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Electrical Discharge in Water Treatment Technology for Micropollutant Decomposition

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Abstract

Hazardous micropollutants are increasingly detected worldwide in wastewater treatment plant effluent. As this indicates, their removal is insufficient by means of conventional modern water treatment techniques. In the search for a cost-effective solution, advanced oxidation processes have recently gained more attention since they are the most effective available techniques to decompose biorecalcitrant organics. As a main drawback, however, their energy costs are high up to now, preventing their implementation on large scale. For the specific case of water treatment by means of electrical discharge, further optimization is a complex task due to the wide variety in reactor design and materials, discharge types, and operational parameters. In this chapter, an extended overview is given on plasma reactor types, based on their design and materials. Influence of design and materials on energy efficiency is investigated, as well as the influence of operational parameters. The collected data can be used for the optimization of existing reactor types and for development of novel reactors.

Keywords: electrode configuration, electrohydraulic discharge, energy yield, organic degradation efficiency, dielectric barrier discharge

1. Introduction

In this introductory section, the current status and limitations of both conventional and advanced water treatment systems are explained in detail, with a focus on their performance on micropollutant removal. This context is necessary to understand the role that plasma technology can play in the future challenges of water purification, which is the main topic of this chapter. Further, it opens a clear perspective on research that still needs to be done in order to turn the plasma treatment of water into a mature technology.

With ongoing improvement of chemical analytical methods, a wide spectrum of compounds and their transformation products are increasingly detected in water bodies and sewage sludge. Many of these compounds occur in low concentrations in the range of microgram to nanogram per liter. They are therefore called micropollutants. Among these are food additives, industrial chemicals, pesticides, pharmaceuticals, and personal care products. Even with such low concentrations, various environmental effects have been observed. Continuous release of antibiotics in the environment leads, for example, to increasing resistance of microorganisms [1]. Chronic exposure of aquatic life to endocrine disruptive compounds causes feminization, masculinization, and immunomodulating effects in fish and frogs, which has tremendous effects on the ecosystem [2, 3]. Additionally, there is growing concern for the direct acute and chronic effects of micropollutants on human health and safety [4–8]. Although more insight is gained on the impact of individual micropollutants, their synergistic, additive, and antagonistic effects are still vastly unknown. Some countries or regions have adopted regulations for a small number of compounds. Nevertheless, effluent limitation guidelines and standards do not exist for most micropollutants.

The primary source of many micropollutants in aquatic systems is the effluent of conventional wastewater treatment plants. An example of such treatment plant is schematically shown in Figure 1. The treatment process occurs in sequential steps:

- Primary treatment consists of a series of mechanical and/or physicochemical treatment steps, which remove solids, oil, and fat. This step is usually common to all wastewater treatment plants [9]. During pretreatment, large debris is eliminated, as it can damage or clog pumps and sewage lines in later steps. Next, abrasive particles are withdrawn, such as grit, sand, oil, and fat. As a third step, a primary clarifier removes the last part of solid material before the wastewater is sent to the secondary treatment unit. With this solid material, as much as possible biodegradable material is removed as well in order to significantly reduce oxygen demand and therefore costs in the later biological treatment unit. Overall, primary treatment removes almost half of the suspended solids in raw wastewater [10]. Sometimes, pH adjustment for neutralization is added as a last step of primary treatment to make the effluent suitable for secondary treatment [11].
- Secondary treatment usually consists of biological conversion of dissolved and colloidal organic compounds into stabilized, low energy compounds, by means of a diversified group of microorganisms in presence of oxygen. Additionally, new cells of biomass are generated during this biological treatment step. The mixture of microorganisms with inorganic and organic particles contained in the suspended solids is referred to as activated sludge. Secondary treatment can differ substantially between wastewater treatment plants, as it depends on the nature of the activated sludge [9].
- Tertiary treatment, also called water polishing, consists of any additional treatment that is carried out to make the effluent quality more suitable for discharge in the receiving environment. Chlorination is the most common method of wastewater disinfection due to its low costs. Nevertheless, it can lead to formation of chlorinated organic compounds that may be carcinogenic or harmful to the environment. Therefore, also ultraviolet disinfection is increasingly finding application in wastewater treatment plants [12]. Additional pollutant

removal can be achieved with sand filtration, biological nutrient removal, adsorption on activated carbon, membrane processes, and advanced oxidation processes [9, 12]. However, many conventional wastewater treatment plants have no or limited tertiary treatment, due to the high costs associated with most of these methods.

As should be noted, organic pollution that enters a wastewater treatment plant has three outlets: effluent water, excess sludge, and exhaust gas in the form of CO₂ or volatile organic compounds. Excess sludge disposal is complex since it contains a high concentration of harmful substances and only a small part of it consists of solid matter. Sludge treatment is required to reduce the water and hazardous organic content and to render the processed solids suitable for reuse or final disposal. Therefore, sludge is processed in sequential steps of thickening, digestion, and dewatering before disposal [10].

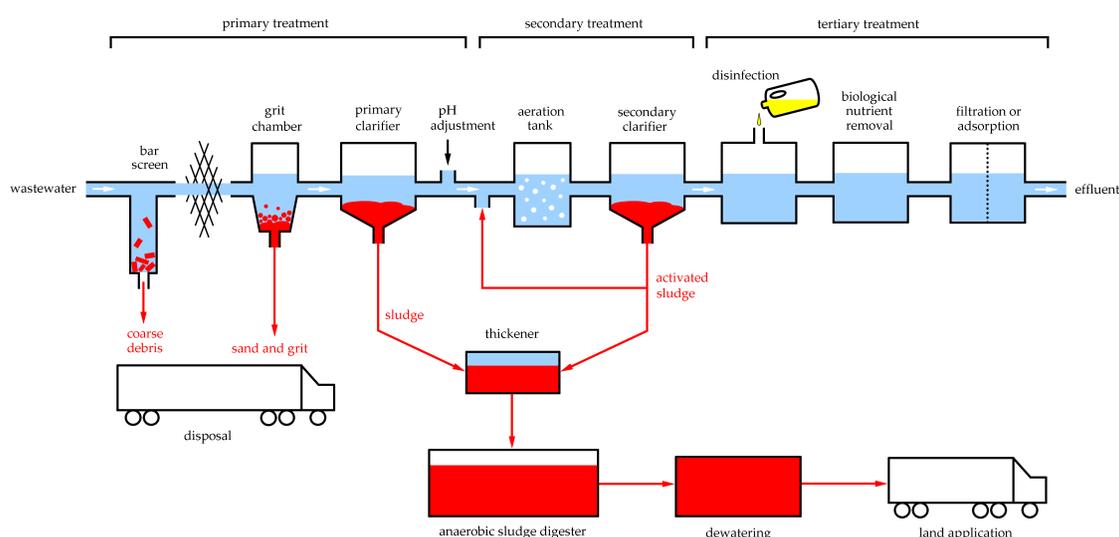


Figure 1. Simplified scheme of a conventional wastewater treatment plant, adapted from Flores Alsina and Benedetti et al. [10, 13].

Up to now, conventional treatment plants cannot sufficiently remove micropollutants, as shown by many studies worldwide [14]. Several options are available to improve the elimination of these contaminants, including:

- Prevention by application of products without micropollutants or only with micropollutants which are easily removed
- Reassessment and optimization of current treatment processes
- Pretreatment of hospital and industrial effluents
- End-of-pipe upgrading of wastewater treatment plants

Preventive measures will always be limited by the increased demand for industrial, pharmaceutical, and personal care products. Moreover, highly stable micropollutants such as the pesticide atrazine are detected even several years after the discontinuation of their

use. Hence, more effective water treatment processes are required. Existing processes in water treatment plants can be optimized by increased sludge ages and hydraulic retention times in conjunction with nutrient removal stages and the varying redox conditions associated with them. Temperature and pH control can also enhance micropollutant removal. According to the reviews by Jones et al. and Liu et al., this is expected to be the most economically feasible approach to increase overall water treatment plant performance [15, 16]. While such measures indeed lead to more effective removal of micropollution in general, they often have limited or negligible effect on several specific persistent micropollutants, as shown in the extended review by Luo et al. [14].

The removal difference among different compounds can be partly ascribed to micropollutant properties. For example, Henry's law constant as a measure of compound volatility gives an indication how easily a contaminant will be removed by aeration and convection. In activated sludge processes, the solid-water distribution coefficient K_d has been proposed as a relative accurate indicator of sorption behavior [17, 18]. It is defined as the partition of a compound between the sludge and the water phase and takes into account both hydrophobicity and acidity of the molecule. The biodegradation of micropollutants is more complex to predict, but compound structure is an important indicator. Highly branched side chains and sulfate, halogen, or electron withdrawing functional groups generally make a contaminant less biodegradable. Also, saturated or polycyclic compounds show high resistance to biodegradation [19, 20].

In order to remove such persistent compounds, an additional secondary or tertiary treatment step for wastewater is required. As a cost-effective alternative, the treatment of hospital and industrial effluent can solve the problem at its source. For these purposes, several advanced treatment techniques have been proposed in recent years. Each removal option has its own limitations and benefits in removing trace contaminants. A complete review on this topic was conducted by Luo et al. [14]. Advanced biological treatment techniques are activated sludge, membrane bioreactors, and attached growth technology. As in the case of conventional biological treatment, these methods are commonly unable to remove polar persistent micropollutants. Coagulation-flocculation processes yield ineffective elimination of most micropollutants. In contrast, electrochemical separation treatment methods such as electrocoagulation and internal microelectrolysis give very good results, as discussed by Sirés and Brillas [21]. Activated carbon, nanofiltration, and reverse osmosis are generally also very effective for removal of trace contaminants. However, they are associated with high energy costs and high financial costs. Moreover, all these separation methods have the additional problem of toxic concentrated residue disposal, as they only remove the compounds without further decomposition into less toxic by-products. Advanced oxidation techniques, on the other hand, are able to oxidize toxic compounds to smaller molecules, ideally with full mineralization to CO_2 and H_2O [22]. Nevertheless, their weakest point is as well their high energy demand. Additionally, they can be hazardous to the environment, by their unwanted production of CO_2 , long-living oxidants, and potentially toxic oxidation products. Therefore, research needs to focus on optimizing existing systems in order to overcome these problems.

Optimal water treatment schemes will eventually be decided upon, achieving effluent limitations set by national or international environmental regulations at a reasonable cost. In their extended reviews, Jones et al. and Liu et al. conclude that it seems unpractical for activated carbon, nanofiltration, reverse osmosis, and advanced oxidation techniques to be widely used in conventional wastewater treatment [15, 16]. However, with more and more shortages of drinking water all over the world, the recycling of wastewater treatment plant effluents as a drinking water source seems just a question of time. For such purpose, these technologies may be advantageous due to their high removal efficiency. Moreover, with the recent developments in energy harvesting in wastewater treatment [23, 24], one needs to consider the possibility to make wastewater treatment plants self-sustainable in power consumption, even with additional implementation of advanced treatment. As mentioned above, the treatment of hospital and industrial effluent can be a cost-effective approach as well. This last approach has gained a lot of attention over the past several years. For an overview of research done in this field for the case of hospitals, the reader is referred to the reviews of Verlicchi et al. [25, 26].

Comninellis et al. propose in their perspective article a strategy for wastewater treatment, depending on the water's total organic content, biodegradability, toxicity, and other physico-chemical requirements, such as transparency [27]. According to this strategy, the use of cost-effective biological treatment is only advised when total organic content is high enough. If such wastewater is not biodegradable, advanced oxidation can be used as pretreatment step, to enhance biodegradability, and reduce toxicity. One needs to consider, however, that presence of oxidant scavengers can sabotage the oxidation efficiency. Therefore, the used oxidation technology needs to be geared toward the wastewater under treatment. In the case that total organic content is low, wastewater possesses little metabolic value for the microorganisms. Then, advanced oxidation technology that effectively mineralizes the targeted pollution can be applied as a one-step complete treatment method. Alternatively, separation treatment can be applied prior to advanced oxidation, where pollutants are transferred from the liquid to another phase and subsequently posttreated.

Following this line of thought, advanced oxidation techniques take a promising place in the quest for micropollutant removal, as they appear the most effective methods for the decomposition of biorecalcitrant organics. However, in this time of a growing energy crisis and concerns over global warming, removal efficiency should not be the only objective. Sustainable development on the whole must to be considered. Therefore, the main objective of research on advanced oxidation technology should be optimization in terms of energy cost and effluent toxicity as well as its compatibility with biological treatment.

Examples of advanced oxidation processes are ozonation, hydrogen peroxide addition, chlorination, Fenton process, UV irradiation, radiolysis, microwave treatment, subcritical wet air oxidation, electrochemical oxidation, homogeneous and heterogeneous catalytic oxidation, ultrasonication, and combinations thereof, such as peroxonation, photocatalysis, and electro-Fenton process.

One type of oxidation method is typically insufficient for micropollutant removal, while a combination of oxidation methods with each other or with other advanced treatment techniques leads to significant improvement up to complete removal, as concluded in many reviews,

such as for antibiotics [28], for pharmaceuticals [29], for UV-based processes [30], and for the general case [31, 32]. Subcritical wet air oxidation is not feasible for micropollutant removal [33].

Oturan and Aaron conclude from their review that chemical methods such as Fenton's process and peroxonation perform worse than photochemical, sonochemical, and electrochemical advanced oxidation techniques [32]. For the latter three technologies, they further conclude the following:

- Among the photochemical methods, photo-Fenton process and heterogeneous photocatalysis possessed in most cases a better efficiency than H_2O_2 and O_3 photolysis. Moreover, the solar photo-Fenton process and solar photocatalysis reduce energy consumption even further. The heterogeneous catalyst TiO_2 has many advantages, as it is chemically highly stable, biologically inert, very easy to produce, inexpensive, and possessing an energy gap comparable to that of solar photons.
- The sonochemical combination of Fenton's process with ultrasonication has effective results at lab scale, but application at the industrial level in real time is needed to demonstrate its economic and commercial feasibility.
- Electrochemical methods have the advantage of minimizing or eliminating the use of chemical reagent. Anode oxidation and electro-Fenton have very good performance when a boron-doped diamond anode is used. They can be combined with other advanced oxidation methods for further improvement of efficiency. Examples of such combinations are photoelectro-Fenton, solar photoelectro-Fenton, sonoelectro-Fenton, and peroxyelectrocoagulation. One needs to consider, however, that boron-doped diamond anodes are very expensive [21].

