{Fe}^{2+}$  generated more  $\cdot\text{OH}$  than the heterogeneous one [34], possibly due to less mass transfer limits of homogeneous catalysis, an unsatisfactory consumption reaction of  $\cdot\text{OH}$  by  $\text{Fe}^{2+}$  also happens (R2); however, heterogeneous catalysis of  $\text{H}_2\text{O}_2$  helps to reduce the consumption of  $\cdot\text{OH}$  by

$\text{Fe}^{2+}$ . Moreover, it is believed that a cycling of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  can be formed through the reduction of  $\text{Fe}^{3+}$  on the catalyst surface by aqueous electrons ( $e_{\text{aq}}^-$ ), which can alleviate the excessive iron sludge production in conventional Fenton oxidation systems, and heterogeneous catalysts also lead to less leakage of metal ions, which are more friendly to the environment. It is very interesting that the ground materials also present different catalytic activities in the liquid phase pulsed discharge process, and higher phenol degradation is obtained by stainless steel ground electrode compared to titanium ground electrode, due to higher catalytic activity of dissolved metal ions from a stainless steel electrode [38]. However, similar to Fenton processes, the pH values of the solutions also affect plasma Fenton/Fenton-like reactions due to the formation of iron oxohydroxides and ferric precipitate at high pH value and the formation of iron complex species  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  at very low pH value [39].



$\text{CeO}_2$  catalyst has been employed in many catalytic reactions including VOC oxidation, water gas shift, reforming, etc due to its unique ability to shuttle between Ce(III) and Ce(IV) states (well-known as oxygen storage capacity).  $\text{CeO}_2$  also plays a very important role in the adsorption of pollutants and  $\text{O}_3$  from water onto its surface for highly efficient plasma catalytic degradation reactions [14]. Doping of other metal components in  $\text{CeO}_2$  creates defect-induced oxygen vacancies which promote the decomposition of ozone, so  $\text{Fe}_2\text{O}_3/\text{CeO}_2$  and  $\text{ZrO}_2/\text{CeO}_2$  composites present better promotional performance on phenol degradation than  $\text{CeO}_2$  in nonthermal DBD plasma technologies [40].

Electric discharge in contact with water produces UV irradiation which originates from  $\cdot\text{OH}$  transitions  $A^2\Sigma^+(v = 0, 1) \rightarrow X^2\Pi(v = 0)$  (287–309 nm) and  $\text{N}_2(\text{C-B})$  transitions (310–440 nm) [41]. Photocatalysts including NiO and  $\text{Ag}_2\text{O}$  [16],  $\text{TiO}_2$  powder/film [16, 42–49] are employed in plasma systems for enhancing the degradation of pollutants. Under UV–vis irradiation of appropriate wavelengths, the valence electrons of photocatalysts transit to the conduction band, leading to the production of oxidative holes ( $h^+$ ) and reductive electrons. Electronegative  $\text{O}_2$  and  $\text{O}_3$  can capture photo-generated electrons ( $e^-$ ) to produce  $\text{O}_2^-$  and  $\text{O}_3^-$  which also can evolve into other reactive radicals (e.g.  $\cdot\text{OH}$ ), and the capture of electrons by  $\text{O}_2$  and  $\text{O}_3$  can inhibit the recombination of  $h^+$  and  $e^-$ ; photogenerated holes react with water molecules and hydroxide anions to produce  $\cdot\text{OH}$ , and they also directly attack pollutant molecules adsorbed on the surface of catalysts to oxidatively degrade pollutants. The gas atmosphere is important for photocatalysis reactions because the gas affects not only the plasma emission spectrum but also the separation of  $e^-$  and  $h^+$ , therefore influencing the activation performance of photocatalysts.  $\text{TiO}_2$  presents a better enhancing effect on phenol degradation and reactive species production in oxygen and air plasma than in nitrogen plasma [47], and little enhancing effect is found in argon plasma [43], which may be

