



Review article

Application of glow discharge plasma for wastewater treatment

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ABSTRACT

During last few years, large number of papers published on direct current glow discharge plasma (GDP) in and in contact with liquids due to the increasing interest for its application for wastewater treatment. In this paper, recent progress of GDP on wastewater treatment has been systematically reviewed, covering the degradation of organic pollutants, the reduction of Cr(VI) and the inactivation of algae. This contribution also provides comprehensive insights into reactors, generation mechanisms, physical characteristics, influence of operating parameters and energy efficiency comparing with other AOPs. The emphasis in this paper is on the mechanism of the removal of hazardous chemicals induced by GDP and the combined process. It ends by shortly mentioning theoretical fundamentals and promising actual application of GDP which call for further study.

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1. Introduction

During last few years, large number of papers published on glow discharge plasma (GDP) in and in contact with liquids due to the increasing interest for its application. Nowadays, it has provided many possible applications, such as hydrogen production [1,2], synthesis [3–8] as well as wastewater treatment [9–15]. The study of glow discharge could trace back to more than a century ago. It is also termed as electrode effect in some references [16–18] depending on which electrode glow discharge takes place. Plasma electrolysis [1], glow discharge electrolysis (GDE) [19–21], contact glow discharge electrolysis (CGDE) [22–28] and diaphragm glow discharge [29–32] are also used in literatures according to different reactors. Early studies suggested that glow discharge had roots in radiation [19,22]. Indeed, glow discharge in and in contact with liquids can dissociate water molecule into hydroxyl radical ($\cdot\text{OH}$) and hydrogen radical ($\cdot\text{H}$) [33–35]. These radicals can diffuse in the surrounding liquid and be used for the removal of dissolved compounds. Especially, $\cdot\text{OH}$ are able to oxidize any organic molecule into “harmless” carbon dioxide in a non-selective way. This makes GDP particularly suitable for decontamination and sterilization proposes. This is the main reason why GDP has been studied extensively as effective method for the removal of hazardous chemicals in aqueous solution.

In recent years, some researchers have reviewed electrical discharge and non-thermal plasmas for water treatment and mentioned GDP briefly [36–40]. However, GDP has its own unique characteristics. Although two reviews about its chemical effect and early application of GDP have published [41,42], large numbers of papers published during the last few years. Both the onset of GDP and its application for the wastewater treatment has been systematically investigated. So far, GDP has been utilized for not only the degradation of organic pollutants [9–15], but also the reduction of Cr(VI) [43–45] and the inactivation of algae [46]. Therefore, in the present contribution, we review current state of research focusing on the application of GDP on wastewater treatment. This paper also reviews generation mechanisms and unique physical characteristics during the onset of glow discharge. The emphasis in this paper is on the mechanism of the removal of hazardous chemicals induced by GDP and the combined process. What's more, reactors commonly used for the generation of GDP are discussed here in details. In addition, GDP is evaluated and compared with other AOPs in energy efficiency, the formation rate constants of active species, removal efficiency of substrate and TOC. The outlook of this emerging technology for the upcoming future is finally envisaged. It should be noted that this paper only reviewed GDP on sustained by direct current in and in contact with liquids.

2. Fundamentals

2.1. The onset of glow discharge

2.1.1. *I*–*V* curve characteristic

Experimentally, GDP is sustained by direct current around the pointed metallic anode or a small hole on diaphragm which separate reactor into two compartments. When the applied voltage is sufficiently high, conventional electrolysis develops spontaneously to generate GDP [22,23,47–49]. *I*–*V* curve (current vs. voltage) is a typical characteristic during the onset of glow discharge. Fig. 1 is the typical *I*–*V* curve during the onset of GDP. Several different regions are usually identified:

$0 < V < V_B$: ohmic region; current linearly increases with the increase of the applied voltage. Conventional electrolysis occurs and electrolysis of water takes place with small bubbles of gas

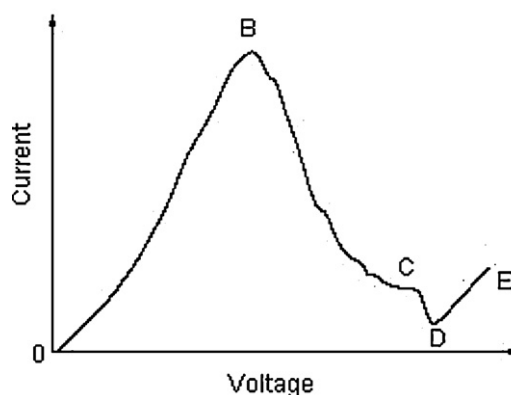


Fig. 1. *I*–*V* characteristic during the onset of glow discharge.

leaving the pointed anode or the small hole. V_B was termed as the breakdown voltage in Refs. [23,47].

$V_B < V < V_D$: transition region; the current starts to decrease with the applied voltage due to the vapor sheath forming around the pointed anode or the small hole. The gas bubbles in vapor sheath undergo the process of formation and collapse, so the oscillation of the current occurs. V_D was the critical voltage (also termed as midpoint voltage in Refs. [22,23,28]). Sometimes, CD region is a horizontal line during the onset of glow discharge when the anode is submersed underwater, as reported in a few Refs. [50,51].

$V > V_D$: glow discharge region; current transport happens through glow discharge. The current begins to increase steadily with the rising voltage and the glow becomes more luminous. In section DE, the color of glow discharge is similar to the flame of metal ion in electrolyte solution.