In conclusion, a synergetic combination of multiple oxidants and oxidation mechanisms is recommended for efficient micropollutant decomposition. Therefore, water treatment by means of plasma discharge takes an interesting and promising place among the advanced oxidation techniques, as it can generate a wide spectrum of oxidative species and processes in proximity of the solution under treatment, including shock waves, pyrolysis, and UV radiation. The hydroxyl radical OH is often named as the most important oxidant, due to its high standard oxidation potential of 2.85 V and its unselective nature in organic decomposition. Further, plasma in contact with liquid can generate significant amounts of O_3 and H_2O_2 . These two oxidants are frequently used in other advanced oxidation methods and lead together to the peroxone process. Other important reactive oxygen plasma species include the oxygen radical O , the hydroperoxyl radical HO_2 , and the superoxide anion O_2^- . When electrical discharge occurs in air, also reactive nitrogen species such as the nitrogen radical, the nitric oxide radical NO , and the peroxyxynitrite anion ONOO^- will play an important role. Oxidants can either enter the liquid phase through transfer from the gas phase or be formed directly in the liquid phase at the plasma–water interface by interaction of plasma species with water or dissolved molecules. Radical hydrogen H , a powerful reducing agent, is directly formed in aqueous phase by the electron collision with water molecules. Plasma discharge also leads to aqueous electrons, which even have a stronger reduction potential. A more detailed overview

of oxidative plasma species and processes without nitrogen-containing oxidants was conducted by Joshi and Thagard [34]. Recent insights on the chemistry of plasma-generated aqueous peroxyxynitrite and its importance in water treatment are given by Brisset and Hnatiuc and Lukes et al. [35, 36].

The presence of different oxidants reduces the selectivity of an oxidation method. Direct oxidation of organics by ozone is, for example, very selective. This is illustrated with the reaction rate constants listed by Jin et al., Sudhakaran and Amy, and Von Gunten [37–39], which range from 10^{-5} to $3.8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. Hydroxyl, on the other hand, is considered unselective in the decomposition of organics, with reaction rate constants from 2.2×10^7 to $1.8 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, as listed in the same 3 references and [40]. Hence, organic oxidation by means of plasma is expected to be rather unselective as well. Nevertheless, the chemistry behind plasma treatment is very complex due to the interactions between the various reactive species in the gaseous phase, in the aqueous phase and at their interface. Moreover, this chemistry is strongly dependent on the used electrode configuration and material, discharge regime, applied voltage waveform, water properties, and feed gas. Therefore, the optimization of plasma reactors for water treatment in terms of energy costs and effluent toxicity is a complicated task, which still requires more research effort and insight. On the positive side, plasma-based water treatment has already shown itself as a versatile technology, which can find application in the treatment of biological, organic, and inorganic contamination, after sufficient optimization has been reached. As an additional advantage, its flexible design allows it to be easily combined with other advanced treatment techniques. Such combinations can lead to interesting synergetic effects and further optimization.

As pointed out already by Sillanpää et al. [41], no information has been reported in scientific literature on the treatment cost of advanced oxidation processes. To our knowledge, plasma technology has only been compared with other water treatment methods in the review of Sirés and Brillas [21]. According to their review, the main drawback of plasma technology would be its high energy requirement. However, the authors did not validate this claim with quantitative data. Comprehensive quantitative assessment is needed to compare different techniques better from both economic and technical points of view, as Luo et al. conclude in their review [14]. For the specific case of plasma technology for water treatment, only 3 reviews have extensively compared different reactors in their energy efficiency for organic decomposition. Malik was the first to do this for dye degradation [42]. Recently, Bruggeman and Locke and Jiang et al. have made a comparison for mostly phenolic compounds [43, 44]. Their findings will be discussed in next sections. Nevertheless, the main comparative parameter in these reviews is energy yield G_{50} for 50% pollutant removal, expressed in g/kWh, which is only used in literature on plasma treatment. Moreover, G_{50} is strongly dependent on the initial pollutant concentration. It is therefore not fit for comparison with other advanced treatment techniques.

In this chapter, several plasma technologies are discussed that can be applied in water treatment. First, different approaches for reactor classification will be analyzed in detail. In Section 3, an overview will be given of different plasma reactor types, where classification is based on reactor design and reactor materials. The influence of multiple working parameters

on reactor energy efficiency is discussed in Section 4. Section 5 gives a summary with future prospects and concluding remarks on the research that is still required in this field.

2. Approaches for reactor classification

Plasma reactors for water treatment can be classified in many ways, depending on several criteria. Such classifications have already been made in a few reviews. One popular approach starts from 2 or 3 main plasma–water phase distributions and subdivides reactors further based on their electrode configuration, as in Bruggeman and Leys and Locke et al. [45, 46]. Here, we will adapt this approach with 6 plasma–water phase distributions, where electrical discharge is generated

1. directly in the water bulk,
2. directly in the water bulk with externally applied bubbles (bubble discharge reactors),
3. in gas phase over water bulk or film,
4. in gas phase with water drops or mist,
5. as a combination of the previous types, or
6. not in direct contact with the solution under treatment.

Accordingly, these reactor types are called (1) electrohydraulic discharge, (2) bubble discharge, (3) gas phase discharge, (4) spray discharge, (5) hybrid, and (6) remote discharge reactors. The basic idea behind this classification is that the total plasma–water interface surface is an important, determining parameter for a reactor's energy efficiency. A larger interface surface is expected to cause higher pollutant degradation efficiency, in agreement with the reviews of Malik, Jiang et al., and Bruggeman and Locke [42–44]. Interface surface can be enlarged by generating plasma in bubbles, by spraying the solution through the active plasma zone, and by making the solution flow as a thin film along the discharge. It can be further enlarged by extending the plasma volume, which has led to many possible choices of electrode configurations and geometries. Additionally, dielectric barriers and porous layers are often introduced in the setup to avoid unwanted energy losses to Joule heating of water and spark formation, while enhancing the local electric field for easier breakdown. In Section 3, this approach for reactor classification will be studied in more detail.

Another popular approach classifies reactors based on the used discharge regime and applied voltage waveform. The following discharge regimes should be considered:

- a. Corona and streamer discharge
- b. Glow discharge
- c. Dielectric barrier discharge (DBD)
- d. Arc discharge

Microdischarge and Townsend discharge are not included in this list, as they are not used for water treatment plasma reactors to our knowledge, except in ozone generation. Spark discharge is to be understood as a transient form of arc discharge and therefore falls in the fourth category. All four discharge regimes can be formed in the gas phase or the liquid phase, although we only found one very short and recent report on submerged DBD discharge without bubbles for water disinfection [47]. In the gas phase, corona discharge needs lowest power input and arc discharge the highest. Underwater discharge requires additional energy for plasma onset by cavitation, but it has the advantage of a large plasma–liquid contact surface. Locke et al. and Jiang et al. suggested in their reviews to apply low-energy plasma such as corona and glow discharge for the treatment of water with low contaminant concentration. On the other hand, high-energetic arc discharge might be more effective for high pollutant concentration [44, 46].

Depending on the voltage waveform used, the following types of discharge can be distinguished:

- i. DC discharge
- ii. AC (low frequency) discharge
- iii. Radio frequency discharge
- iv. Microwave discharge
- v. Monopolar pulsed discharge
- vi. Bipolar pulsed discharge

Variations are possible, such as periodically interrupted AC discharge to avoid excessive heating of the plasma gas [48]. Multiple voltage-related parameters can influence reactor energy efficiency, such as voltage amplitude and polarity, sinusoidal or pulse frequency, and pulse rise time and width. Their influence will be discussed in more detail in Section 4. By combining different voltage waveforms with the different discharge regimes in either the liquid or the gas phase, a list of discharge types can be obtained. Malik, for example, identified 27 distinct reactor types in his literature study, using this approach [42]. Locke et al. made a classification into 7 types [46]:

- Pulsed corona and corona-like electrohydraulic discharge
- Pulsed spark electrohydraulic discharge
- Pulsed arc electrohydraulic discharge
- Pulsed power electrohydraulic discharge
- Gas phase glow discharge
- Gas phase pulsed corona discharge
- Hybrid gas–liquid electrical discharge

This classification partly overlaps with the 6 types of plasma–water phase distribution mentioned above, where bubble discharge is included in hybrid gas–liquid discharge. Jiang et al. add 4 more types [44]:

- DC pulseless corona electrohydraulic discharge
- Dielectric barrier discharge
- Gas phase gliding arc discharge
- DC arc discharge torch

While the first 3 types generate plasma in or in contact with the liquid, the last type introduces the water under treatment directly in the torch, where it subsequently gets vaporized and becomes the plasma forming gas. It can therefore be classified as a subtype of spray discharge reactors. For more summarized information on the basic chemistry and physics of the discharge types in this list, the reader is referred to [43, 46].

The list illustrates how the 6 reactor types based on plasma–water phase distribution can be further split into subtypes. This has been done in a more extensive way by Locke and Shih, who identified more than 30 subtypes during their comparative study for the reactor energy efficiency of H_2O_2 production [49]. While this method has proven to be useful for their purpose, it disregards the influence of reactor design, materials, and working parameters. As Locke and Shih point out, studying this influence is a challenging task, but it will reveal valuable information on reactor optimization.

A small number of reviews have been made on plasma reactor energy efficiency for organic decomposition, which mostly focused on the influence of plasma–water phase distribution, discharge type, and a few working parameters. Nevertheless, no comprehensive overview is found in literature up to now on reactor design and reactor materials. The next section will deal with this topic. While the section is not meant to be fully comprehensive, we want to give a broader overview of reactor types reported in literature than has been done in prior reviews. Such overview is not only useful to get easier and faster understanding of reactor operation and development but also serves as source of inspiration for future reactor designs. Moreover, it reveals the close relationship between electrode configuration and discharge type. Both popular and more exotic, unique designs will be discussed, with extra focus on several general working parameters in Section 4. This review also includes plasma reactors that have been used for inorganic removal or biological treatment, as these reactors are also valuable candidates for aqueous organic decomposition.

3. Overview of reactor types

3.1. Electrohydraulic discharge reactors

Electrohydraulic discharge reactors have been studied for many years due to their importance in electrical transmission processes and their potential for water treatment. From theoretical

point of view, they are attractive for water treatment due to the relatively high ratio of plasma–water contact surface to plasma volume and proximity of plasma to the water surface. Moreover, they generate shock waves that can aid in organic decomposition. Nevertheless, electrohydraulic discharge reactors are usually less efficient than other reactor types for water decontamination [42, 50]. This is likely due to the additional input energy required for cavitation, i.e., gas phase formation during discharge onset.

Most commonly reported types of electrohydraulic discharge are pulsed arc and pulsed corona discharge. To our knowledge, all arc electrohydraulic discharge reactors reported in literature have pulsed input power. Mostly, a rod-to-rod electrode configuration is used (Figure 2a), but there are also reports on a reactor with a grounded L-shaped stationary electrode and a vibrating rod electrode (Figure 2b) [51, 52]. As learned from personal communication with Dr. Naum Parkansky, the vibrating electrode has the purpose to facilitate electrical breakdown and mix the treated solution. Apart from organic degradation, pulsed arc electrohydraulic discharge is also gaining more recent attention for biological treatment [53, 54]. Often, refractory metal such as tantalum, titanium, tungsten, or a corresponding alloy is selected as electrode material, as it needs to be sufficiently resistant to corrosion and shock waves. Tungsten has proven to be less corrosive than titanium and titanium alloy [53]. Particles that eroded from titanium electrodes enhanced methylene blue decomposition during aging in one study. The authors explained this enhancement with titanium peroxide formation from interaction of H_2O_2 with the particle surface [55]. In contrast, particles that eroded from low carbon steel electrodes diminished the decomposition of the same pollutant, possibly through the catalytic decomposition of H_2O_2 and scavenging of OH radicals [52]. While an increasing energy efficiency is reported for the decomposition of 2,4,6-trinitrotoluene [56] and methyl-tert-butyl ether [57] when the electrode gap is reduced, the opposite effect has been observed for atrazine degradation in another study [58]. Further investigation is needed to understand this apparent contradiction. In a small comparative study, Hoang et al. found the energy efficiency of 4-chlorophenol decomposition of this type of reactor to be one order of magnitude lower than degradation efficiency with UV, UV/ H_2O_2 , and O_3 systems [59].

Submerged pin-to-pin electrode configuration, as in Figure 2c, is uncommon in scientific literature. Such reactor has been used with high frequency bipolar pulsed power with reduced voltage and low pulse energy by Potocký et al. [61], to lower temperature loading of the electrodes and to clean both electrode tips continuously from any possible adjacent products. With addition of a high inductance in series with the discharge, transition from glow type to arc type discharge can be suppressed [62]. For sufficiently large interelectrode distance and low voltage amplitude, unbridged nonarc discharge was observed. For closer electrodes and higher voltage, bridged arc discharge was obtained, which, according to the authors, was initiated with spark formation at both electrodes [63].

A pin-to-plate electrode configuration (Figure 2d) is often used in electrohydraulic discharge reactors, either for DC glow [64, 65] or pulsed corona [66–68] discharge with positive polarity. The pin curvature radius determines the local electric field strength and is therefore an important parameter that influences discharge initiation [69]. For pulsed corona discharge, the anode pin material has been reported to lead to catalytic effects for organic decomposition.