**Table 2.** Degradation performance of pollutant by plasma/catalyst.

Pollutants	Plasma	Feed gas (l min <sup>-1</sup> )	Catalyst	pH <sub>0</sub>	C <sub>0</sub> (μS cm <sup>-1</sup> )	k (min <sup>-1</sup> )	DE (%)	EY(g kWh <sup>-1</sup> )	Ref.
Endosulfan: 15 mg L <sup>-1</sup> ; 100 ml	Cylindrical tube DBD, quartz dielectric; 1.82 W	Air 0.2	No catalyst	—	—	8.5 × 10 <sup>-2</sup>	82.4%, 60 min	0.678	[14]
			CeO <sub>2</sub> 1 g L <sup>-1</sup>	—	—	1.45 × 10 <sup>-1</sup>	95%, 60 min	0.782	
4-chlorophenol: 100 ppm; 100 mL	Multi-needle to plate pulsed discharge; 14 kV, 150 Hz	O <sub>2</sub> 1.667	No catalyst	6.5–7	34	9.6 × 10 <sup>-2</sup>	~80%, 18 min	337.8 (G <sub>50</sub> )	[33]
			Fe <sup>2+</sup> 0.2 mM	—	—	1.74 × 10 <sup>-1</sup>	~96%, 18 min	634 (G <sub>50</sub> )	
			Fe <sup>3+</sup> 0.2 mM	—	—	1.5 × 10 <sup>-1</sup>	~94%, 18 min	550.8 (G <sub>50</sub> )	
Methylene blue: 20 mg L <sup>-1</sup> ; 100 ml	Needle to needle alternate current corona, 45.91 W	O <sub>2</sub>	No catalyst	3.5	—	4.5 × 10 <sup>-2</sup>	~96%, 40 min	~0.063	[35]
			Pyrite 0.13 g L <sup>-1</sup>	—	—	6.9 × 10 <sup>-1</sup>	~95%, 10 min	~0.25	
Methyl violet 10B: 100 mg L <sup>-1</sup> ; 430 ml	Gliding arc	Air 13.33	No catalyst	5.5	<40	5 × 10 <sup>-4</sup>	6.7%, 60 min	—	[36]
			γ-Fe <sub>2</sub> O <sub>3</sub> 1 g L <sup>-1</sup>	—	—	3.6 × 10 <sup>-2</sup>	48.1%, 60 min	—	
4-chlorophenol: 100 mg L <sup>-1</sup>	Multi-needle to plate pulsed discharge	O <sub>2</sub> 1.667	No catalyst	6.5–7	2–4	9.36 × 10 <sup>-2</sup>	—	0.95 (G <sub>50</sub> )	[37]
Phenol: 100 ppm	Cylindrical tube DBD, quartz dielectric; 18 kV	Air 0.2	No catalyst	—	—	0.071	59.99%, 30 min	6.03	[40]
			CeO <sub>2</sub>	—	—	0.076	72.9%, 30 min	8.05	
			Fe <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub>	—	—	0.081	84.49%, 30 min	9.25	
			ZrO <sub>2</sub> /CeO <sub>2</sub>	—	—	0.084	91.48%, 30 min	10.03	
Acid blue 25: 20 mg L <sup>-1</sup> , 500 ml	Direct current glow discharge	Argon atmosphere	No catalyst	6.7	—	—	78%, 60 min	—	[42]
			TiO <sub>2</sub> 0.5 g L <sup>-1</sup>	—	—	—	90%, 60 min	—	
Phenol: 250 mL, 100 mg L <sup>-1</sup>	Multi-needle to plate pulsed discharge; 21 kV, 50 Hz	Air 5	No catalyst	7.0	100	—	66.9%, 60 min	—	[43]
			TiO <sub>2</sub> film	—	—	—	77.5%, 60 min	—	
		O <sub>2</sub> 5	No catalyst	—	—	—	80%, 60 min	—	
		TiO <sub>2</sub> film	—	—	—	98.1%, 60 min	—		
Phenol: 5 mg L <sup>-1</sup> ; 150 ml	Multi-needle to plate pulsed discharge; 20 kV, 100 Hz, 1.48 W	—	No catalyst	—	—	1.7 × 10 <sup>-2</sup>	63%, 60 min	0.744 (G <sub>50</sub> )	[44]
			TiO <sub>2</sub> nano-tube film	—	—	4.3 × 10 <sup>-2</sup>	98%, 60 min	1.895 (G <sub>50</sub> )	
Leachate: COD 540–580 mg L <sup>-1</sup> , 100 ml	Multi-needle to plate pulsed discharge; 40 kV, 400 Hz	Air 0.3	No catalyst	7.5–8.2	4.05–4.53 × 10 <sup>3</sup>	—	28.6%, 30 min	—	[45]
			TiO <sub>2</sub> powder 1.5 g L <sup>-1</sup>	—	—	—	58.9%, 30 min	—	
Phenol: 10 mg L <sup>-1</sup>	Pulsed diaphragm discharge	—	No catalyst	6.34	5.24 × 10 <sup>3</sup>	—	74%, 20 min	—	[46]
			TiO <sub>2</sub> film	—	—	—	80%, 20 min	—	
Acid orange 7: 300 mg L <sup>-1</sup> , 100 ml	Gliding arc discharge; 200 W	O <sub>2</sub> 6.67	No catalyst	—	—	1.437 × 10 <sup>-1</sup>	~94%, 20 min	—	[47]
			TiO <sub>2</sub> powder 1 g L <sup>-1</sup>	—	—	2.117 × 10 <sup>-1</sup>	~98%, 20 min	—	
Textile wastewater: COD 147.8 mg L <sup>-1</sup>	Gliding arc discharge	Air 15	No catalyst	4.9	315.8 × 10 <sup>3</sup>	1.3 × 10 <sup>-2</sup>	86.4%, 180 min	—	[48]
			TiO <sub>2</sub> 3 g L <sup>-1</sup>	—	—	3.3 × 10 <sup>-2</sup>	94.6%, 180 min	—	
Phenol: 100 mg L <sup>-1</sup> ; 250 ml	Multi-needle to plate pulsed discharge; 21 kV, 50 Hz	O <sub>2</sub> 5	No catalyst	7	100	3.1 × 10 <sup>-2</sup>	—	4.95 (G <sub>50</sub> )	[49]
			TiO <sub>2</sub> film	—	—	5.2 × 10 <sup>-2</sup>	—	7.86 (G <sub>50</sub> )	
2-nitrophenol: 4.4 × 10 <sup>-2</sup> mM, 1.5 l	Double quartz tube DBD	Air 3	No catalyst	3	51.3	—	56.8%, 80 min	—	[50]
			TiO <sub>2</sub> powder 0.8 g Carbon-doped TiO <sub>2</sub>	—	—	—	52.2%, 80 min	—	
						—	69.4%, 80 min	—	