2.1.2. Critical voltage

In *I*–*V* curve, V_B and V_D are two significant points marking the breakdown of normal electrolysis and the onset of glow discharge. Initially, Sengupta and Singh studied the onset and location of CGDE and found that V_B was significantly sensitive to variation in the anolyte surface tension, the anode wire dimension and the anode material [23]. V_B was 125 V with equi-conducting electrolytes when platinum wire diameter was 0.35 mm and temperature is $70 \pm 2^\circ\text{C}$. V_D was 420 V in anodic CGDE and was unaffected by the electrolyte's composition, concentration, temperature and surface tension [23,28].

Recently, it has been reported that initial conductivity of the solution is one of the most important parameters for the onset of glow discharge. V_B and V_D decrease with the increasing conductivity and then maintain a certain value [48,49]. What's more, much attention has been paid to V_D in CGDE, since glow discharge takes place and large amount of active species form only when the applied voltage is above V_D . It was found that V_D decreased from 542 V to 438 V when the conductivity of Na_2SO_4 solution was in the range of 1.00–5.99 mS/cm. When the conductivity of Na_2SO_4 solution was 7.00, 8.20, 9.25, 10.48 and 11.38 mS/cm, the values of V_D were 432, 431, 425, 420 and 425 V, which were close to 420 V, obtained from Sengupta's experimental result. That is, when the conductivity of solution was in the range of 7.00–11.38 mS/cm, the effect of conductivity on V_D was largely insignificant. In addition, CGDE was also conducted in different electrolyte with the same conductivity (5.00 mS/cm). It was also found that all values of V_D were very close in different electrolytes with the same initial conductivity of solution. That is, V_D was unaffected by the electrolyte's composition if the conductivity of solution was given a specific value in a certain range.

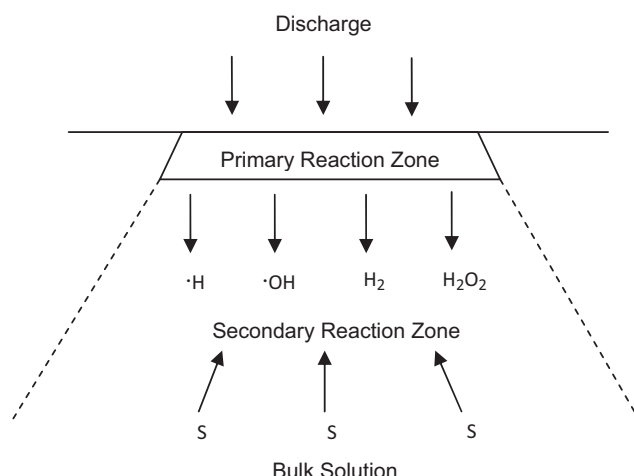


Fig. 2. Hickling's theory about GDP (S denotes substrate in the solution).

The critical voltage in multi-anode CGDE was also investigated. It was noted that critical voltages with multi-anode were similar to that with single anode, since multi-anode was parallel connected in the circuit after all [13].

2.2. Energetic species in glow discharge plasma

Initially, Hickling and Ingram thought that GDP was analogous to alpha particles in radiation chemistry [19,22]. As shown in Fig. 2, within the primary reaction zone, water was ionized or activated, and then bombard each other to break up by charge transfer. The ultimate result was the production of free $\cdot\text{OH}$ radicals and sometimes $\cdot\text{H}$. They may interact each other to form H_2O_2 , $\text{HO}_2\cdot$ and H_2 . Thus, a mixture of $\cdot\text{OH}$, $\cdot\text{H}$, H_2O_2 and H_2 diffused out of the primary zone (that was called plasma later) and interacted each other or was scavenged by substrate in the secondary reaction zone. They thought that the primary reaction zone may be likened to a spur in radiation chemistry. The reaction zone might be considered as a single spur, which was located in a fixed position and constantly renewed. Later, the production of $\cdot\text{OH}$ radical in the liquid was proved by an ESR study using 5,5-dimethylpyrroline-1-oxide (DMPO) as the spin trap [33,34]. Emissions of $\cdot\text{H}$ and $\cdot\text{OH}$ radicals were also observed using a photo-multichannel analyzer with a wavelength range from 200 to 900 nm [35].

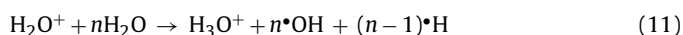
Sengupta et al. paid much attention to nonfaradaic yields of anodic CGDE. They found that nonfaradaic yields of anodic CGDE originated in two different reaction zones: the plasma around the anode and the liquid phase near the plasma-anolyte interface [24,28]. In the reaction zone within the plasma around the anode, H_2O vapor molecules dissociated into H_2 and O_2^{E} (O_2 in excess of the Faradaic yield), according to the following mechanism.



In the liquid-phase reaction zone near the plasma-anolyte interface, several liquid H_2O molecules broke up into H_2 and H_2O_2 plus O_2^{E} by being bombarded by each $\text{H}_2\text{O}^+_{\text{gas}}$ from the anodic plasma following Hickling's radiolytic mechanism.



Recently, the dissociation of water molecules in GDP has often been written as following equation [43,44]:



The value of n was estimated by using ferrous ion and cerous ion as $\cdot\text{OH}$ scavenger and the results were 7.9–10.6 mol [22] and 12 mol [27] $\cdot\text{OH}$ radicals for the passage of each mol electron of electricity, respectively. Using iso-propanol, n-propanol, n-butanol and acetone as $\cdot\text{H}$ scavenger, the value of n is estimated to be as high as 9.8 [52]. Hydroxyl radical is a short lived species, and they can recombine into H_2O_2 . Therefore, $\cdot\text{OH}$ and H_2O_2 can be continuously produced in GDP in and in contact with liquids. $\cdot\text{OH}$ and H_2O_2 are all oxidative agents, especially $\cdot\text{OH}$ with higher oxidation potential (2.8 V), which could mineralize nearly most of organic pollutants.