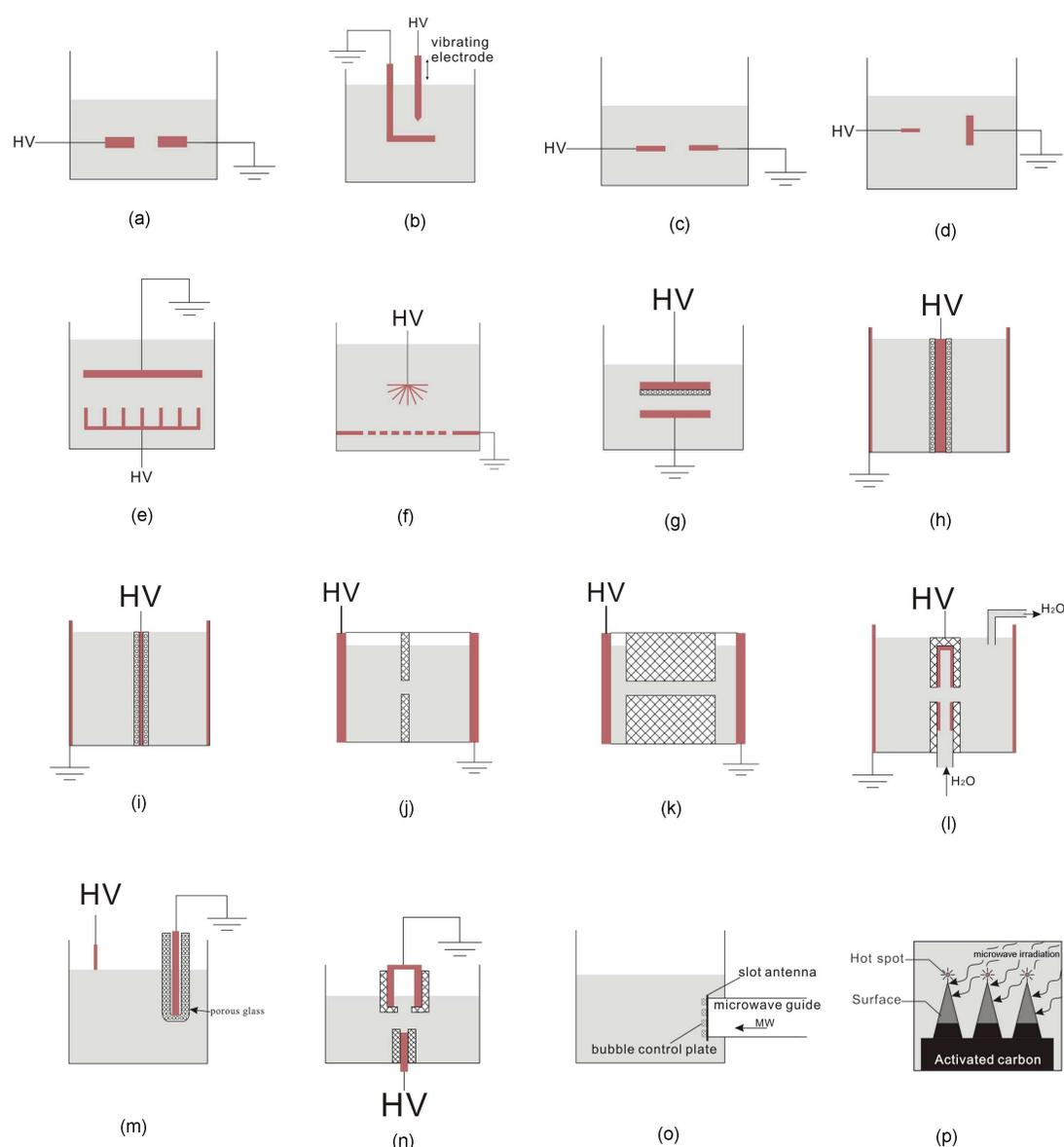


Figure 2. Types of electrohydraulic discharge reactors: (a) pulsed arc, (b) pulsed arc with vibrating electrode, (c) pin-to-pin, (d) pin-to-plate, (e) multi-pin-to-plate, (f) brush-to-plate, (g) plate-to-plate with porous ceramic coating, (h) coaxial rod-to-cylinder with ceramic coating on rod, (i) coaxial wire-to-cylinder with ceramic coating on wire, (j) diaphragm discharge, (k) capillary discharge, (l) coaxial diaphragm discharge reactor from Šunka et al. [60] with perforations in tubular electrode covered by polyethylene layer, (m) contact glow discharge electrolysis, (n) RF-discharge in cavitation bubble on electrode, (o) microwave bubble plasma from waveguide with antenna slot, and (p) “hot spot” plasma formation on activated carbon surface under influence of microwave irradiation.

Platinum enhances pollutant degradation as compared to a NiCr, but only in combination with certain electrolytes. In the case of ferrous salts, this is due to reduction of Fe^{3+} to Fe^{2+} by erosion particles from the platinum electrode [66, 67]. Erosion of tungsten, on the other hand, causes catalysis of oxidation by plasma-generated H_2O_2 [70].

To achieve a higher plasma volume, the pin electrode can be replaced by a multipin electrode [71], a brush electrode [72], or a plate electrode coated with a thin ceramic layer [73], respec-

tively, shown in Figures 2e–g. The concentration of predischARGE in the pores of the ceramic layer enhances the electric field strength on the electrode surface [68]. Due to inhomogeneities such as entrapped microbubbles inside the ceramic layer, the electric field can be locally even higher. As a result, a large number of streamers can be generated with lower input voltage as compared to uncoated electrode systems. Moreover, a ceramic coating does not only facilitate an upscale of the system but also serves as a support for a suitable catalyst of the plasma chemical reactions. Also, certain ceramic materials can enhance organic decomposition by catalytic effects [74]. Usually, positive high-voltage pulses are applied to the coated electrode. In some cases, negative high voltage is used to avoid arc formation, as this can damage the coating [73]. However, bipolar pulses are advised since monopolar pulses cause a polarized charge buildup on the ceramic, which can quench the electrical discharge [75].

To enlarge the plasma volume even further, coaxial geometry has been used, where either a coated rod [75] or wire [68, 74] high-voltage electrode is located at the symmetry axis of the grounded cylindrical electrode (Figures 2h–i). Analog to the curvature of pin electrodes, the diameter of the inner electrode is an important system parameter.

When a submerged anode and cathode are separated from each other with a perforated dielectric barrier, electrohydraulic discharge will occur through cavitation at the perforation. For larger ratio of perforation diameter to thickness, this type of discharge is called diaphragm discharge (Figure 2j), while for lower values, the term capillary discharge is used (Figure 2k). DC glow discharge [76, 77] and pulsed corona discharge [78] are commonly used for this reactor, but also AC power input is possible. The strongly inhomogeneous electric field during plasma onset has a similar structure to the one in pin-to-plate geometry. Therefore, similar plasma features can be expected. Energy efficiency for dye and phenol degradation with a single diaphragm is the same as in the case of a pin-to-plate electrode system [46]. Also, similarities with contact glow discharge electrolysis are reported [77]. As an important difference, diaphragm discharge is not in direct contact with the electrodes, which prevents electrode erosion [76]. Sunka et al. developed a coaxial reactor where a polyethylene covered tubular anode with perforations was placed inside a cylindrical cathode (Figure 2l) [60]. The generated plasma was reported to be similar as well.

Another common type of electrohydraulic discharge is contact glow discharge electrolysis. As depicted in Figure 2m, a pointed anode is placed with its tip in the water surface. It is separated from the submerged cathode by means of a sintered glass barrier. In such reactor, glow discharge is generated at the anode tip in a vapor layer surrounded by water. Plasma volume can be increased by increasing the anode number. Stainless steel performed better as anode material than platinum for Acid Orange 7 decoloration [79].

Electrohydraulic discharge can also be generated with RF or microwave power, but such reactor types are less common. Figure 2n shows a reactor where plasma is generated in a cavitation bubble on the tip of an RF electrode [80]. Producing cavitation bubbles by means of microwave power is more complicated. Therefore, a slot antenna can be placed in between the liquid and a microwave guide, as illustrated in Figure 2o. The electric field intensity can be enhanced by installing a quartz plate with holes, a so-called bubble control plate, on the slot antenna. Ishijima et al. reported an increase of methylene blue decomposition efficiency with

a factor of 20 after installation of the bubble control plate and tripling the amount of slot antennas [81]. Another way to produce underwater plasma with microwave power is by adding a microwave-absorbing material with high surface area, such as activated carbon, to the solution under treatment. Under influence of microwave irradiation, delocalized π -electrons on the activated carbon surface gain enough energy to jump out of the surface and generate confined plasmas (Figure 2p), also called hot spots, which are known to increase organic decomposition efficiency [82].

3.2. Bubble discharge reactors

Since electrohydraulic discharge generally has low energy efficiency due to the difficulty of initiating discharge directly in the water phase, a lot of attention has gone to enhancing efficiency by discharge formation in externally applied bubbles. Bubbling has the additional advantage of mixing the solution. Moreover, discharge initiation in the gas phase minimizes electrode erosion, which lengthens the lifetime of the system. Bubbling gas through the discharge region greatly increases radical density in the plasma, as for example observed by Sun et al. [69] for O₂ and Ar bubbles. Obviously, feed gas plays a determining role. Yasuoka et al. measured highest efficiency for Ar bubbles, in which plasma spread extensively along the inner surface, while lowest efficiency was obtained with He plasma, which has smallest plasma–water contact surface [83]. The importance of the working gas in plasma reactors in general will be further discussed in Section 4.

A common method is to pump gas upward through a nozzle anode, located underneath a grounded electrode [69], as shown in Figure 3a. Often, the nozzle electrode is placed inside a dielectric tube up to its tip, to avoid any energy leakage toward the water. Alternatively, a pin anode is sometimes placed inside a dielectric nozzle which transports the feed gas (Figure 3b) [86]. The pin tip can be placed below or above the nozzle extremity. Many variations can be encountered in literature, such as a pin anode inside a perforation in a dielectric plate (Figure 3c) [87] and different nozzle orientations (Figures 3d–e) [88, 89]. All choices in nozzle or perforation material, shape, dimensions, and orientation determine the bubble shape during formation and its position after detachment, which significantly influences the electric field in the interelectrode region and therefore the plasma characteristics. This complicates comparison of different reactors. Another option is to place the high-voltage electrode underneath the perforated dielectric plate, as shown by Yasuoka et al., Sato et al., and Yamatake et al. [83, 90, 91] (Figures 3f–h), where the ring-shaped grounded electrode is located around the bubble. Also, here, electrode geometry and position influence the electric field. Yasuoka et al. found their single hole reactor (Figure 3h) to be more energy efficient than advanced oxidation with photochemical persulfate, photocatalyst heteropoly acid, photodegradation, and ultrasonic cavitation for the decomposition of 2 surface active compounds [83]. By increasing the number of nozzles or holes, energy efficiency can be enhanced. In a study by Sato et al. [90], a reactor with a single hole (Figure 3f) was compared to a reactor with 9 holes (Figure 3g). Discharge power deposited per hole was lower in the reactor with 9 holes, which seemed to minimize self-quenching of OH radicals, resulting in higher efficiency. Following this line of thought, a multibubble system as in Figure 3i with a high-voltage mesh in the gas phase attached to a

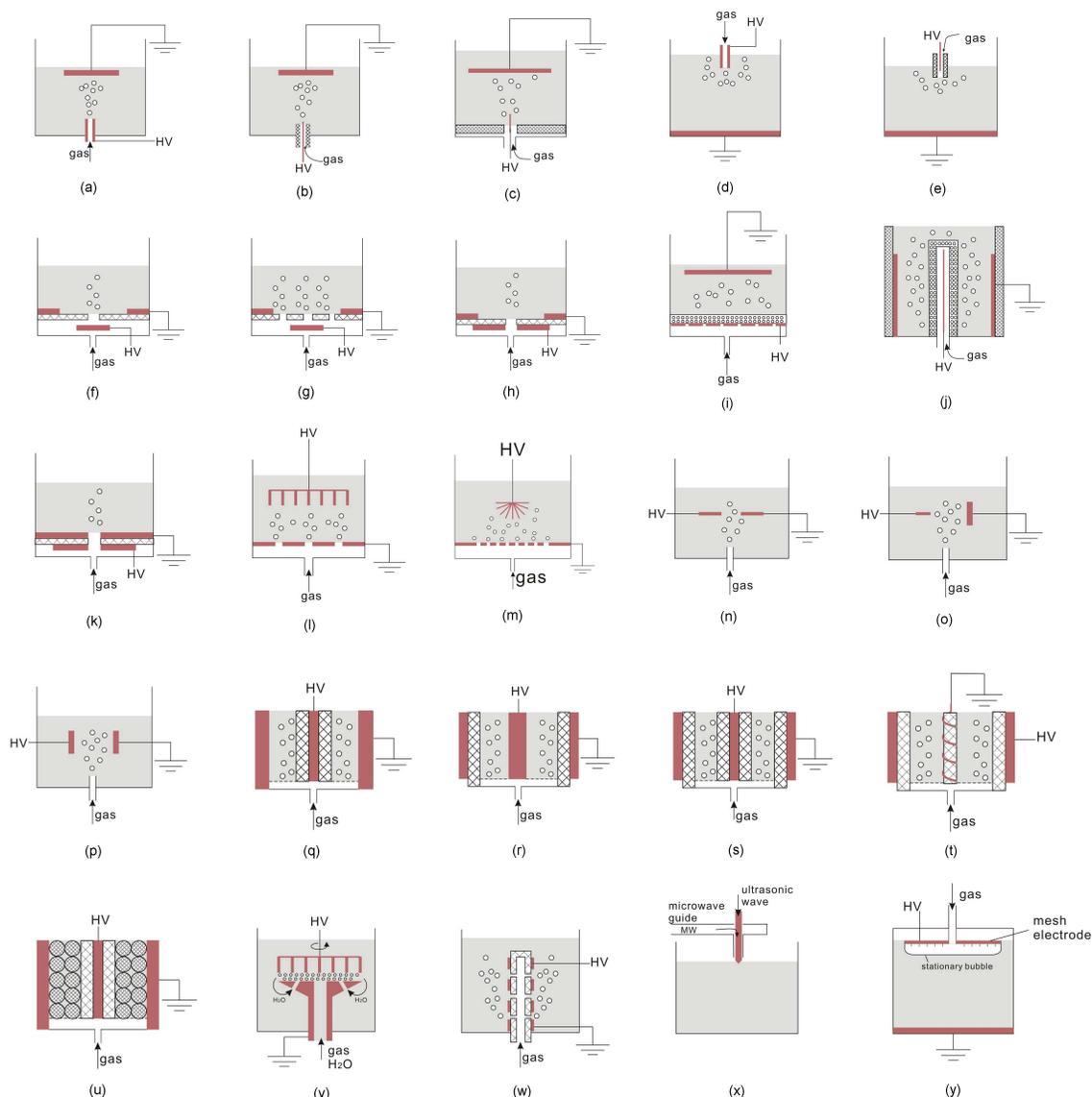


Figure 3. Types of bubble discharge reactors: (a) upward nozzle electrode-to-plate, (b) upward nozzle containing needle electrode-to-plate, (c) hole containing needle electrode-to-plate, (d) downward nozzle electrode-to-plate, (e) downward nozzle containing needle electrode-to-plate, (f–h) hole above electrode and inside circular ground electrode, (i) multibubble discharge on porous ceramic with high-voltage mesh, (j) multibubble discharge on porous ceramic tube surrounding a high-voltage wire electrode, (k) bubble discharge on hole in grounded electrode, (l–m) bubbles rising toward high-voltage electrode, (n–p) bubbles rising in between electrodes, (q) DBD reactor with inner barrier, (r) DBD reactor with outer barrier, (s) DBD reactor with double barrier, (t) DBD reactor with spiral electrode from Aoki et al. [84], (u) glass bead packed-bed DBD reactor, (v) coaxial arc discharge reactor with rotating multipin electrode from Johnson et al. [85], (w) multielectrode slipping surface discharge reactor, (x) microwave discharge in ultrasonic cavitation bubble, and (y) stationary bubble under high-voltage mesh.

porous ceramic seems a promising alternative [92]. Similarly, bubbling gas through a porous ceramic tube containing a high-voltage wire electrode [93] (Figure 3j) gives a large plasma–water contact surface as well. Increasing gas flow rate had no influence in this reactor on decomposition efficiency of phenol, while energy efficiency was enhanced for Acid Orange II removal.