Table 2. (Continued.)

Pollutants	Plasma	Feed gas (l min <sup>-1</sup> )	Catalyst	pH <sub>0</sub>	C <sub>0</sub> (μS cm <sup>-1</sup> )	k (min <sup>-1</sup> )	DE (%)	EY(g kWh <sup>-1</sup> )	Ref.
Reactive blue: 100 mg L <sup>-1</sup> , 10 mL	Plate-plate DBD, quartz dielectric, 62 W	—	Carbon/TiO <sub>2</sub> (350 °C)	6.28	—	—	77.5%, 80 min	—	[52]
			Carbon/TiO <sub>2</sub> (400 °C)			—	72.5%, 80 min		
			Fe/TiO <sub>2</sub>			2.8 × 10 <sup>-1</sup>	~96%, 10 min		
Phenol: 100 mg L <sup>-1</sup> , 100 mL	Multi-needle to plate pulsed discharge; 20 kV, 50 Hz, 9 W	Air 0.833	No catalyst	~6.3	100	—	48%, 120 min	—	[53]
			TiO <sub>2</sub> powder 0.2 g L <sup>-1</sup>	—	—	57%, 120 min	—		
			Fe <sup>3+</sup> 10 mg L <sup>-1</sup>	—	—	58%, 120 min	—		
			TiO <sub>2</sub> (0.2 g L <sup>-1</sup> ) /Fe <sup>3+</sup> (10 mg L <sup>-1</sup> )	—	—	73%, 120 min	—		
Triclocarban: 10 mg L <sup>-1</sup> , 100 ml	Plate to plate DBD, quartz dielectric, 38 W	Air atmosphere	TiO <sub>2</sub> /ACF sheet	—	—	—	84.9%, 30 min	0.045	[55]
Acetaminophen: 20 mg L <sup>-1</sup> , 180 mL	Cylindrical DBD, quartz tube dielectric	Air 3.33	No catalyst	7.5	Tap water	—	50%, 18 min	0.057	[56]
			TiO <sub>2</sub> /rGO 0.25 g L <sup>-1</sup>	—	—	92%, 18 min	0.113		