3. Experimental features

3.1. Glow discharge reactors

A variety of different types of reactors have been studied for the generation of GDP in and in contact with liquids. The reactors can be divided into two groups according to the location of the glow discharge. The first group is around the pointed metallic anode in and in contact with liquid. Another is around the small hole on diaphragm which separate reactor into two compartments.

With anode in contact with liquids, GDP takes place around the pointed anode and interface between gaseous and liquid phase, which is often termed as CGDE and the most commonly used configuration listed in Fig. 3(a), where the anodic compartment and cathodic compartment are separated by a sinter glass disk of medium porosity [9,12,53–70]. Pointed platinum wire is often used as the anode. The cathode such as platinum wire, carbon rod and stainless steel stick are usually preferred. H type reactor with two equal volume compartments in references [10,71–73] also belongs to this kind of reactor. Multiple anodes are used to generate large volume GDP in contact with liquids. An improved reactor has been developed by replacing platinum wires with stainless steel wires [13].

When the anode is placed in liquid shown in Fig. 3(b), it has ever been termed as direct glow discharge electrolysis [11,74] or submersed glow discharge [75], glow discharge electrolysis [50,51,76,77] in literatures. Some researchers believe that reactor (b) could prolong the lifetime of platinum anode when the anode was placed underwater. But, sometimes, the anode wire still melts due to excess heat. The anode is still a pointed platinum wire and the cathode can be graphite stick. Similarly, multiple anodes are used to generate large volume GDP underwater [78].

When GDP occurs around a small hole on diaphragm shown in Fig. 3(c), it is termed as diaphragm discharge or diaphragm glow discharge (DGD) [29–32]. A quartz (1.0 mm in thickness) and PET diaphragm (thickness of 0.25 mm) are used as diaphragm. The diameter of small hole is in the range of 0.25–2.0 mm. Two graphite electrodes act as the same role in normal electrolysis and are placed in each compartment, respectively. GDP occurs around the small hole which can induce chemical reactions in both anodic and cathodic compartment. The role of small hole in reactor (c) is similar to the pointed needle anode in other reactor.

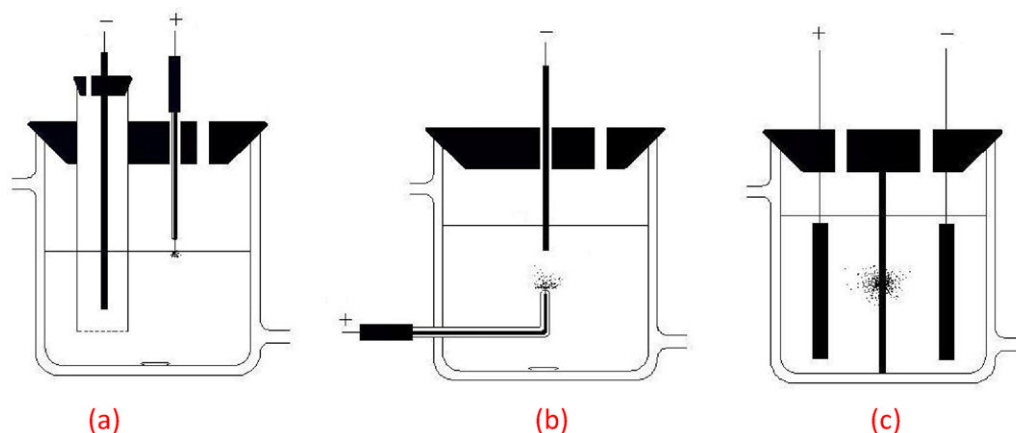


Fig. 3. Overview of experimental setups developed for GDP.

3.2. Influence of operating parameters

3.2.1. Applied voltage

The chemical reactivity of GDP depends on operating parameters such as applied voltage, current, conductivity, pH value of solution and electrolyte constituents. Most of these parameters are optimized for achieving the higher efficiency and lower energy cost. Applied voltage is key parameter for the chemical reactivity of GDP, since glow discharge takes place only when the applied voltage is above the critical voltage [22–28,48,49]. The applied voltage can be a certain value above the critical voltage. Some experimental results showed that increasing applied voltage facilitated the treatment process [79], since the rise in applied voltage accelerate the formation of energetic species [77]. However, it was also found that when the applied voltage increased to a certain value, the concentration of H_2O_2 and the degradation of substrate in both compartment of reactor (c) increased little [30]. Furthermore, the applied voltage cannot be too high in terms of energy efficiency. In addition, erosion of the anode and the small hole appeared when applied voltage was too high. Table 1 lists the voltage usually applied for different reactors. In practice, 500 V is usually employed as the applied voltage for the generation of GDP in contact with liquid [9,12,13,53–68], 600 V for GDP in liquid [11,50,51,74,75,78], 750 V for DGD [30], respectively.