Another situation is found when bubbles are formed on the grounded electrode, as shown by Yamatake et al. and Nikiforov [91, 94] (Figure 3k). Reactor from Figure 3h has more aggressive reaction with water and improved durability of electrode in comparison to the reactor from Figure 3k, as concluded by Yamatake et al. [91]. Nevertheless, one needs to take into account the applied voltage type. While for most of the reactors above positive pulsed corona discharge is used, less commonly AC voltage [94] or positive DC voltage [89, 91] is applied, leading to significantly different phenomena. As Yamatake has shown, plasma can be stably generated in the reactor from Figure 3h even without gas flow since O_2 gas is generated from electrolysis by application of positive DC voltage, while this is not the case for the reactor from Figure 3k. The microdischarge channel makes plasma more stable than that in the study of Kurahashi et al. [89], where the same phenomenon has been studied. Therefore, the system of Figure 3k requires higher gas flow due to the short lifetime of the oxygen radical, while in the reactor of Figure 3h decomposition did not depend on flow rate due to direct reaction with water.

Gas can also be bubbled from the ground electrode toward a multipin or brush high-voltage electrode, as shown by Chen et al. and Wang et al. [72, 95] (Figures 3l–m), or in between 2 sideways positioned electrodes, as shown by Lee et al., Miichi et al., and Vanraes et al. [96–98] (Figures 3n–p). The discharge systems are often very similar to the ones described in Section 3.1 without bubbles. For a plate-to-plate configuration, pulsed streamer discharge mostly occurred inside bubbles adjacent to the electrodes [97].

A last common type of bubble discharge reactor has a coaxial DBD geometry. The cylindrical dielectric barrier can either be placed at the inner [99] or at the outer electrode [91], or at both [91] (Figures 3q–s). For a single barrier, a reticulate electrode can be placed in contact with the water in order to enhance the local electric field [99]. With double barrier, unwanted erosion of the electrodes can be avoided. In the study of Yamatake et al. [91], a double-barrier reactor was found to have higher decomposition efficiency of acetic acid in comparison to a single barrier reactor with similar dimensions, which is most likely caused by a difference in energy density. Monopolar pulsed, bipolar pulsed, and AC high-voltage are most commonly applied to the inner electrode. In the study of Aoki et al. [84], however, the reactor from Figure 3t was used to generate RF glowlike plasma in bubbles. The grounded spiral electrode impeded the motion of the bubbles in the small gap between the electrodes, which increases the probability of discharge in the bubbles. Nevertheless, most of the input energy seems to be dissipated as heat in this system, resulting in low energy efficiency. Bubble movement can also be impeded by adding obstacles in the water bulk. For the single barrier reactor of [100] (Figure 3u), the addition of spherical glass beads significantly enhanced the energy efficiency of indigo carmine decomposition. Porous ceramic sphere gave worse performance than glass beads, but better one than inert conductive fragments. As an interesting research question, it is still unclear whether bubbles in contact with the electrodes in these DBD systems give rise to a better efficiency than freely rising bubbles or not.

A more exotic and patented reactor design is investigated by Johnson et al. [85] (Figure 3v). In this reactor, the high-voltage electrode is a pin array that can rotate at speeds up to 2500 rpm. Oxygen is pumped through the stationary electrode and nebulized to form a bubble mist between the electrodes. DC voltage is applied to the system, generating arc discharge. Rotating

the electrode distributes erosion particles evenly on the stationary electrode, preventing pitting and unwanted changes in the relative distance between the electrodes. Moreover, it reduces mass transfer limitations that are apparent in pin-to-plate reactors. Additionally, it lowers the inception voltage by abating the effective distance between the pin electrodes and the stationary electrode. Energy efficiency for methyl tert-butyl ether decomposition increased with an increase in spin rate. The system was found to be more energy efficient than many corona-based technologies but still requires further optimization.

Anpilov et al. developed the multielectrode slipping surface spark discharge system depicted in Figure 3w [101]. A series of cylindrical electrodes are mounted on the outside of a dielectric tube. One of the extreme electrodes is grounded, and high-voltage pulses are applied to the other extreme electrode. All other electrodes are on floating potential. To increase system efficiency, the outer surface of the electrodes is coated with a thin insulating layer. Gas is pumped into the electrode gaps through drilled holes in the dielectric tube. When a high-voltage pulse is applied, plasma discharge occurs initially in the first interelectrode gap adjoining the high-voltage electrode. The breakdown of this gap quickly transports the high-voltage potential to the next electrode, which leads to the breakdown of the second gap. The process repeats itself until the grounded electrode has been reached. This way, the discharge load on each electrode can be kept low, enhancing erosion resistance and increasing the system lifetime. The effectiveness of the system has been demonstrated for disinfection of biological wastewater, methane conversion, and aqueous organic waste decomposition [102].

Apart from bubble cavitation by electrical discharge, the classical gas pumping method, and gas formation by electrolysis, bubbles can also be generated with ultrasonic cavitation. Since microwave power cannot easily generate cavitation bubbles, a combination of ultrasound and microwave discharge can be an attractive method. An example is given by Horikoshi et al. [103] (Figure 3x). Stationary bubbles, however, are not commonly used in bubble discharge reactors, unless for diagnostic purposes. An example is given by Yamabe et al. [104], with the reactor of Figure 3y. This reactor was used to investigate plasma formation and propagation along the gas–water interface, which is a common feature for bubble discharge reactors and which makes it, therefore, different in nature than most gas phase discharge reactors.

3.3. Gas phase discharge reactors

Electrical discharge in the gas phase is usually more energy efficient for organic degradation than discharge in the liquid phase [42, 43, 50]. In this section, we will distinguish 4 subgroups of gas phase discharge reactors: corona and glow discharge over a horizontal water surface (Figure 4), DBD over a horizontal water surface (Figure 5), falling water film reactors (Figure 6), and arc discharge over a water surface (Figure 7).

3.3.1. Corona and glow discharge over water surface

The most standard version of a discharge over water surface has a pin-to-water configuration with a grounded water electrode, as depicted in Figure 4a. The type of discharge produced in this reactor, corona, glow, or transient glow-to-spark, depends on the applied voltage, pin

curvature, interelectrode distance, and voltage polarity [105, 106]. For the application of water treatment, both positive and negative DC and monopolar pulsed voltage have been reported. AC input power is less common but has been used as well [107]. Plasma volume can be increased by replacing the high-voltage pin electrode with a multipin [108], a brush [72], or a horizontal wire [109] (Figures 4b–d). In the study of Miyazaki et al. [108] with a multipin electrode, the energy efficiency for a certain amount of phenol decomposition was independent of the type of discharge, the voltage amplitude, the polarity of the applied voltage, and the amount of pin electrodes.

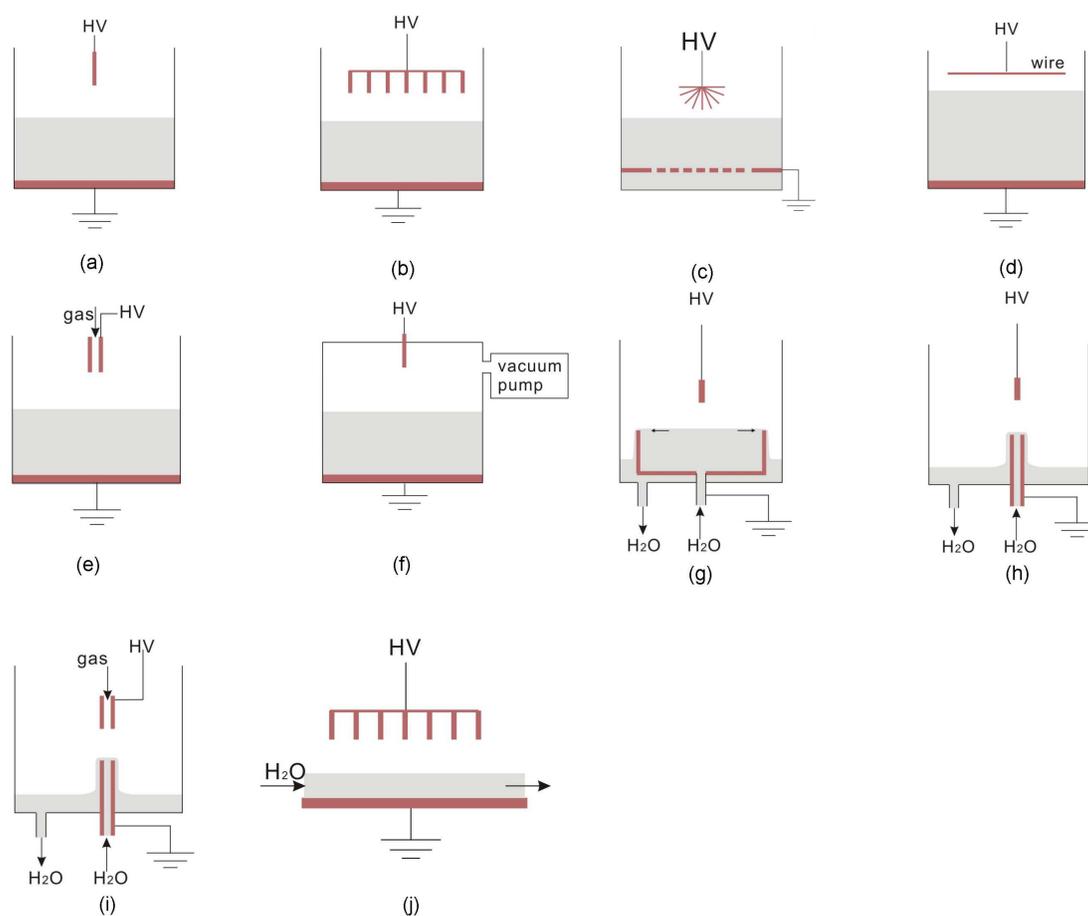


Figure 4. Types of reactors with corona or glow discharge over water surface: (a) pin-to-water, (b) multi-pin-to-water, (c) brush-to-water, (d) wire-to-water, (e) nozzle electrode-to-water, (f) low-pressure pin-to-water glow discharge reactor, (g) pin above radial water flow, (h) pin above flowing liquid electrode, (i) miniature microjet above flowing liquid electrode, and (j) multipin above water flow.

According to Dors et al., atmospheric pressure glow discharge in air produces gaseous nitrogen oxides, leading to formation of undesirable aqueous nitrates and nitrites, while DC positive corona produces ozone in air without any traces of nitrogen oxides [110]. The energy efficiency of phenol oxidation in their system, depicted in Figure 4e, was comparable to the results obtained in pulsed corona discharge systems. Sharma et al., however, compared their low-pressure negative DC glow discharge reactor (Figure 4f) with bench scale data of atmospheric

pressure corona discharge and concluded that the power cost for pentachlorophenol decomposition was lower for their system [111]. Additionally, the operating cost of their reactor was found to be comparable with power cost of UV-based advanced oxidation technologies. Yet it is unclear how feasible such low-pressure system is for applications with large water volume or continuous water flow.

It is important to note that dimensions and movement of the water phase in this type of reactors can influence energy efficiency significantly. In the system of Sharma et al., for example, stirring rate increased the rate of pentachlorophenol removal [111]. Water movement also plays an important role in radial flow reactors (Figure 4g). In the reactors from Jamróz et al. [112] with small sized flowing liquid cathode (Figures 4h–i), degradation efficiency depended strongly on the water flow rate, while the Ar flow rate from the miniature flow Ar microjet (Figure 4i) gave negligible effect on methyl red decomposition. The importance of water and gas flow rates will be further discussed in Section 4.3. As mentioned above, making the solution flow as a thin film along the discharge is another way to enhance the oxidation process. Promising results from a pilot-scale system with negative pulsed corona from multiple carbon fiber cathodes above a flowing water film (Figure 4j) have been published by Even-Ezra et al., Gerrity et al., and Mizrahi and Litaor [113–115]. The system was similar or more efficient than a pilot-scale UV/H₂O₂ advanced oxidation process and achieved similar energy efficiency to those reported in the literature for other advanced oxidation processes [113, 114]. Moreover, the plasma pilot system with additional ozone injection was more cost-effective than three other commercialized advanced oxidation systems (O₃/H₂O₂, O₃/UV, and O₃/H₂O₂/UV) [115]. However, the total capital costs and reliability of large-scale gas discharge reactors for water treatment are still relatively unclear.

3.3.2. DBD over water surface

DBD over horizontal water surface is most commonly powered with AC voltage, but occasionally pulsed high voltage has been used as well. Often, glass is used as dielectric barrier, especially quartz glass, while Al₂O₃ ceramic barriers have also been reported less frequently. Interestingly, reactors with DBD over water often have energy efficiency for organic decomposition that increases with input power [116–118]. The most standard reactor design for DBD in the gas phase over a water surface is shown in Figure 5a. In the study of Hu et al. [116], energy efficiency in such reactor was found to increase by decreasing the distance between the dielectric barrier electrode and the water surface. This can be explained with a decrease in plasma volume and thus in unused plasma reactions far from the water surface. A water batch can also be placed in between two dielectric barriers to avoid erosion of one of the electrodes, as in the study of Hijosa-Valsero et al. [119] (Figure 5b). A more exotic way of bringing DBD over a water surface is shown in Figure 5c, where water is kept on floating potential. However, this device has not been applied for organic degradation and is instead used for biomedical applications [120]. In another less common design, the water can be located above the dielectric barrier, with an uncovered high-voltage electrode positioned above the water surface, as in the wire-to-water reactor of Marotta et al. [121] (Figure 5d). In this reactor, the energy efficiency of phenol decomposition was 3.2 times higher with stainless steel wires as compared to Ni/Cr

wires. However, it is unclear whether this effect should be attributed to the larger diameter of the Ni/Cr wires or their possible inhibiting effect on ozone or other oxidants. The material of the ground electrode in contact with water in many DBD reactors is, on the other hand, clearly important. In the study of Lesage et al. [122], the use of a stainless steel substrate resulted in a better decomposition efficiency in comparison to the use of brass. This is explained with corrosion of the brass substrate under influence of nitrate, leading to formation of aqueous nitrite, which scavenges OH radicals and thus inhibits the degradation process. Stainless steel, as a more inert metal, does not have this effect.