attributed to the higher efficiency of electronegative oxygen than argon and nitrogen in trapping photogenerated electrons; moreover, the emission spectrum of argon plasma which mainly falls in the visible light region (except for those from ·OH transitions) may also affect the photocatalytic reactions on a TiO<sub>2</sub> surface. In addition, there is an optimal TiO<sub>2</sub> dosage which enhances the pollutant degradation by discharge plasma, and excessive TiO<sub>2</sub> decreases its promotional performance [42, 47, 48]; the calcination temperature of TiO<sub>2</sub> also affects its catalytic performance, due to the influence on the micropore area and the Brunauer–Emmett–Teller surface area [50].

Doped/modified Ti-based catalysts including composite NiO/TiO<sub>2</sub> [16], metal (Fe, Mn, Ce, etc) doped TiO<sub>2</sub> catalysts [51, 52], Fe<sup>3+</sup>/TiO<sub>2</sub> [53], carbon-doped TiO<sub>2</sub> [50], TiO<sub>2</sub>/ACF composite [54, 55], and TiO<sub>2</sub>-reduced graphene oxide (TiO<sub>2</sub>-rGO) nanocomposite [56] usually present better performance in pollutant degradation and mineralization than a single TiO<sub>2</sub> catalyst. Figure 3 shows a schematic of the TiO<sub>2</sub> photocatalysis mechanism based on EDPs. Carbon/metal doping and their composites with TiO<sub>2</sub> can enhance the production of reactive species [51] or restrict the recombination of e<sup>-</sup> and h<sup>+</sup> [50, 53] through trapping e<sup>-</sup> by O<sub>2</sub> adsorbed on the carbon surface [54]; moreover, catalyst modification through doping or composite pathways may affect the pH<sub>pzc</sub> of catalysts, and therefore has an influence on the adsorption and degradation of pollutants on the surface of catalysts.

Like heavy metals, nanocatalysts in water environments may also pose a potential threat to aquatic animals and human beings, so prevention of the leakage of metal ions and nanoparticles into water systems should be considered for plasma-catalysis technologies, but the installation of facilities to remove nanocatalysts, especially homogeneous catalysts, is a major cost factor in the application of the plasma-catalysis process in wastewater treatment.

### 2.3. Plasma/oxidant technologies

Ozone is very efficient for the disinfection of drinking water and the decolorization of dye wastewater, but the relatively low solubility and slow oxidation of recalcitrant compounds in water limit its application. Since electric discharge in water also produces UV irradiation and H<sub>2</sub>O<sub>2</sub> which can convert O<sub>3</sub> to stronger ·OH, ozone is injected into water for promoting the degradation of pollutants by EDP [57, 58]. Vanraes *et al* [29] and Bradu *et al* [59] also studied the degradation of herbicides by discharge plasma followed by ozonation (namely, the produced ozone in the gas phase during water treatment process is input into the treated water), and the degradation and mineralization of herbicides are apparently improved. Similar to O<sub>3</sub>, the addition of H<sub>2</sub>O<sub>2</sub> in water also increases the generation of the concentration of ·OH through photolysis of H<sub>2</sub>O<sub>2</sub> by UV irradiation emitted from EDP, and H<sub>2</sub>O<sub>2</sub> oxidant has also been employed as the enhancing oxidant in water treatment by the pulsed discharge process [60, 61]. Table 3 shows that O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> apparently promote and accelerate the degradation of pollutants and the energy efficiency compared to discharge plasma treatment alone. The enhanced removal of pollutants in the plasma/O<sub>3</sub> process is mainly attributed to the greater production of ·O through ozone decomposition by electron collisions, pyrolysis, UV photolysis, and the greater production of ·OH through the reaction of ·O with H<sub>2</sub>O [57].

Peroxydisulfate (PDS) is a strong oxidant with a redox potential ( $E = 2.01$  V) close to O<sub>3</sub>, but far higher than H<sub>2</sub>O<sub>2</sub>. PDS is very stable at room temperature and atmospheric conditions, so direct oxidation of organic compounds by PDS in water is very slow; however, after PDS can be activated into sulfate radical anion (SO<sub>4</sub><sup>-</sup>) through the electron transfer pathway or direct cleavage of O = O band of PDS. Sulfate radical anion, a strong oxidative radical with a redox potential of 2.5–3.1 V, reacts with pollutants in water also through electron transfer, hydrogen abstraction, or radical addition.