3.2.2. Current

The effect of current on the degradation of substrates was only investigated with reactor (a). The current was increased by the increasing depth of the anode. The concentration of H_2O_2 and removal rate of substrate increased with the increase of current [63]. As an example, when the current was 100 mA, about 60% of nitrobenzene could be removed and 2.3 mmol of hydrogen peroxide produced after 50 min treatment. However, when the current increased to 400 mA, more than 90% of nitrobenzene could be removed and 4.0 mmol of hydrogen peroxide produced within 25 min. Accordingly, the first-order rate constant linearly increased with the increase of current [15,55,62]. Liu et al. thought that the

increase in the plasma zone in contact with the solution explained the increase in the degradation rate of chlorobenzene [62]. But Jiang et al. believed plasma zone was so small and could be negligible in comparison with that in the bulk zone. The increase of current actually increased the concentration of $\bullet OH$ and H_2O_2 in bulk solution [15]. In practice, current fluctuates due to the change of solution conductivity. Therefore, much attention was paid to the initial conductivity of electrolyte solution.

3.2.3. Initial conductivity of solution

Since the glow discharge is transferred by ions, it is evident that the conductivity of the solution has an influence on the onset of GDP. Therefore, the initial conductivity of solution is an important parameter for GDP. It has been reported that the critical voltage in CGDE decreased with the increasing conductivity of solution, and then maintained a certain value [49]. If the initial conductivity is too low, there are only few charge carriers in system, and subsequently the resistance is so high that the applied voltage must be high enough to initiate for GDP generation. For example, when the initial conductivity of solution in reactor (c) is 0.1 mS/cm, only when the applied voltage is 2.2 kV, the discharge phenomenon appears [80]. However, when the initial conductivity increased to 6.4 mS/cm, 750 V is enough for the onset of DGD [30]. Furthermore, it has been found that the concentration of active species such as $\bullet OH$, $\bullet H$ and H_2O_2 increased with the increasing initial conductivity of solution [77]. The discoloration rate of crystal violet increased from 20% to about 95% when the concentration of Na_2SO_4 increased from 1 g/L to 4 g/L after 20 min GDP treatment with reactor (b) [79]. However, the erosion of the platinum anode is evident when the concentration of Na_2SO_4 was 4 g/L. Therefore, too higher initial conductivity should be avoided. In addition, the conductivity of solution changes during the treatment. Usually, conductivity increases due to the formation of organic acids with organic pollutants as substrate [68,69]. Therefore, too high or too low initial conductivity should be avoided in terms of energy efficiency. Usually, 3–7 mS/cm is selected for the initial conductivity of electrolyte solution. Therefore, GDP treatment has the advantage for real wastewater containing salts.

3.2.4. Initial pH value of solution

The initial pH value is an important factor in wastewater treatment. The effect of initial pH of the solution has been investigated by many researchers. For different substrates, pH value shows different effects. The removal rate of some substrates was not influenced by pH [62,71]. For example, pH had little effect on the first-order rate constants of chlorobenzene and the rate constants were all about $1.96 \times 10^{-2} \text{ min}^{-1}$ when initial pH value were 3.0, 5.0, 6.5 and 9.0 [62]. However, many authors think that pH of the solution plays

Table 1
Summary for different reactors.

| Reactor | a | b | c |
|-----------------------------|------------------------------------|-------------------------|----------------------|
| Location of GDP around | Pointed anode gas/liquid interface | Pointed anode in liquid | Small hole in liquid |
| Voltage usually applied (V) | 500 | 600 | 750 |
| Supporting electrolyte | 2 g/L Na_2SO_4 | 2 g/L Na_2SO_4 | 4 g/L Na_2SO_4 |

a significant role in the oxidation power of GDP. Some experimental results showed that the faster removal rate could be obtained at a relatively lower pH value, since more $\bullet\text{OH}$ and H_2O_2 are generated [77] and the oxidative potential of $\bullet\text{OH}$ is stronger in acid solution (the oxidative potential of the hydroxyl radical is 2.70 V at pH 3.0 and 2.34 V at pH 9.0) [15,29,30,74,75,81]. Especially for GDP combined with Fenton process, the degradation of substrate proceeded rapidly in acid condition. But for some dyes such as alizarin red S and crystal violet, it has been reported that higher discoloration rate is achieved under alkalinity condition [51,79]. In fact, pH value of electrolyte solution changed during GDP treatment. The value of pH usually decreased because of the formation of carbonic acid. In practice, the initial pH value of wastewater often varies in a large range. Usually, pH adjustment was unnecessary before treatment if substrate was not a given organic pollutant and the wastewater was acidic or neutral. Otherwise, the optimal of pH is necessary.

3.2.5. Electrolyte constituents

Usually, wastewater often contains various organics and inorganic substances. Hydroxyl radical scavenger can consume the radicals and decrease the degradation process. Any organics that can compete with target pollutant for the available hydroxyl radicals, consequently, decrease the degradation rate of the target pollutant. Methanol and n-butanol have been reported as hydroxyl radical scavengers [29,64,66]. For example, the presence of methanol decreases the degradation rate of substrate according to the following reaction.

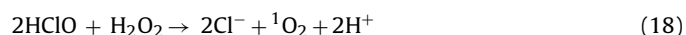


Similarly, the carbonate ions and bicarbonate ions consume the available hydroxyl radicals by the following reactions [15,29]



Although $\bullet\text{CO}_3^-$ is an oxidizing agent, it reacts much more slowly with substrates as compared with hydroxyl radicals. As a result, carbonate ions also decelerate the decomposition of substrates. The presence of a small quantity of Na_2CO_3 and NaHCO_3 in solution has slight influence on the degradation of substrates.