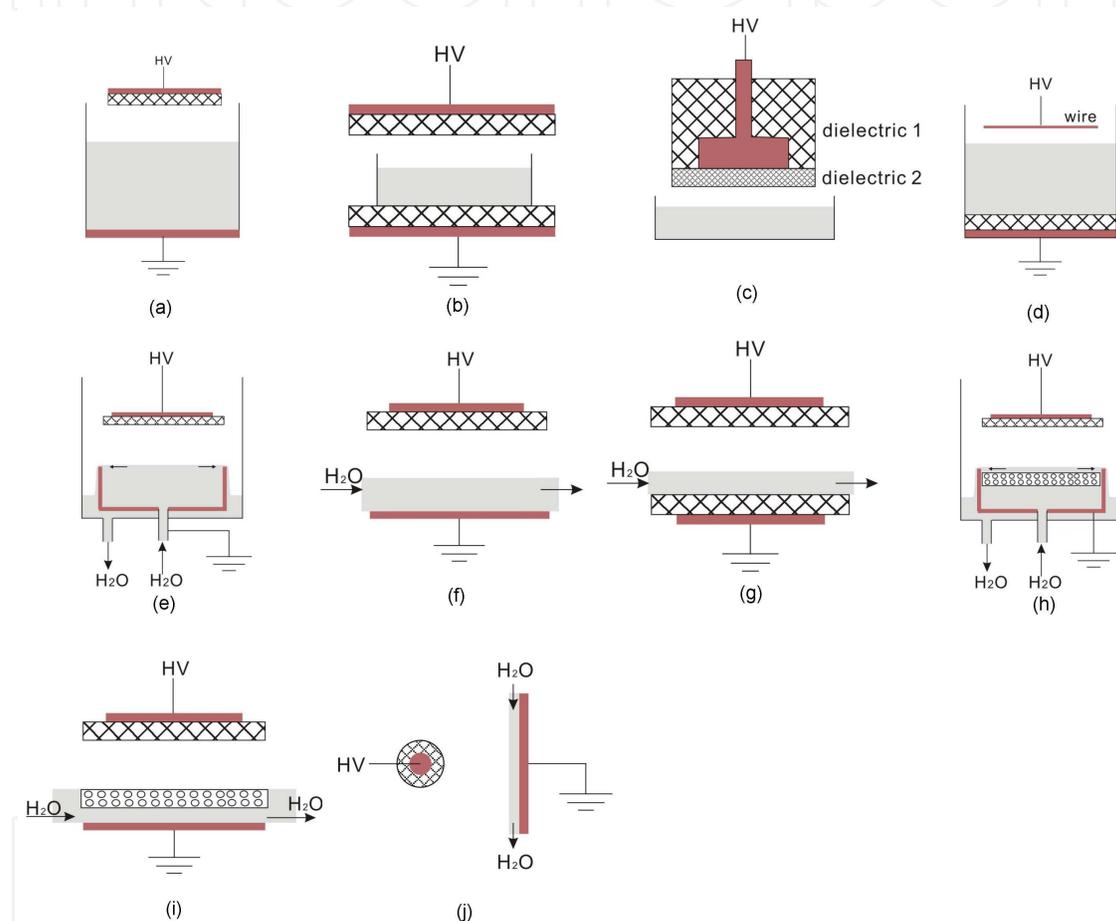


Figure 5. Types of reactors with DBD over water surface: (a) DBD-to-water, (b) water batch in between DBD, (c) DBD above floating electrode, (d) wire-to-water DBD, (e) DBD above radial water flow, (f) DBD above water flow, (g) water flow in between DBD, (h) DBD over radial water flow on porous ceramic, (i) DBD over water flow on porous ceramic, and (j) DBD rod to falling water film.

Also for DBD-based systems, the movement of water influences the degradation efficiency. Reactors with radial flow [117] or flowing water films [118, 123] are investigated in literature for organic decomposition (Figures 5e–g). Both situations have also been reported with incorporation of a porous ceramic segment in the zone between electrodes (Figures 5h–i) [124, 125]. This porous segment serves as guide for the flowing water. It allows the water to remain undisturbed by the electrical discharge due to hydrophilic force. This enables a reduction of

the discharge gap and subsequently an increase in the intensity, stability, homogeneity, and efficiency of the discharge. Under such a configuration, a transition from filamentary mode to semi-homogeneous mode of the plasma discharge can be realized [125]. Moreover, such ceramic can be effectively used as substrate for photocatalysts, where both substrate and catalyst remain unchanged after use [124].

An exotic reactor type where a rod high-voltage electrode with dielectric cover is placed next to a falling water film has been investigated by Lesage et al. [122, 123] (Figure 5j). The reactor was found to be significantly more efficient than a gliding arc (see Section 3.3.4) over the same falling water film, partly due to less corrosion of the brass substrate in contact with the water.

3.3.3. Coaxial reactors with falling water film

A relatively common falling water film reactor that does not use DBD is shown in Figures 6a–b and is often referred to with the term wetted-wall reactor. Either a rod [126] or more commonly a wire [127–130] high-voltage electrode is placed along the axis of a grounded cylindrical electrode. The falling water film flows along the inner wall of the cylinder electrode where it comes in contact with streamer or corona discharge. Mostly, positive pulsed power is applied on the inner electrode, but also negative DC [127] has been reported. Usually, corona discharge is formed in such reactors for all voltage waveforms, while spark discharge is undesired due to excessive energy dissipation to Joule heating. To prevent spark formation, it is necessary to have the entire inner wall area covered by the water flow [130]. The choice of gas flow direction is important, as concluded by Faungnawakij et al. [131] for negative DC corona. Experiments showed a downward airflow to be more effective than upward airflow for acetaldehyde degradation. In the study of Sano et al. [127], the energy efficiency of a wetted-wall reactor with negative DC voltage applied to the inner wire was calculated to be 3 to 4 times higher than in a wire-to-water corona reactor (Figure 4d) over flowing water with negative DC voltage. For the same reactor, energy efficiency was found to be highest for conditions of a smooth water surface, i.e., for a minimal water flow rate where the flow entirely covers the anode inner wall and for an optimal current, which does not disturb the flow by strong ion wind. There is an optimal wall radius, where decomposition efficiency is maximal. For higher radius, many plasma-generated short-lived radicals cannot reach the water film in time, while for smaller radius, the plasma–water contact surface decreases [127]. Sato et al. compared four kinds of coaxial reactors with falling water film and positive pulsed power. They found phenol most energy efficiently removed with the configuration of Figure 6b [128]. Sealing such reactor seems beneficial for energy efficiency, due to better confinement of the produced ozone [129].

Most falling water film reactors generate plasma by DBD, either with AC or monopolar pulsed high voltage. Pulsed DBD in coaxial configuration using O_2 is considered as one of the most efficient electrical discharge systems evaluated because of the large surface area and small electrode distance [50]. Several configurations are possible, but in the most common design, the water film flows over the surface of an inner stainless steel rod electrode placed inside a glass cylindrical vessel which acts as dielectric barrier. The outer electrode can be a metal mesh or a metal painted layer which is located around the vessel. Four versions of this reactor design

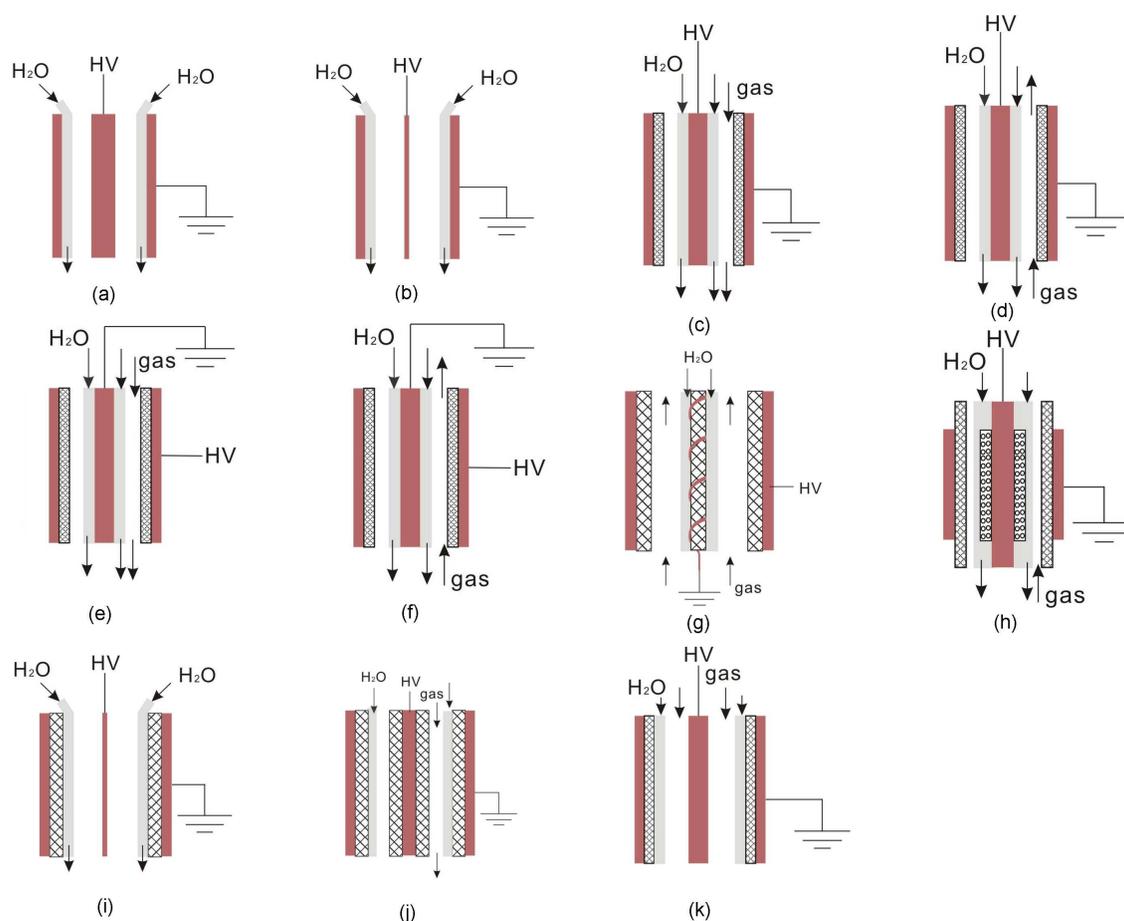


Figure 6. Types of coaxial reactors with falling water film: (a) wetted-wall reactor with rod electrode, (b) wetted-wall reactor with wire electrode, (c–f) 4 variations of falling water film DBD reactor with outer barrier, (g) falling water film DBD reactor with inner spiral electrode, (h) falling water film on glass fiber fabric in DBD reactor with outer barrier, (i) wetted-wall DBD reactor with wire electrode, (j) wetted-wall DBD reactor with double barrier, and (k) configuration of coaxial whirlpool reactor of [132].

are found in literature, where the inner electrode is either grounded or connected to the high voltage and with an upward or downward gas flow (Figures 6c–f). With the reactor of Figure 6f, energy efficiencies of micropollutant decomposition are about one order of magnitude higher than for a water batch in between a DBD reactor (Figure 5b) [119]. A slightly different configuration was used by Ognier et al. [133], where a tungsten wire that was rolled around a dielectric rod served as inner grounded electrode (Figure 6g). In this study, volatile aqueous compounds were treated. The more volatile the compound was, as expressed with the Henry's law constant, the more efficiently it was removed. Therefore, degradation processes of pollutants in the gas phase should be considered in plasma reactors, depending on the volatility of the compound. In the study of Bubnov et al. [134], the inner electrode of a coaxial DBD reactor was covered with a 1-mm-thick porous hydrophilic glass-fiber fabric (Figure 6h). This fabric allows a more homogeneous water flow and higher water retention time. Moreover, it can function as substrate for catalysts, such as Cu and Ni compounds, which enhanced the decomposition efficiency in the research of Bubnov et al. [134].

Less frequently, the water film is chosen to flow along the inner wall of the dielectric barrier. Morimoto et al., for example, investigated the effect of placing a dielectric barrier inside the wetted-wall reactor of Figure 6b, as shown in Figure 6i. Addition of the barrier allows to decrease the interelectrode gap without formation of spark discharge, which is expected to increase energy efficiency. With the application of positive nanosecond pulsed high voltage on the inner wire, the treatment efficiency of the DBD system was found to be, surprisingly, less energy efficient for indigo carmine decomposition as compared to the normal wetted-wall reactor. Another type of wetted-wall DBD reactor with falling water film is investigated by Rong et al. [135], for a reactor with double dielectric barrier (Figure 6j). A more exotic type of DBD reactor with modified water-gas mixing is reported by Chen et al. [132]. The system is powered with high frequency bipolar tailored voltage pulses. It has a configuration as shown in Figure 6k, but water and air are introduced in the reactor with high flow rate of 5 L/min and 100 to 200 L/min, respectively, causing a whirlpool. For this reactor, gas flow rate was shown to have negligible effect on decomposition efficiency of methyl orange.

3.3.4. Arc discharge over water surface

Gliding arc discharge above a water surface (Figure 7a) is a popular approach for water treatment with plasma. In this reactor type, two diverging electrodes are placed above a water solution. An electric arc forms at the shortest electrode gap and glides along the electrode's axis under influence of a gas flow directed toward the water surface. The arc length increases on moving and its temperature decreases, turning the arc from thermal plasma into quenched plasma while breaking into a plume. A new arc then forms at the narrowest gap and the cycle continues. Unfortunately, many publications on this type of reactor are unclear about the use of AC or DC voltage, but AC power is definitely a common choice. Important research in this field has focused on enlarging the plasma treated water surface with adjustments in design. One possibility is to use a couple of controlled electrodes in between the electrode gap to facilitate breakdown, increasing current intensity and allowing a larger interelectrode distance [136]. Another option is to use three main electrodes supplied by two power sources, as proposed by Burlica et al. [137] (Figure 7b). Both approaches have shown to increase reactor efficiency. Gliding arc discharge can also be used for the treatment of falling water films, as shown by Lesage et al. [123] (Figure 7c). Arc discharge with an active water electrode is less commonly researched (Figure 7d). According to Janca et al. [138], the energy efficiency of such system was found to be strongly dependent on the type of discharge produced, such as arc or gliding arc. For more detailed information on water treatment by means of gliding arc, the reader is referred to the review by Brisset et al. [136].