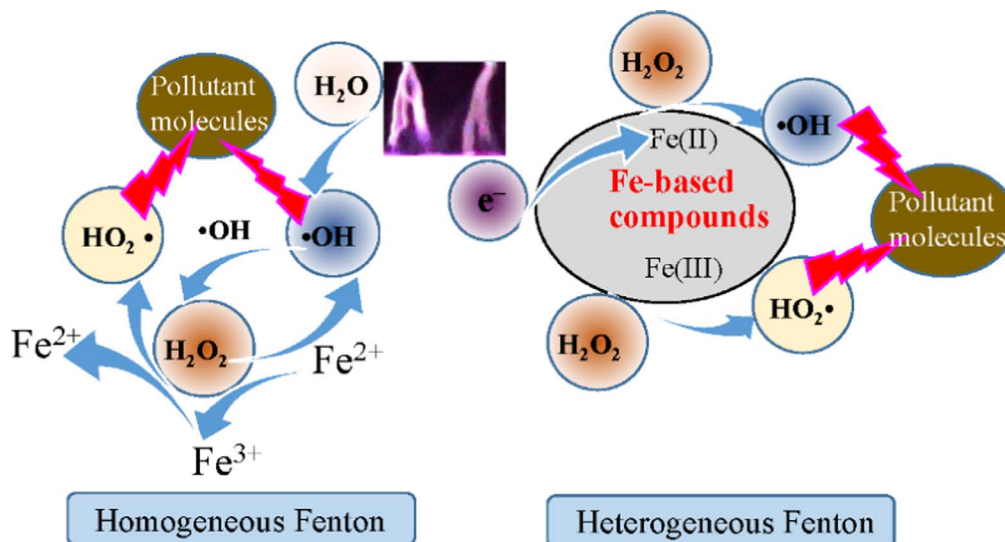


Figure 2. Homogeneous and heterogeneous catalysis of H<sub>2</sub>O<sub>2</sub> by Fe-based catalysts.

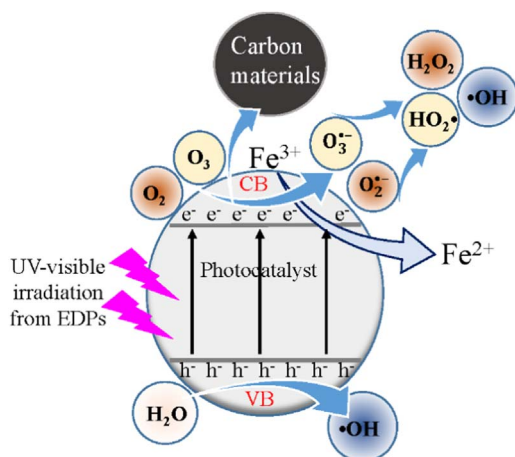


Figure 3. Schematic of TiO<sub>2</sub> photocatalysis mechanism based on EDPs.

We innovatively studied activating PDS by discharge plasma to enhance the degradation of pollutants. The hybrid plasma/PDS system simultaneously generates the strong radical species,  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$ , and the oxidation efficiency of the pollutants is apparently improved [15, 62, 63]. Sodium percarbonate ( $\text{C}_2\text{H}_6\text{Na}_4\text{O}_{12}$ , SPC) is usually employed as an alternative for  $\text{H}_2\text{O}_2$  in the Fenton system due to its safer and easier storage performance. Wang *et al* [64] studied the effect of SPC on the degradation of dimethyl phthalate (DMP) by DBD plasma, and a Fenton-like chemistry via self-decomposition into  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{CO}_3$  enhances the production of reactive species including  $\cdot\text{OH}$ ,  $\text{O}_2^{\cdot-}$ ,  $^1\text{O}_2$  and  $\text{CO}_3^{\cdot-}$ , which promotes the degradation of DMP.

Compared to the plasma/adsorbent and plasma/catalyst technologies, the advantage of the hybrid plasma/oxidant process is that the degraded products of  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , PDS, etc are less harmless for the environment, so the secondary treatment of wastewater (e.g. recovery of nanocatalysts and adsorbents and leaked metal ions) is not required.