It have been reported that the presence of Cl^- has enhancing effect on the degradation rate of pollutants [64,66,70]. Cl^- can react with $\bullet\text{OH}$ and produce chlorine radical. Two chlorine radicals react with each other to form one molecular of chlorine. Then, HClO is formed and it also can react with H_2O_2 to produce singlet oxygen.



The singlet oxygen is strongly oxidizing and can oxidize substrates. As a result, the presence of Cl^- accelerates the degradation process. Similar results are achieved in solutions containing other halogen anions [31].

However, another study shows that the presence of low concentrations of Cl^- ions in the solution may have inhibitory effects on dye degradation, and that only higher concentrations of Cl^- ions ($>0.02 \text{ M}$) can significantly enhance the dye degradation efficiency during GDP treatment but not increase dye mineralization. In addition, the presence of Cl^- results in the formation of adsorbable organic halogens (AOX) [81]. Although the results indicated that AOX could be abated with prolonged treatment, this observation is significant for the assessment of the environmental impact of GDP in the presence of Cl^- .

Metal ions such as Fe^{2+} , Fe^{3+} , Cr(VI) , Co^{2+} , Mn^{2+} and Cu^{2+} displays enhancing effects on the degradation rate of organic pollutants [10,15,64,70,71]. All of these metal ions except Cr(VI) can decompose H_2O_2 into $\bullet\text{OH}$, which accelerate the degradation of substrate. The enhancing effects of Fe^{2+} , Fe^{3+} and Cr(VI) are more apparent than Co^{2+} , Cu^{2+} and Mn^{2+} , which is discussed in the following parts, accordingly.

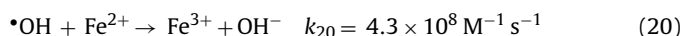
3.3. Combined process

3.3.1. Fenton process

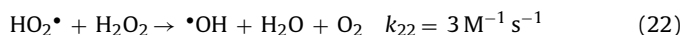
Since a lot of H_2O_2 form during GDP treatment, it is useful to add iron salts to convert H_2O_2 into $\bullet\text{OH}$ and enhance the removal of pollutants through Fenton's reactions. Many researchers employ ferric and ferrous ions as catalyst in GDP and both of them show apparent catalytic effect on the removal of pollutants, which are shown in Table 2. The addition of Fe^{2+} produces additional hydroxyl radicals through the following reaction:



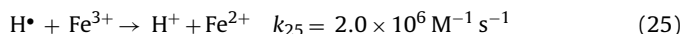
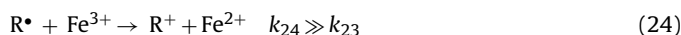
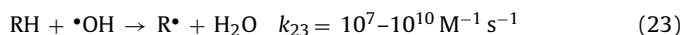
As shown in Table 2, Fe^{2+} shows apparent catalytic effect on the degradation of dyes, phenols and other organic pollutants [10,11,29,30,50,51,62–71,75,79,82]. At the same time, the optimum dosage of Fe^{2+} is also investigated, since too higher concentration of Fe^{2+} also consumes $\bullet\text{OH}$ due to the following reaction:



The effect of Fe^{3+} is also investigated. It seems that, for dyes, the catalytic effect of Fe^{2+} is more evident than that of Fe^{3+} [68,70]. It has been reported that only when the concentration of Fe^{3+} ion is over 120 mg/L, its catalytic effect is better than that of Fe^{2+} ion during GDP treatment for polar brilliant B [64]. Many researchers believe that the catalytic effect of Fe^{3+} is not apparent than that of Fe^{2+} , since the rate constant of Fe^{2+} ion with H_2O_2 ($76 \text{ M}^{-1} \text{ s}^{-1}$) is almost four orders of magnitude larger than that of Fe^{3+} ion with H_2O_2 ($0.01 \text{ M}^{-1} \text{ s}^{-1}$). And the oxidative ability of $\text{HO}_2\bullet$ is much lower than that of $\bullet\text{OH}$.



But Wang et al. found that Fe^{3+} showed better catalytic effect than Fe^{2+} during the degradation of aromatic organic substrate [29,30,62,63,65–67]. The possible mechanism may be the following reactions besides the aforementioned reactions:



The hydroxyl radicals in GDP can both react with RH to produce $\text{R}\bullet$ radicals and with Fe^{2+} ions to produce Fe^{3+} ions. As for $k_{24} \gg k_{23}$, Fe^{3+} ion can be quickly transformed to Fe^{2+} ion by $\text{R}\bullet$. As a result, a lot of Fe^{2+} ions were formed in the solution and the newly formed Fe^{2+} ions further react with H_2O_2 in the solution to produce more hydroxyl radicals. On the other hand, Fe^{3+} has the scavenging ability for $\text{H}\bullet$ shown in Eq. (25), which makes more hydroxyl radical available for the oxidation of substrate. The fact that H_2 produced in the anodic compartment is reduced with the addition of Fe^{3+} verified this [45].