3.4. Spray discharge reactors

3.4.1. Low-energy spray discharge reactors

Although spray discharge reactors have received more attention in recent years due to their high reported energy efficiencies [42–44], still more research is required to characterize and optimize them. One of the most common spray reactors has a wire-to-cylinder geometry

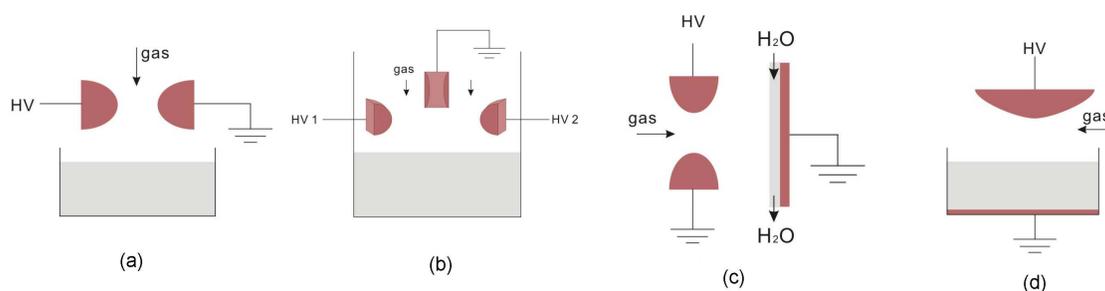


Figure 7. Types of gliding arc discharge reactors over water surface: (a) standard configuration, (b) configuration with extra main electrode, (c) gliding arc discharge to falling water film, and (d) gliding arc discharge with active water electrode.

(Figure 8a), similar to wetted-wall reactors. This reactor type is always operating with positive pulsed corona or streamer discharge, according to our literature review. In the study of Kobayashi et al. [139], different spraying nozzles were used to investigate the influence of water location on the energy efficiency of indigo carmine decomposition. As the results showed, spraying water as droplets into the discharge area is more effective than making it flow as a water film on the inner reactor wall. Moreover, droplets that were sprayed close to the reactor wall underwent 1.5 times faster decolorization than droplets near the wire electrode. Energy efficiency was found to be independent of droplet size for same water flow rate [140].

Sugai et al. adjusted this reactor by addition of packed-bed of pellets (Figure 8b) or fluorocarbon wires (Figure 8c) in order to increase the droplet retention time in the discharge space [141]. The packed pellets were hollow polyethylene balls with 14 holes per ball to increase discharge. The fluorocarbon wires were woven as insulation grids in the outer cylindrical electrode. Addition of the pellets decreased the energy efficiency significantly, due to the narrowing of the discharge space. The fluorocarbon wires, however, kept the discharge space unaltered and increase the energy efficiency with 2–10%.

In the study of An et al. [142], a similar electrode configuration was used as in Figure 8a, but with tooth wheels assembled on the inner electrode (Figure 8d). Here, droplets were not created by spraying, but due to condensation of steam under influence of up-flowing air. Alternatively, positive pulsed corona can also be generated in a spray reactor around wire anodes in parallel with two grounded plate cathodes [143], as depicted in Figure 8e. In another approach, water is sprayed in between rod electrodes that are each surrounded with a dielectric barrier (Figure 8f). Monopolar pulsed voltage of both polarities is reported in literature [144, 145]. In the study of Wang et al. [146], grounded water was sprayed from dielectric nozzles in proximity of a high-voltage dielectric barrier plate electrode (Figure 8g). When AC high voltage was applied to the plate, the by electrostatic induction generated electrostatic force pulled the water droplets to the glass dielectric layer. The energy efficiency of indigo carmine decomposition depended on both voltage amplitude and air gap distance, for which optimal values were found. Another interesting reactor type is based on the electrospray process to simultaneously generate and treat water spray under influence of high voltage, as shown in Figure

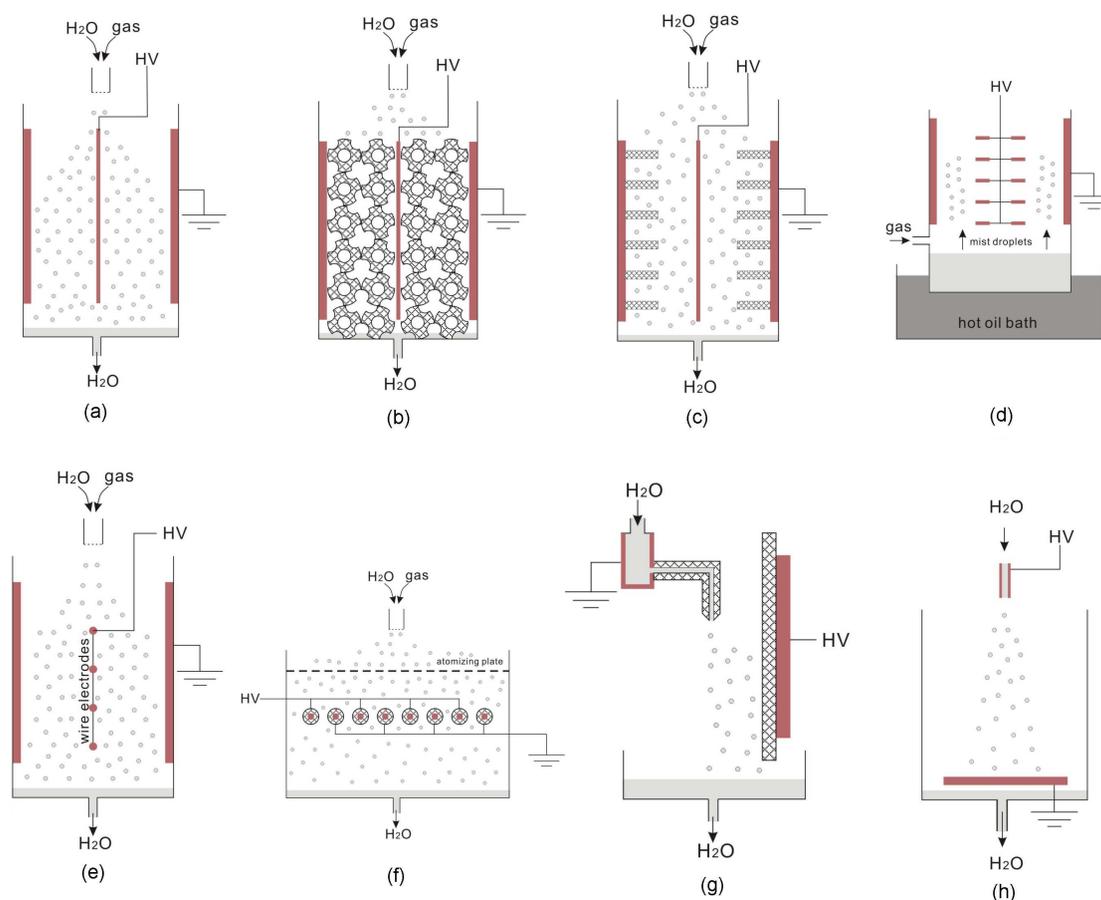


Figure 8. Types of low-energy spray discharge reactors: (a–c) wire-to-cylinder corona or streamer reactor without or with packed-bed of pellets or fluorocarbon wires for increased droplet retention, (d) mist droplets in tooth wheel-to-cylinder corona reactor, (e) multi-wire-to-plate corona reactor, (f) spray through DBD rods, (g) spray from grounded electrode to DBD plate, and (h) electrospray reactor.

8h. In the study of Elsawah et al. [147], water is treated that way with positive pulsed corona electrospray.

3.4.2. Spray arc reactors

Water spray can also be introduced in gliding arc discharge for treatment, as depicted in Figure 9a. This method is found to be more energy efficient than gliding arc discharge over a water surface as discussed in Section 3.3.4 [136, 137]. The decomposition of 4-chlorophenol in such spray reactor became more energy efficient with increasing gas–water mixing rate [148]. Efficiency is higher with electrodes from stainless steel than for aluminum or brass electrodes. Also here, extending the plasma volume by the use of a controlled electrode couple or an extra main electrode enhances energy efficiency (Figure 9b) [137]. The process can also be optimized by introducing the water with a flat spraying nozzle perpendicular to the gas flow to improve the contact with the plasma (Figure 9c) [149]. For more detailed information on water treatment by means of gliding arc spray reactors, the reader is referred to the review by Brisset et al. [136]. Water can be treated as well with a DC plasma torch, where it is usually directly introduced

into the torch as plasma forming gas. A discussion on this treatment method is provided by Brisset et al. [44].

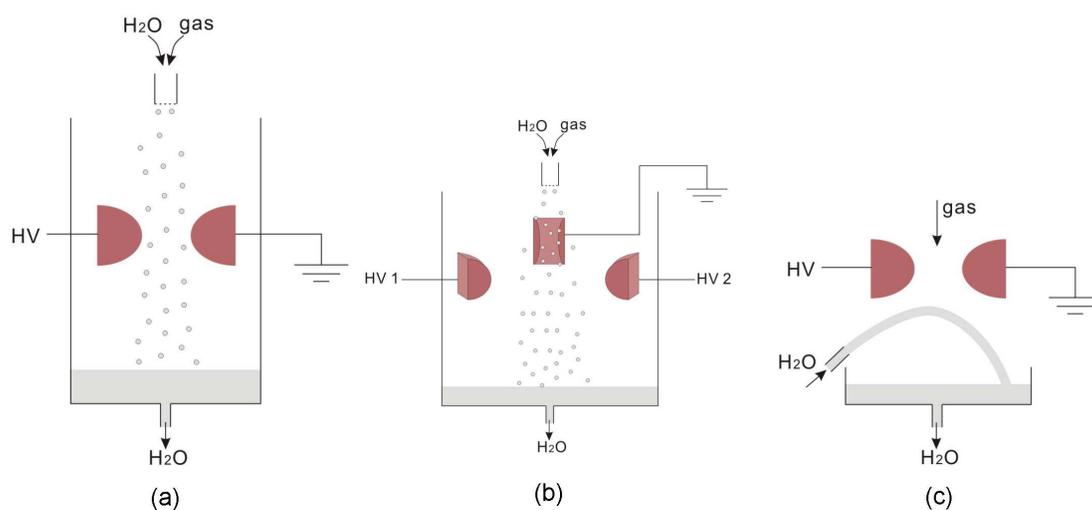


Figure 9. Types of spray gliding arc reactors: (a) standard configuration, (b) configuration with extra main electrode, and (c) water jet under angle through gliding arc discharge.

3.5. Hybrid reactors

Electrohydraulic discharge and gas phase discharge can simultaneously be generated when a high-voltage electrode is placed in the water phase with a grounded electrode above the water surface in the gas phase. Mostly, positive pulsed corona is generated in these systems reported in literature. Several electrode configurations are possible, such as an underwater pin to plate in gas [150] (Figure 10a) and an underwater pin to multipin in gas [151] (Figure 10b). In some reactors, a second high-voltage electrode is placed in the gas phase, either powered by the same high-voltage source [151] (Figure 10c) or by a second one [152] (Figure 10d). Also here, energy efficiency can be enhanced by discharge formation in externally applied bubbles, leading to hybrid reactors that combine bubble discharge with gas phase discharge. One example is given by Ren et al. [153], where bubbles are formed on high-voltage nozzle electrodes located underneath a plate electrode in the gas phase (Figure 10e). Hybrid reactors with discharge in both water and gas phase are sometimes proposed for the treatment of gaseous and aqueous pollutants simultaneously, as in the case of volatile pollutants [44, 46]. Their energy efficiency for organic decomposition is moderately higher than the one of hydraulic discharge reactors [42, 43].

Another type of hybrid reactor combines the treatment of a falling water film and droplets. This situation naturally occurs by spraying water from a shower nozzle at an angle. In the study of Kobayashi et al. [139], a wetted-wall hybrid reactor with inner wire anode was used, where water solutions from the falling film and from the droplets were collected separately (Figure 10f). Indigo carmine was decomposed 0.57 times faster in the droplets than in the water

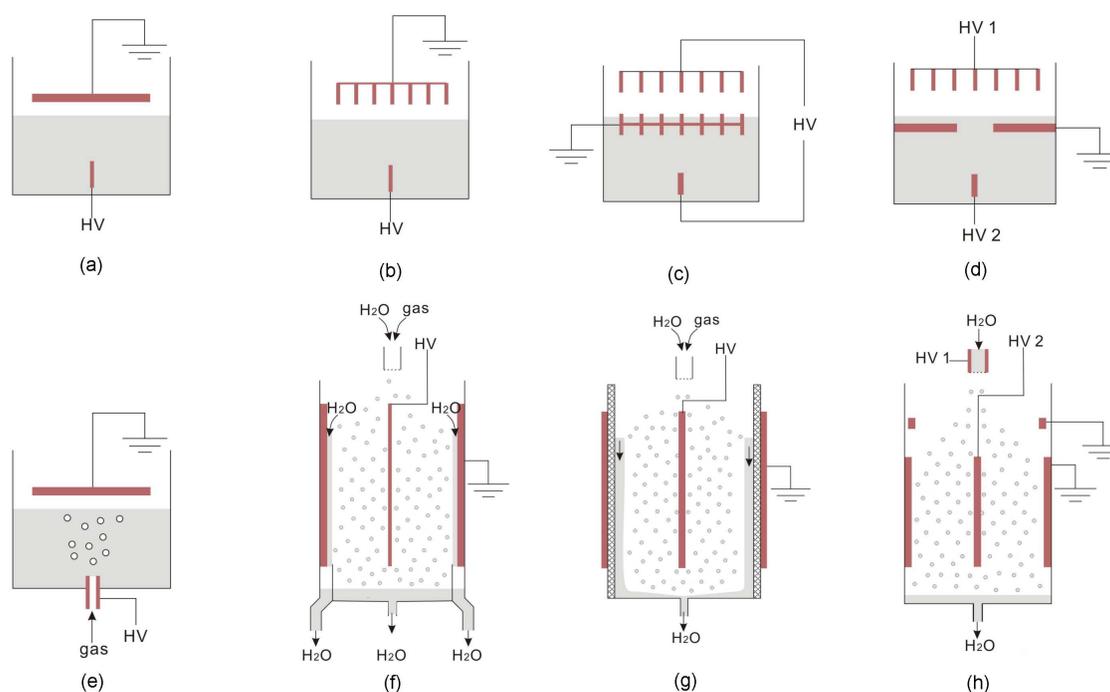


Figure 10. Types of hybrid reactors: (a, b) underwater high-voltage pin to plate or multipin in gas, (c) reactor from Lukes et al. [151], (d) reactor from Lukes et al. [152], (e) bubble discharge on underwater nozzle electrode to plate in gas, (f) wetted-wall spray corona reactor with inner wire electrode, (g) wetted-wall spray DBD reactor with outer barrier, and (h) electrospray through wire-to-mesh corona reactor.

film, as could be expected from the higher energy efficiency of spray discharge reactors as compared to falling water film reactors. In the study of Nakagawa et al. [154], the water film was formed on the dielectric barrier which separated the inner rod anode and the grounded mesh surrounding the barrier (Figure 10g). For low water flow rate, the energy efficiency of rhodamine B decomposition was similar for 3 of such reactors with different inner diameter and barrier thickness. For higher flow rates, however, one reactor performed significantly better. This reactor had larger inner diameter and equal barrier thickness compared to one of the other reactors.