#### 2.4. Other hybrid technologies

The combination of discharge plasma with ultrasound is also employed for enhancing the sterilization of water, but an obvious enhancing performance is only observed for submerged systems without aeration [65], due to the promotional ignition of electric discharge by cavitation from ultrasound and an elimination of the enhancing effect by aeration. At present anaerobic and/or aerobic biological technologies are employed in most wastewater treatment facilities due to their lower operational costs and no secondary pollution, but biological treatment technologies are usually slow and may be obstructed by refractory chemicals because their toxicity is resistant to microbes. Ozone [66] and EDP [67] are combined with biological treatment to remediate organic wastewater. The pretreatment of wastewater by ozone and EDP enhances the biodegradability and the treatment performance of wastewater by biological technologies. However, only a few studies have reported the feasibility of plasma-biological process for wastewater treatment, and there are no data on whether the residue ozone and reactive species in plasma will kill the microbes in biological processes for water treatment, but the ozone dosage and electric discharge intensity should be safely controlled to prevent the microbes from their harm.

### 3. Conclusions and perspective

EDP has shown very good treatment efficiency for various organic compounds in water, but most of the obtained results are from laboratories, and the water samples in laboratory studies are much different from actual wastewater. Actual wastewater usually has higher conductivity and turbidity, more complex inorganic/organic components, and various pH values, so the generation of discharge plasma in actual wastewater is very different from that in laboratory studies. In future studies greater emphasis should be put on the feasibility of treating actual wastewater by discharge plasma, so



**Table 3.** Degradation performance of pollutant by plasma/oxidant.

Pollutants	Plasma	Oxidant	$C$ pH <sub>0</sub>	$k$ ( $\mu\text{S cm}^{-1}$ )	$k$ ( $\text{min}^{-1}$ )	$DE$ (%)	$EY$ ( $\text{g kWh}^{-1}$ )	Ref.
4-chlorophenol: 250 mg L <sup>-1</sup> , 100 ml	Needle-plate pulsed discharge; 30 kV, 100 ml	O <sub>2</sub> 200 mL min <sup>-1</sup>	7.0	—	—	~72%, 30 min	~0.6	[57]
	50–150 Hz, 60 W	O <sub>3</sub> 8.87 mg L <sup>-1</sup> , 0.3 L min <sup>-1</sup>	—	—	—	96%, 30 min	0.8	
Phenol: 25 mg L <sup>-1</sup> , 250 mL	Point to plane pulsed discharge, 2.2 W	O <sub>2</sub> 10 mL min <sup>-1</sup>	6.1	20	—	16%, 240 min	0.373	[58]
		O <sub>3</sub> 10 mL min <sup>-1</sup>	—	—	—	64%, 240 min	1.456	
Phenol: 15 mg L <sup>-1</sup>	Needle-plate pulsed discharge (spark); 20 kV, 2.54 Hz	0 mM	—	—	—	—	0.778	[60]
		H <sub>2</sub> O <sub>2</sub> 4.4 × 10 <sup>-2</sup> mM	—	—	—	—	2.34	
Acid orange: 5 mg L <sup>-1</sup> , 200 mL	Plate to plate DBD, glass dielectric; 3.3–3.6 W	0 mM	6.12	1.5	0.5	34.7%, 50 min	0.18	[62]
		K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 1 mM	5.69	98	2.52	89.8%, 50 min	0.47	
p-nitrophenol: 5 mg L <sup>-1</sup> , 100 mL	Multi-needle to plate pulsed discharge; 18 kV, 50 Hz, 10–10.5 W	0 mM	6.46	1.1	—	48.5%, 60 min	0.022	[63]
		K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 2.87 mM	—	987	—	70.4%, 60 min	0.035	
Dimethyl phthalate: 30 mg L <sup>-1</sup> , 500 mL	Indirect injection of reactive species by AC DBD reactor; 18 kV, 50 Hz	0 mM	—	—	0.029	~73%, 45 min	—	[64]
		C <sub>2</sub> H <sub>6</sub> Na <sub>4</sub> O <sub>12</sub> 0.12 mM	—	—	0.067	97%, 45 min	1.08	

the development of highly efficient discharge plasma technologies free of the effect of water properties is very important for wastewater treatment. This can be realized by (1) the development of high performance gas–liquid phase plasma reactors with better gas–liquid diffusion transfer and low sensitivity to water properties (e.g. water spraying reactors and falling film reactors with a narrow discharge gap); and (2) development of hybrid processes of adsorption/membrane filter followed by plasma (catalytic) regeneration of adsorbents and membranes, etc. In addition, a scale-up of the discharge plasma facilities including the power supply and the discharge device is a great challenge for the treatment of vast quantities of wastewater. Therefore, an enrichment of micropollutants in water by adsorption or membrane filter process followed by plasma treatment of the concentrate can also solve the scale-up problem of discharge plasma facilities.