3.3.2. TiO_2 film

As GDP enables the generation of numerous high energy particles integrated with light, electricity and chemical oxidation, functioning as a multiple energy field, there exist the conditions

Table 2

GDP treatment of organic pollutants combined with iron salts.

| Type | Substrate | C ₀ | Reactor | C (Fe ²⁺) | Conditions | Time (min) | Degradation rate (%) | Ref. |
|-------------------------|----------------------|----------------|---------|--|---|------------|----------------------|------|
| Dyes | Acridine Orange | 20 ppm | a | Fe ²⁺ : 6.94 × 10 ^{−4} M | 500 V; 2 g/L Na ₂ SO ₄ ; pH ₀ = 2; anode: 0.5 mm platinum wire; cathode: stainless steel; 175 mL | 5 | 89.0 | [71] |
| | Brilliant red B | 16 mg/L | a | Fe ²⁺ : | | 2 | 94.99 ^a | [10] |
| | Weak acid flavine G | | | 8.76 mg/L | | | 95.55 ^a | |
| | Cationic Blue | 25 mg/L | a | Fe ²⁺ : 20 mg/L | 500 V; 2 g/L Na ₂ SO ₄ ; pH ₀ = 6; anode: 0.3 mm platinum wire; cathode: stainless steel; 303 K; 200 mL | 3 | 99.7 | [68] |
| | Acid Orange 7 | 25 mg/L | a | Fe ³⁺ : 20 mg/L | 515 V; 2 g/L Na ₂ SO ₄ ; pH ₀ = 3; anode: 0.3 mm platinum wire; cathode: graphite stick; 303 K; 200 mL | 10 | 68.6 | [70] |
| | | | | Fe ²⁺ : 40 mg/L | | 5 | 95.33 ^a | |
| | | | | Fe ³⁺ : 40 mg/L | | | 79.75 ^a | |
| | Polar brilliant B | 50 mg/L | a | Fe ²⁺ : 20 mg/L | 500 V; 100 mA; 4 g/L Na ₂ SO ₄ ; anode: 0.6 mm platinum wire; cathode: stainless steel plate; pH ₀ = 2.5; 150 mL | 2 | 80 ^a | [64] |
| | | | | Fe ³⁺ : 80 mg/L | | | 60 ^a | |
| | Crystal violet | 6 mg/L | b | Fe ²⁺ : 4 × 10 ^{−4} M | 600 V; 2 g/L Na ₂ SO ₄ ; anode: 0.5 mm platinum wire; cathode: graphite plate; pH ₀ = 6.7; 250 mL | 5 | 91.4 ^a | [79] |
| Phenols | Alizarin red S | 30 mg/L | b | Fe ²⁺ : 2 × 10 ^{−4} M | | 10 | 80 ^a | [51] |
| | Brilliant Green | 30 mg/L | b | Fe ²⁺ : 2 × 10 ^{−4} M | | 10 | 95 | [50] |
| | Phenol | 100 mg/L | b | Fe ²⁺ : 60 mg/L | 600 V; 2 g/L Na ₂ SO ₄ ; anode: 0.5 mm platinum wire; cathode: graphite plate; 300 mL | 30 | 55 | [11] |
| | | 100 mg/L | a | Fe ²⁺ : 37 mg/L | 500 V; 100 mA; anode: 0.6 mm platinum wire; cathode: stainless steel plate; initial conductivity: 6.4 mS/cm; pH ₀ = 3; 298 K; 150 mL | 6 | 75 | [64] |
| | | | | Fe ³⁺ : 37 mg/L | | | 84 | |
| | 4-Nitrophenol | 300 mg/L | c | Fe ²⁺ : 60 mg/L | 900 V; 110 mA; diameter of small hole: 2 mm; pH ₀ = 2.8; initial conductivity 6.5 mS/cm; 298 K; 250 mL | 20 | 85 | [29] |
| | | | | Fe ³⁺ : 60 mg/L | | | 95 | |
| | | 1000 mg/L | a | Fe ²⁺ : 40 mg/L | 500 V; 100 mA; anode: 0.6 mm platinum wire; cathode: stainless steel; initial conductivity 6.4 mS/cm; pH ₀ = 2.5; 298 K; 150 mL | 10 | 32 | [67] |
| | | | | Fe ³⁺ : 40 mg/L | | | 45 | |
| | 4-Chlorophenol | 100 mg/L | c | Fe ²⁺ : 40 mg/L | 750 V; diameter of small hole: 1.5 mm; initial conductivity 6.4 mS/cm; pH ₀ = 3.0; 303 K; 300 mL | Q = 40 C | 84 | [30] |
| Other organic compounds | 4-Nitrophenol | 70 mg/L | b | Fe ³⁺ : 30 mg/L | | | 95 | [75] |
| | 2,4-Dinitrophenol | 40 mg/L | | Fe ²⁺ : | 600 V; 2 g/L Na ₂ SO ₄ ; anode: 0.5 mm platinum wire; cathode: graphite plate (diameter: 20 mm); 303 K | 20 | >75 | |
| | 2,4,6-Trinitrophenol | 108 mg/L | | 4 mg/L | | | >65 | |
| | Chlorobenzene | 100 mg/L | a | Fe ²⁺ : 30 mg/L | 500 V; 100 mA; initial conductivity 6.4 mS/cm; pH ₀ = 2.6; anode: 0.6 mm platinum wire; cathode: stainless steel plate; 298 K; 150 mL | 6 | 58 | [62] |
| | Nitrobenzene | 100 mg/L | a | Fe ³⁺ : 20 mg/L | 500 V; 100 mA; 4 g/L Na ₂ SO ₄ ; anode: 0.6 mm platinum wire; cathode: stainless steel plate; pH ₀ = 3.5; 298 K; 150 mL; | 6 | >90 | [63] |
| | | | | Fe ²⁺ : 30 mg/L | | | 85 | |
| | | | | Fe ³⁺ : 20 mg/L | | | >90 | |
| | 2-Naphthylamine | 30 mg/L | b | Fe ²⁺ : 30 mg/L | 600 V; 2 g/L Na ₂ SO ₄ ; anode: 0.5mm platinum wire; cathode: graphite plate; 250 mL | 2 | 98 | [82] |

^aDiscoloration rate.

for the combination of TiO_2 and GDP [14]. Initially, TiO_2 was immobilized on glass by using sol–gel method to couple with GDP with reactor (a). The results showed that the TiO_2 film with 5 layers had high catalytic activity and good durability. Using the coupling system, the degradation efficiency of methylene blue ($C_0 = 5 \text{ mg/L}$) reached up to 95% after 15 min treatment [83].