A special case is found when droplets from an electrospray are treated a second time with plasma discharge. In the study of Njatawidjaja et al. [155], electrostatically atomized droplets passed through pulsed corona discharge in between a wire-to-mesh electrode configuration (Figure 10h). In both parts of the reactor, positive polarity performed better than negative one for the decomposition of Chicago sky blue dye. In the electrospray, positive DC voltage produced a larger number of finer droplets with a wider spray angle than in the case of negative voltage.

3.6. Remote discharge reactors

The concept of remote discharge reactors for water treatment is not new. An early example is ozonation, where ozone is generated by means of plasma discharge in gas phase and subsequently transported toward the solution under treatment. More recently, electrical discharge

reactors have been developed where remotely generated plasma gas is bubbled through the solution. As main difference, the plasma gas does not only contain ozone, but also other reactive species, such as H_2O_2 and OH . In the study of Tang et al. [156], this is accomplished by using humid air as feed gas of a DBD gas phase reactor (Figure 11a). With corona discharge in dry air, positive and negative ions can be generated in addition to ozone for water treatment, as in the air ionization device reported by Wohlers et al. [157]. Yamatake et al. compared the bubble discharge reactor from Figure 3k with ground electrode in contact with water to a reactor where plasma is generated separately from the water and subsequently bubbled through the solution (Figure 11b) [158]. Both reactors had identical electrode configuration, used oxygen as feed gas, and were powered by the same positive DC voltage source. Acetic acid was not decomposed in the remote discharge reactor, while decomposition was significant in the bubble discharge reactor. This difference was explained with the production of oxygen radicals, which acted as main oxidant during bubble discharge but had too short lifetime to reach the water in the remote discharge reactor.

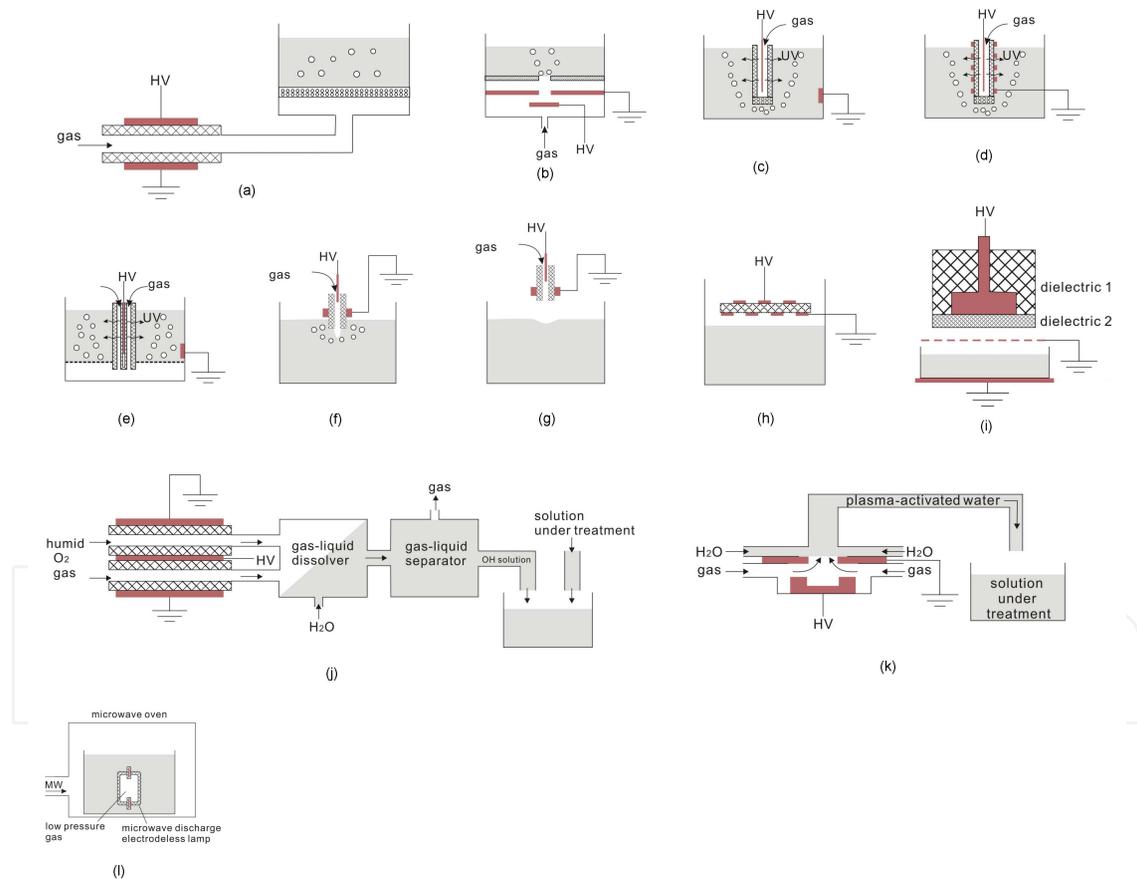


Figure 11. Types of remote discharge reactors: (a, b) plasma gas bubbling reactors, (c–e) plasma gas bubbling reactors with UV irradiation through quartz barrier, (f) underwater DBD plasma jet, (g) DBD plasma jet over water surface, (h) metal strips on quartz disc for DBD above water surface, (i) setup from Dobrynin et al. [159] with removable grounded mesh, (j) reactor from Zhang et al. [160] for production of hydroxyl radical solution, (k) gliding arc reactor from Kim et al. [161] for plasma-activated water production, and (l) reactor with tungsten-triggered microwave discharge electrodeless lamp.

Plasma gas bubbling can be combined with UV irradiation by generating plasma inside a quartz tube submerged in the solution. Several variations are reported in literature, where the high-voltage electrode inside the tube is a screw [162], a spiral wire [163], a rod covered by dielectric barrier [164], or a glass tube filled with NaCl solution [165]. A metal mesh surrounding the tube [162] or a metal rod in contact with the water [165] serves as ground electrode (Figures 11c–d). DBD plasma is usually generated inside the tube with AC power. The working gas is pumped in the tube and subsequently bubbled through the solution by means of a gas diffuser or a series of air distribution needles (Figure 11e) [164]. Comparison with other oxidation techniques has indicated that such reactors may be competitive technology to other plasma systems such as the hybrid reactor by Nakagawa et al. [154] (Figure 10g) and to photocatalytic oxidation [165, 166].

A system closely related to these plasma gas bubbling reactors is a submerged DBD plasma jet for water treatment. In the study of Foster et al. [167], a nanosecond pulsed DBD plasma jet is investigated for oxidation of aqueous organic pollutants (Figure 11f). Its decomposition efficiency was higher than the one reported in literature for glow discharge and pulsed corona discharge [167]. The energy efficiency of methylene blue decomposition significantly dropped with increasing treatment time. As the results suggest, using multiple plasma jets powered in parallel can improve the process significantly. The plasma jet can also be placed above the water surface (Figure 11g), as is done for the production of plasma-activated water by Ma et al. [168]. Nevertheless, application of non-thermal plasma jets for water treatment is relatively uncommon for now.

A few systems are reported in literature where plasma is generated above a water surface without direct contact with the solution. In the study of Olszewski et al. [169], copper strips adhered to both sides of a quartz disc were used as electrode configuration for methyl orange decomposition with AC DBD plasma (Figure 11h). In the study of Dobrynin et al. [159], inactivation of spores was investigated by means of the DBD electrode system of Figure 5c above a removable mesh for reference experiments (Figure 11i). Experiments with and without the mesh were compared to reveal the role of UV irradiation.

Recently, a new approach is gaining popularity in which water treated with plasma, often termed plasma-activated water, is added to the solution under treatment. Plasma-activated water contains several long-living oxidants that are able to inactivate biological organisms. According to Zhang et al., long-living aqueous hydroxyl radicals were produced in their setup by mixing DBD-treated humid O₂ gas with water (Figure 11j) [160]. This hydroxyl radical solution was sprayed in a sea enclosure to effectively inactivate red tide organisms. Plasma-activated water can be produced by means of any of the reactors mentioned above, but gliding arc discharge is most commonly used. Figure 11k depicts the gliding arc reactor used by Kim et al. [161] for plasma-activated water generation utilizing a vortex flow with two circular disk electrodes. Introducing the produced water–air mixture in the solution under treatment through microbubble generators significantly enhanced the process. Up to now, plasma-activated water is used for disinfection of water, while its effects on organic contamination are still largely unknown.

In principle, plasma technology is also frequently used in water treatment technology solely as UV source in plasma lamps or excimer lamps. An upcoming new technology is the microwave discharge electrodeless lamp, which self-ignites under influence of microwave power. As an example, Figure 11l schematically shows a tungsten-triggered microwave discharge electrodeless lamp proposed by Horikoshi et al. [170] for low microwave power levels. The tungsten wire was embedded in a synthetic quartz tube attached to the lamp system to act as a trigger. In that manner, the high microwave power usually required for self-ignition in aqueous medium is avoided.

4. Influence of working parameters on energy efficiency

In addition to reactor design and materials, there are several other factors that influence reactor energy efficiency, which need to be considered for reactor optimization. Roughly, these factors can be split into two groups: working parameters determining reactor operation and solution parameters. Since solution parameters, such as water temperature, pH, conductivity, and water matrix, are hard to control, especially for large volume of influent water, they are not discussed in this chapter. For a discussion on their influence, the reader is referred to [44]. In contrast, operational parameters such as applied voltage characteristics, working gas, and flow rates of gas and solution are easier to adjust. Therefore, they deserve additional attention for further reactor optimization. In this section, we will shortly review the importance of voltage waveform, working gas, and gas and water flow rates. Their influence on reactor efficiency for organic decomposition will be illustrated with examples from literature.

For a given reactor, energy efficiency depends on voltage-related parameters. In the pulsed bubble discharge reactor of [92] and the positive pulsed streamer discharge in wetted-wall reactor of [129], energy efficiency increased for rising voltage amplitude. In a negative pulsed DBD falling water film reactor [171] and a positive pulsed corona electro spray reactor [147], however, increasing voltage amplitude reduced the energy efficiency. In the gas phase DBD reactor of [169], the interruption period of pulse-modulated AC voltage had no effect on methyl orange degradation, while lowering its duty cycle from 100% to 25% increased energy efficiency 2.11 times. The authors explained the latter effect with additional dye degradation during plasma off time under influence of long living reactive species such as O_3 and H_2O_2 . Sinusoidal voltage frequency is an important parameter, as it can lead to different plasma phenomena, which explains the distinction of AC, radio frequency, and microwave discharge. Nevertheless, very limited information is available in literature on the dependence of the energy efficiency of the sinusoidal frequency for a given reactor design. In the study of Lesage et al. [122], no change in energy efficiency was observed for 4-chlorobenzoic acid decomposition with voltage frequency increase from 500 Hz to 2000 Hz for AC powered DBD over moving water film. Increasing AC frequency from 1.5 kHz to 15.6 kHz kept the energy efficiency of a coaxial falling water film DBD reactor in the same order of magnitude as well, in spite of the additional heating that resulted from the higher frequency [172]. In the case of pulsed discharge, pulse properties such as rise time and width are expected to be important. For pulsed

positive corona discharge in humid O₂/N₂ atmosphere, the energy efficiency of radical and excited species production increases with decreasing pulse width [173]. This is in agreement with the higher efficiency of indigo carmine decomposition for shorter pulse width observed by Sugai et al. [174] for a positive pulsed streamer discharge spray reactor. A faster pulse rise rate generated thicker streamers and a higher energy efficiency in the same reactor [175]. Positive pulsed arc electrohydraulic discharge was reported to have increased the energy efficiency of sulfadimethoxine when pulse duration was brought back from 100 μs to 20 μs [51]. Remarkably, also pulse frequency can influence reactor efficiency. In a bubble reactor with positive pulsed corona, the energy efficiency of 2,4-DCP degradation increased with increasing pulse frequency [176]. In contrast, the energy efficiency of indigo carmine reduction dropped for increasing pulse frequency in a positive pulsed streamer wetted-wall reactor [129], in a negative pulsed DBD spray reactor [144], and in a positive pulsed DBD hybrid film and spray reactor [154]. In a negative pulsed DBD falling water film reactor [177] and a positive pulsed corona spray reactor [143], no influence of the frequency was observed. In bipolar pulsed electrohydraulic reactors, breakdown voltage decreases with frequency [62, 96]. Reversing voltage polarity can also cause significant changes in plasma properties and thus treatment efficiency. In the study of Lee et al. [96], positive polarity of pulsed corona in electrohydraulic discharge greatly enhanced the energy efficiency of methyl orange decomposition in pin-to-plate electrode configuration in comparison with negative polarity. The authors explain this observation with the space charge effect, which causes positive corona streamers to be faster and longer, hence increasing radical production and plasma–water contact surface. In the study of Yasuoka et al. [178], higher efficiency was observed as well for positive polarity in a DC bubble discharge reactor. For phenol decomposition in gas phase discharge reactors with a 20% O₂ and 80% N₂ atmosphere, negative DC was found to be more efficient than positive one by Sano et al. [179], while according to Miyazaki et al. [108], no significant difference was seen for both polarities with pulsed power. In a pulsed DBD falling water film reactor, better results were obtained with negative polarity as compared to positive one [171]. In the bubble discharge reactor of Figure 3h with O₂, He, Ar, or Ne bubbles, positive DC voltage performed better than negative one for the decomposition of interfacial active agents [83]. For negative polarity, electrolysis occurred with formation of hydrogen and oxygen gases. For positive polarity, the interfacial anion agents were more concentrated at the bubble surface due to electrostatic attraction. Positive plasma species collided with the water surface, where a cathode drop is formed. These unknown species likely enhanced the decomposition of the agents.