Moreover, although adsorbents, catalysts and oxidants can improve the decontamination efficiency of wastewater by discharge plasma treatment, a complete mineralization of organic compounds, especially recalcitrant compounds, is difficult. Therefore, more efficient composite catalysts, which can fully couple with the plasma effects such as UV–vis irradiation, local high temperature, electrons, reactive species, etc, should be developed. Furthermore, if nanocatalysts are used, their leakage into water should be prevented to induce secondary pollutions. Installation of additional filters to capture the leaked catalysts may be a solution.

In addition, electric discharge in water with air bubbling or over a water surface will produce NO<sub>x</sub> in air, and the

dissociation of NO<sub>x</sub> in water leads to a significant increase of nitrates and nitrites, so a biological treatment process followed after wastewater pretreatment by EDPs or hybrid plasma oxidation technologies may be a good choice for simultaneous removal of the inorganic/organic pollutants in wastewater. If the biological filter bed is used in hybrid plasma-biological treatment process, it may also play a role in capturing nanocatalyst or adsorbent materials.

## Acknowledgments

This research is supported by National Natural Science Foundation of China (No. 21577011) and the China Scholarship Council.

## References

- [1] Oturan M A and Aaron J J 2014 *Crit. Rev. Environ. Sci. Technol.* **44** 2577
- [2] Lukes P *et al* 2014 *Plasma Sources Sci. Technol.* **23** 015019
- [3] Bruggeman P and Leys C 2009 *J Phys. D Appl. Phys.* **42** 053001
- [4] Shang K F *et al* 2016 *Jpn. J. Appl. Phys.* **55** 01AB02
- [5] Wang H J *et al* 2016 *Vacuum* **128** 99
- [6] Foster J E 2017 *Phys. Plasmas* **24** 055501
- [7] Malik M A, Ghaffar A and Malik S A 2001 *Plasma Sources Sci. Technol.* **10** 82
- [8] Sato M *et al* 2008 *IEEE Trans. Ind. Appl.* **44** 1397
- [9] Ruma *et al* 2018 *Catalysts* **8** 213