Recently, TiO_2 film has been developed to newly generate in situ with Ti electrode as the anode [14]. TiO_2 film was formed on the Ti anode, which then broken down when GDP occurred. The system realizes the process of electrode catalysis, as well as electrolyte catalysis. Under optimum conditions (550 V; electrode depth: 2 mm, supporting electrolyte: 5 g/L Na_2SO_4 ; pH = 2), the maximum decolorization ratio of 100 mL of 20 mg/L brilliant red B solution was 97.8% after 40 min treatment. GDP integrated with TiO_2 catalysis system on the electrode creates a mutually coupling and self-exciting system showed the synergic function of the multiple energy fields, which had promising prospects for practical application.

4. Environmental applications of glow discharge plasma

GDP has been applied for the degradation of wastewater containing dyes, phenols, benzene derivatives, algae and so on. Most of these studies are to demonstrate the viability of GDP for wastewater treatment. In addition, much attention has been paid to the detection of intermediates, degradation mechanism and kinetic behavior.

4.1. Environmental applications

4.1.1. Dyes

Effluents from textile dyeing industry cause severe environmental problems due to the characteristics of strong color, high chemical oxygen demand (COD) and low biodegradability. Being toxic to microbes, dyes-containing wastewater cannot be treated well by biological processes. In addition, aquatic metabolism is suppressed due to the shortage of sunlight, which in turn lowers the self-purification ability of the wastewater. Therefore, the treatment of dyeing wastewater is becoming a matter of great concern. GDP has proven effective for the discoloration of dyeing wastewater.

The discoloration of dyeing wastewater has been carried by different reactors shown in Fig. 3, as well combined with Fenton process. Different kinds of dyes have been employed as target pollutants for the viability of GDP [10,13,14,31,32,50,51,64,68–71,73,78,79,81,83]. Most of researchers employ GDP combined with Fe^{2+} for dye discoloration in short time, which is displayed in Table 2. For example, wastewater containing cationic blue dye (25.0 mg/L) underwent efficient degradation with reactor (a) assisted by Fe^{2+} . The degradation ratio was about 99.7% after 3 min treatment under 500 V when the concentration of Fe^{2+} was 20 mg/L. The removal of COD reached up to 58.7% after 10 min treatment, which was prior to 55.7% after 90 min treatment without Fe^{2+} [68].

Gao et al. investigated the discoloration of Brilliant Green, with reactor (b). COD removal reached more than 95% within 10 min with Fe^{2+} ($2.0 \times 10^{-4} \text{ mol/L}$). GC–MS was used to identify the intermediates and found that benzoic acid, 1,2,3,4,5,6-cyclohexanhexaol and organic acid formed after 5 min treatment. Then possible pathway was assumed that Brilliant Green molecule was cleaved into benzoic acid and 1,2,3,4,5,6-cyclohexanhexaol at first, and further producing lots of smaller molecule of organic acids after opening the ring [50].

Reactor (c) is also used for dye discoloration such as Direct Red 79. It was found that higher degradation efficiency was obtained in the anodic compartment of the diaphragm reactor where final

decomposition efficiency reached 80% after 30 min treatment. The decomposition products were also analyzed by HPLC–MS during the GDP treatment. It was found that five main compounds in the anolyte and another three ones in the catholyte [32].

4.1.2. Phenol and phenolic compounds

Phenol and phenolic compounds are widely used in the manufacture of antioxidants, disinfectants, pesticides, and other synthetic materials. Therefore, such contaminants are commonly found in industrial wastewater. Reactor (a), (b) and (c) are used for phenol degradation and GDP has proven efficient for the remediation of effluents containing these pollutants. Especially, by GDP combined with Fenton process, phenols can be degraded in short time shown in Table 2. Furthermore, more attention is paid to the degradation pathway of phenol, kinetics and energy efficiency, besides the study of the optimum condition with different reactors.

The degradation of phenol has been systematically investigated with GDP without catalysts and in the presence of Fe^{2+} and Fe^{3+} . Without catalysts, the degradation of phenol proceeded smoothly induced by GDP [9,11]. The concentration of phenol decreased exponentially with the discharge time and approximately 80% phenol disappeared after 2 h with reactor (a). Three isomeric dihydroxybenzenes and hydroxyhydroquinone were identified and the distribution of dihydroxybenzene intermediates was catechol > hydroquinone >> resorcinol. In addition, catechol, hydroquinone and hydroxyhydroquinone did not disappear after 2 h treatment. It was also found that both oxalic and formic acids were detected as major products. Other dicarboxylic acids, such as tartaric acid, malic acid and malonic acid were also detected during GDP treatment. Based on the intermediate products, Tezuka believed that the collapse of phenol proceeded in a successive manner as follows: (1) hydroxylation of benzene ring, (2) oxidative ring cleavage leading to the formation of carboxylic acids and ultimately, (3) oxidation to inorganic carbon. The reaction pathway of phenol without catalysts was shown in Fig. 4(a).