The working gas determines many plasma features for a given input voltage waveform, such as breakdown voltage, electron density and temperature, plasma homogeneity and intensity, generated reactive species, etc. Air is the most frequently used working gas for water treatment plasma reactors due to its wide availability. Pure oxygen gas, however, is often found to give more efficient organic degradation, while nitrogen gas leads to lower efficiency [42, 44, 50]. This can be partly explained with formation of OH radicals and O₃ in oxygen. In N₂ containing gases, however, toxic aqueous nitric products are generated, which decrease solution pH and

act as scavengers of oxidants such as OH radicals [50]. Noble gases like helium and argon are sometimes used, especially in bubble discharge reactors. Often, argon leads to the faster decomposition of phenols but performs worse than oxygen for other compounds [50]. In a wetted-wall reactor (Figure 6b) with argon, streamer discharge has been observed which had slightly better phenol decomposition energy efficiency than corona in oxygen [128]. Noble gases, however, are expected to be less economically feasible for use on larger scale due to their high price. Interestingly, treatment efficiency of electrohydraulic discharge reactors can also be altered by bubbling different gases through the solution under treatment, where bubbles are kept away from the discharge zone. Sahni and Locke observed a decrease in nitroform anion decomposition by pulsed underwater corona when the solution was oxygenated with O₂ gas or deoxygenated with N₂, He, or Ar gas as compared to discharge without prior bubbling, but the authors could not explain this effect [180]. Also, water content of the working gas should be taken into account, as it influences formation of important oxidants such as OH and H₂O₂.

Gas flow rate is another factor that needs to be taken into consideration. In three bubble discharge reactors, increasing bubble flow rate enhanced the decomposition process [158, 181, 182], while according to Reddy et al. [183] no significant effect was observed. In the hybrid reactor with bubbles from Figure 10e, oxidation rate first increased and then reached a stationary value with rising gas flow rate [153]. In the remote discharge reactor with bubbling from Chen et al. [184], increasing gas flow also enhanced decomposition. For gas phase discharge reactors, the influence of gas flow rate seems less pronounced. In a positive pulsed corona-like discharge over water, phenol decomposition was slower with increasing oxygen flow and slightly dropped with increasing airflow, while argon flow rate had no influence [185, 186]. In a pulsed DBD falling water film reactor, the effect of the oxygen flow rate on methylene blue degradation was not significant [171].

In reactors with moving solution, the water flow rate often influences the decomposition process. In coaxial falling water film reactors with corona discharge, phenol degradation rate was unchanged with faster water flow for positive pulsed voltage [128], while it dropped in case of negative DC, which was attributed to higher roughness of the water surface [127]. In a pulsed DBD falling water film reactor, the energy efficiency of methylene blue degradation decreased with increasing water flow rate [171]. In contrast, 4-chlorobenzoic acid was decomposed faster with increasing water flow for AC gliding arc discharge over falling water film [123]. Measurements in spray discharge reactors indicate the existence of an optimal water flow rate. In a positive pulsed streamer spray reactor, the energy efficiency of indigo carmine decomposition initially increased and then stabilized with increasing water flow rate due to saturation of aqueous ozone [140]. Moreover, the efficiency was independent of droplet size. In a similar corona reactor, the energy efficiency of oxalic acid decomposition first increased with rising water flow rate, reached a maximal value and subsequently dropped again [187]. The optimal water flow rate increased with applied pulse frequency. Rising water flow rate decreased breakdown voltage in a positive pulsed DBD spray reactor [145]. For the hybrid positive pulsed DBD spray and falling water film reactor of Figure 10g, the energy efficiency of rhodamine B decomposition enhanced with increasing water flow [154].

5. Summary and concluding remarks

Removal of hazardous micropollutants is often insufficient by means of modern conventional wastewater treatment plants. Preventive measures and optimization of conventional biological treatment are suggested as most cost-effective solutions. Nevertheless, preventive measures are limited by increasing demand, while the optimization of conventional techniques often has negligible effect on many persistent micropollutants. Therefore, advanced treatment techniques such as electrochemical separation, activated carbon, nanofiltration, and reverse osmosis have recently received more attention for their effective removal of micropollutants. These techniques, however, are associated with high costs and the additional problem of hazardous concentrate disposal. Advanced oxidation techniques are a promising alternative, as they are the most effective available methods to decompose biorecalcitrant organics. As a main drawback, their energy costs are high up to now, preventing their implementation on large scale. Alternatively, their application can be limited to the treatment of important micropollutant sources, such as hospital and industrial effluent.

Among the advanced oxidation techniques, water treatment by means of electrical discharge takes an interesting place since it is able to generate a wide spectrum of oxidative species, leading to a low selectivity of the degradation process. Further, the optimization of this technology is complex due to the wide variety in reactor design and materials, discharge types, and operational parameters. In this chapter, plasma reactors are comprehensively classified based on their design and materials, in contrast to other reviews where focus lies more on applied voltage and discharge type. Six main reactor types are distinguished. In electrohydraulic discharge reactors and bubble discharge reactors, plasma is generated directly in the liquid bulk, respectively, without and with external application of bubbles. In gas phase discharge reactors and spray discharge reactors, plasma is generated in the gas phase, respectively, over a water bulk or film and in contact with water drops or mist. Reactors that use a combination of these types simultaneously are classified as hybrid reactors. In the last type of reactors, referred to as remote discharge reactors, plasma is not generated in direct contact with the solution under treatment.

Most commonly, electrohydraulic discharge reactors use pulsed arc or positively pulsed corona discharge, where electrode material can have substantial influence on organic decomposition after plasma contact due to formation of erosion particles in water. For the case of arc discharge, energy efficiency is reported to be dependent on interelectrode distance. For pulsed corona, high-voltage pin curvature radius is an important parameter as well. The corona plasma volume can be enlarged by replacing the high-voltage pin with a multipin electrode or a high-voltage electrode covered with a thin porous ceramic layer. Diaphragm and capillary discharge are expected to have similar plasma features to corona discharge in pin-to-plate electrode configuration, which is in agreement with the similar energy efficiency. Contact glow discharge electrolysis is another common type of electrohydraulic discharge, where electrode material also plays an important role. In more exotic types of electrohydraulic discharge reactors, plasma formation is preceded by cavitation under application of RF or microwave power.

Adding external bubbles in the water bulk has the advantages of easier plasma onset, immediate mixing of the solution, minimizing electrode erosion and increasing radical density. Most commonly, bubbles are generated by pumping gas through a dielectric or an electrode, which is shaped as a nozzle, perforated plate, or porous ceramic. Choices in bubble gas, nozzle or perforation material, shape, dimensions, and orientation strongly influence plasma properties, which complicates reactor comparison. Often, the high-voltage electrode is positioned directly in contact with the bubble or in the gas phase in contact with the bubble. In that case, energy efficiency can be enhanced by increasing the number of nozzles or holes. Alternatively, bubbles can be positioned in between submerged electrodes. Some common bubble discharge reactors use a coaxial DBD configuration, where the gas is bubbled in axial direction. Energy efficiency in these systems can be increased by using a double barrier or adding glass beads in the water bulk. More exotic types of bubble discharge reactors have been reported in literature, with promising first results.

Corona and glow discharge in gas phase over grounded water bulk or film is mostly generated with pulsed power. Negative pulsed corona over flowing water film in a pilot system has been shown to have better or comparable energy efficiency than other advanced oxidation processes. Based on one report, energy efficiency of organic decomposition seems to be independent of the type of discharge, voltage amplitude, polarity of the applied voltage, and amount of pin electrodes. In contrast, DBD over water bulk or film has an energy efficiency that is reported to increase with increasing voltage amplitude and decreasing interelectrode distance. Interelectrode distance can be decreased substantially by adding a porous ceramic segment at the water surface. Movement of the water phase by stirring or by making it flow as a film along the discharge increases energy efficiency substantially, making water flow rate an important parameter for optimization. Based on this principle, coaxial reactors with falling water film are gaining more popularity. Such reactors can be further optimized by adjusting gas flow direction and electrode and barrier dimensions. A last common gas phase discharge reactor uses arc discharge over the water bulk or film. Larger arc-treated water surface and energy efficiency can be reached by using a couple of controlled electrodes or a second high-voltage electrode.

Spray discharge reactors have received more attention in recent years due to their high reported energy efficiencies. In the case of positive pulsed corona, treatment is more efficient for droplets near the inner reactor wall, while droplet size has no influence on energy efficiency. Such reactors can be further optimized by adding fluorocarbon wires along the inner reactor wall for larger droplet retention time. Other spray discharge reactors treat droplets with DBD, electrospray or arc discharge. In the case of gliding arc, the process can be optimized by addition of a couple of controlled electrodes or a second high-voltage electrode and by introducing the water perpendicular to the gas flow to improve contact with plasma. DC plasma torches can also be used for water treatment by injecting the solution into the torch as plasma forming gas.

One type of hybrid reactor is designed by placing a high-voltage electrode in the water phase and a ground electrode or second high-voltage electrode in the gas phase above the water surface, without or with the addition of bubbles. Their energy efficiency for organic decom-

position is moderately higher than the one of hydraulic discharge reactors. Another hybrid reactor type naturally occurs by spraying water from a shower nozzle at an angle, causing a falling water film in combination with spray. In such case, organic decomposition in droplets is more efficient than in the water film. A more exotic hybrid reactor that deserves more attention consists of a spray discharge reactor where droplets are formed by electrospray with additional plasma treatment afterwards.

Remote discharge reactors can be encountered in many configurations. In the most standard design, plasma gas is remotely generated and sequentially bubbled through the solution, as in the well-known example of ozonation. Plasma gas bubbling can be combined with UV irradiation by generating plasma inside a quartz tube submerged in the solution. Research has indicated that such reactors may be competitive technology to systems with direct plasma treatment. Plasma can also be used solely for UV irradiation, as in plasma lamps, excimer lamps and microwave discharge electrodeless lamps. Recently, the generation and application of plasma-activated water for water disinfection is gaining popularity, while its effects on organic contamination are still largely unknown.

Additionally, the importance of voltage waveform, working gas and flow rates of gas, and water for further optimization are shortly reviewed in this chapter. Energy efficiency has different dependency for different reactor types on voltage parameters, such as voltage type, amplitude, polarity, sinusoidal frequency, pulse rise time, pulse duration, and pulse frequency. For example, positive polarity causes higher efficiency of electrohydraulic and bubble discharge reactors in all considered cases, explained with the space charge effect. On the other hand, negative polarity gives better performance in gas phase discharge reactors. The choice of working gas can significantly alter plasma chemistry and therefore treatment efficiency and by-product formation. While atmospheric air is often chosen due to its wide availability, oxygen generally enhances the process. Argon often performs better for phenol degradation but is expected to be less economically feasible for use on large scale. Increasing gas flow rate typically enhances decomposition in bubble discharge and remote discharge reactors, whereas its effect is less pronounced in gas phase discharge reactors. Also, adjustment of water flow can significantly increase energy efficiency. Measurements in spray discharge reactors, for instance, indicate the existence of an optimal water flow rate. While dependency of a few of these parameters on energy efficiency seems adequately established for a limited number of reactor types, a deeper literature study and more experimental investigation are required for additional confirmation and a better understanding in most of the cases. Due to the wide variety in plasma reactors and the distinct, unique features of every reactor, researchers are motivated to report new results in this field, including clear descriptions of reactor design and materials.

One needs to keep a few additional influences in mind when interpreting energy efficiencies reported in literature. First of all, solution parameters such as water temperature, pH, conductivity, and water matrix can have significant effect on plasma chemistry and reactions in the water bulk. Often, deionized water at room temperature is used as solvent in plasma reactors. In other cases, however, deviations in energy efficiency can be caused by a difference in solution parameters. Also, it should be remarked that micropollutant measurement is

generally performed a certain time after plasma treatment with analytical chemistry methods, such as gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry. During this time, postreactions with long-living oxidants can occur, decomposing the micropollutant to a greater extent. This effect is usually neglected by researchers, complicating accurate comparison between reported energy efficiencies. On the positive side, this aging effect can be beneficial in applications where sufficiently long hydraulic retention time is possible after plasma treatment. Last but not least, most of the reported electrical discharge reactors only treat small water volumes in batch mode without or with recirculation of water. As a result, the determined energy efficiency can be significantly different for the same reactor type in single-pass mode, where water is flowing through the system only once. The latter case is more representative for industrial application and thus deserves more attention.

In this chapter, only improvement of the plasma process in terms of reactor design, materials, and working parameters is discussed. Further optimization can be achieved by combining plasma discharge with other advanced treatment methods, such as adsorption, Fenton's reagent, photocatalysis, and ultrasonication. Such combinations have been reported before but require additional attention and further exploration. As should be noted, plasma technology can also be used for synthesis, pretreatment, regeneration, and posttreatment of materials and matter involved in water treatment processes, such as nanotubes, membranes, activated carbon, excess sludge, and organic concentrate from filtration. In-line application of these methods during the water treatment process needs to be considered as a possible alternative to direct water treatment with advanced oxidation processes since energy demand and overall costs can be pressed significantly this way. However, more experimental investigation and thorough cost analysis is necessary to confirm this claim.

Future application of plasma discharge for water treatment will largely depend on its effectiveness and energy efficiency as compared to other advanced oxidation processes and treatment methods in general, but additional criteria need to be taken into consideration as well. Sustainability, ease of operation, capital costs, and costs related to maintenance, gas input, and additional energy for pumps will also determine whether a system will be adopted on a large scale. Moreover, an extensive study of generated oxidation by-products and long-living oxidants in treated water is necessary to assure that overall toxicity is consistently and sufficiently decreased after plasma treatment. Up to now, reports on these topics are largely lacking in literature or limited to only a few specific cases.

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