- [10] Šunka P 2001 *Phys. Plasmas* **8** 2587
- [11] Minamitani Y et al 2008 *IEEE Trans. Plasma Sci.* **36** 2586
- [12] Du C M et al 2014 *IEEE Trans. Plasma Sci.* **42** 2221
- [13] Kodama S et al 2017 Optimization of persistent organic pollutants treatment in wastewater using by nanosecond pulsed non-thermal plasma *Proc. of the 2017 IEEE 21st Int. Conf. on Pulsed Power* (Brighton, UK: IEEE) 2017
- [14] Reddy P M K, Mahammadunnisa S and Subrahmanyam C 2014 *Chem. Eng. J.* **238** 157
- [15] Shang K F et al 2017 *Chem. Eng. J.* **311** 378
- [16] Bobkova E S et al 2012 *Plasma Chem. Plasma Process.* **32** 703
- [17] Zhao Y et al 2017 *Plasma Sci. Technol.* **19** 034001
- [18] Gao Q S, Liu Y J and Sun B 2017 *Plasma Sci. Technol.* **19** 115404
- [19] Li J et al 2013 *High Voltage Eng.* **39** 2119
- [20] Foster J E et al 2018 *J. Phys. D Appl. Phys.* **51** 293001
- [21] Lukes P, Locke B R and Brisset J L 2012 Aqueous-phase chemistry of electrical discharge plasma in water and in gas-liquid environments ed V I Parvulescu, M Magureanu and P Lukes *Plasma Chemistry and Catalysis in Gases and Liquids* vol 2012 (Weinheim: Wiley) p 243
- [22] Vanraes P et al 2015 *J. Hazard. Mater.* **299** 647
- [23] Qu G Z et al 2014 *Plasma Sci. Technol.* **16** 608
- [24] Qu G Z et al 2009 *J. Hazard. Mater.* **172** 472
- [25] Xin L et al 2016 *Chemosphere* **144** 855
- [26] Shang K F et al 2015 *Ozone Sci. Eng.* **37** 178
- [27] Wang T C et al 2016 *Environ. Sci. Pollut. Res.* **23** 13448
- [28] Zhou R S et al 2016 *J. Taiwan Inst. Chem. Eng.* **68** 372
- [29] Vanraes P et al 2015 *Water Res.* **72** 361
- [30] Knopp G et al 2016 *Water Res.* **100** 580
- [31] Hao X L, Zhang X W and Lei L C 2009 *Carbon* **47** 153
- [32] Neta P, Huie R E and Ross A B 1988 *J. Phys. Chem. Ref. Data* **17** 1027
- [33] Hao X L et al 2007 *Chemosphere* **66** 2185
- [34] Zhu X Y et al 2017 *J. Chem. Technol. Biotechnol.* **92** 1970
- [35] de Brito Benetoli L O et al 2012 *J. Hazard. Mater.* **237–238** 55
- [36] Tiya-Djowe A et al 2015 *J. Environ. Chem. Eng.* **3** 953
- [37] Lei L C et al 2007 *Plasma Process. Polym.* **4** 455
- [38] Banaschik R et al 2017 *Electrochim. Acta* **245** 539
- [39] Babuponnusami A and Muthukumar K 2014 *J. Environ. Chem. Eng.* **2** 557
- [40] Reddy P M K et al 2013 *Plasma Process. Polym.* **10** 1010
- [41] Sarani A, Nikiforov A Y and Leys C 2010 *Phys. Plasmas* **17** 063504
- [42] Ghodbane H et al 2015 *Open Chem.* **13** 325
- [43] Wang H J et al 2007 *J. Hazard. Mater.* **141** 336
- [44] Zhang Y et al 2013 *Chem. Eng. J.* **215–216** 261
- [45] Zhang C et al 2017 *J. Hazard. Mater.* **326** 221
- [46] Duan J J et al 2015 *Plasma Sci. Technol.* **17** 303
- [47] Liu Y A et al 2014 *Plasma Chem. Plasma Process.* **34** 1403
- [48] Ghezzar M R et al 2009 *J. Hazard. Mater.* **164** 1266
- [49] Wang H J et al 2008 *Appl. Catal. B Environ.* **83** 72
- [50] Tijani J O et al 2017 *Plasma Chem. Plasma Process.* **37** 1343
- [51] Chen Y D et al 2014 *Environ. Sci. Pollut. Res.* **21** 9948
- [52] Sun Y et al 2015 *IEEE Trans. Plasma Sci.* **43** 3234
- [53] Duan L J et al 2018 *Appl. Catal. B Environ.* **221** 521
- [54] Zhang Y Z et al 2010 *Chem. Eng. J.* **162** 1045
- [55] Wang J et al 2016 *Chem. Eng. J.* **300** 36
- [56] Zhang G Y et al 2017 *J. Hazard. Mater.* **323** 719
- [57] Wen Y Z, Jiang X Z and Liu W P 2002 *Plasma Chem. Plasma Process.* **22** 175
- [58] Malik M A et al 2002 *Plasma Sources Sci. Technol.* **11** 236
- [59] Bradu C, Magureanu M and Parvulescu V I 2017 *J. Hazard. Mater.* **336** 52
- [60] Sun B, Sato M and Clements J S 2000 *Environ. Sci. Technol.* **34** 509
- [61] Sugiarto A T et al 2003 *J. Electrostatics* **58** 135
- [62] Shang K F et al 2017 *Top. Catal.* **60** 973
- [63] Shang K F et al 2017 *Plasma Sci. Technol.* **19** 064017
- [64] Wang T C et al 2018 *Chem. Eng. J.* **346** 65
- [65] Chen C W et al 2009 *Environ. Sci. Technol.* **43** 4493
- [66] de Arruda Guelli Ulson de Souza S M, Bonilla K A S and de Souza A A U 2010 *J. Hazard. Mater.* **179** 35
- [67] Yee D C et al 1998 *Biotechnol. Bioeng.* **59** 438