Initially, much attention has been paid to the addition of Fe^{2+} , since Fe^{2+} can convert hydrogen peroxide in solution to $\cdot\text{OH}$, which apparently accelerates the degradation of phenol. When the concentration of Fe^{2+} was 60 mg/L, the degradation efficiency of phenol was up to 55% after 30 min treatment under 600 V with reactor (b). The intermediate products were determined by HPLC. It was found that benzoquinone (not detected without Fe^{2+}) was detected in considerable amounts besides *o*-dihydroxybenzene, hydroxyhydroquinone, *p*-dihydroxybenzene, and carboxylic acids [11]. According to the intermediate products aforementioned, the reaction pathway of phenol in the presence of Fe^{2+} was proposed, which is shown in Fig. 4(b).

Wang and Jiang found that both Fe^{2+} and Fe^{3+} showed the catalytic effect on the degradation of phenol [29,65]. COD and TOC sharply decreased in the presence of iron salts. In addition, the catalytic effect Fe^{3+} was better than that of Fe^{2+} . 100 mg/L phenol solution was treated with reactor (a) assisted by Fe^{2+} and Fe^{3+} , respectively. The phenol removal was 84% with Fe^{3+} and 75% with Fe^{2+} after 6 min treatment when their concentrations were both 37 mg/L. Possible mechanism is shown in Fig. 4(c). When phenol underwent GDP treatment, dihydroxycyclohexadienyl radicals formed due to the attack of the hydroxyl radicals on benzene ring. Possessing reducing nature, the dihydroxycyclohexadienyl radicals can rapidly reduce Fe^{3+} to Fe^{2+} . A lot of Fe^{2+} were formed in the solution and further reacted with H_2O_2 to produce more hydroxyl radicals. The concentration of H_2O_2 in solution verified this. There was a lot of H_2O_2 accumulated in the solution in the presence of Fe^{2+} only, Fe^{3+} only, Fe^{2+} plus phenol. However, no H_2O_2 accumulated in the presence of Fe^{3+} plus phenol. The intermediate products such as benzoquinone, hydroquinone and catechol formed during

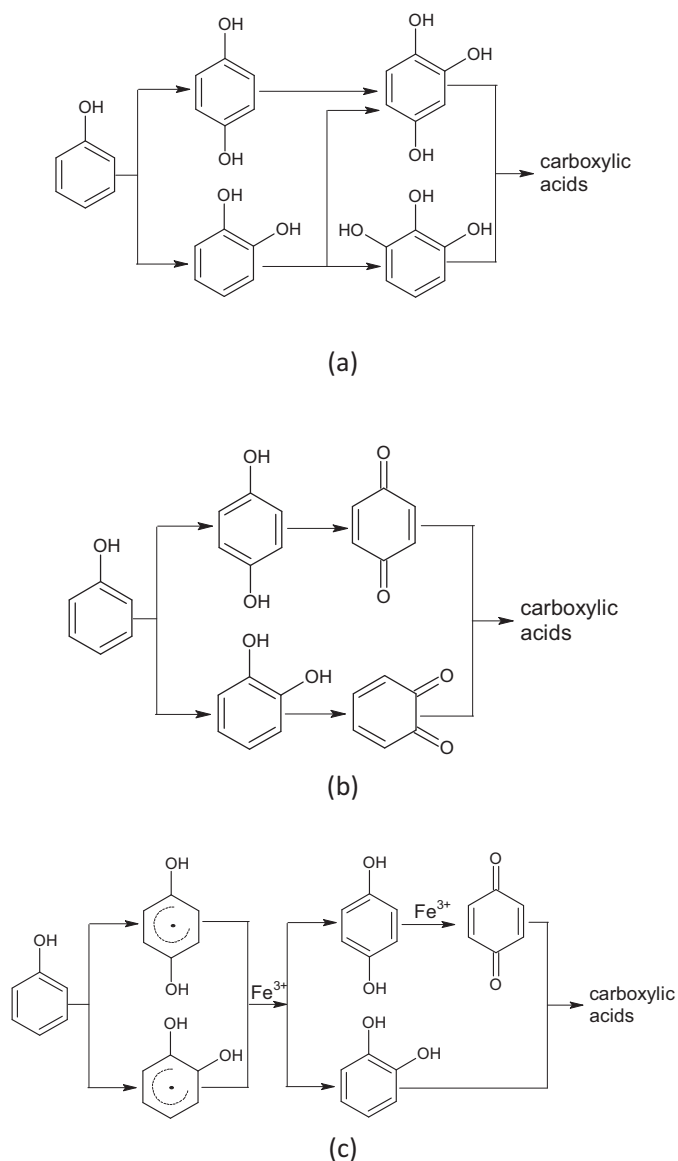


Fig. 4. Reaction pathway for phenol oxidation in GDP (a) without catalyst (b) in the presence Fe^{2+} (c) in the presence of Fe^{3+} .

the first 10 min GDP treatment when the concentration of Fe^{3+} was 37 mg/L.

In addition, Tezuka investigated kinetics of phenol degradation with reactor (a). The experimental results showed that the initial rate of phenol degradation might be governed by the first-order rate law, when the initial concentration was sufficiently low and, vice versa, the zero-order rate law [58].

Liu and Jiang also investigated the degradation of phenol under acidic, neutral, and basic conditions with reactor (c) [29]. In a basic medium, the phenol degradation rate was slower and the byproducts were less abundant than those in acidic medium. The product distribution was also different in basic medium as compared to that in neutral or acidic medium. In basic medium, the phenols exist in phenolate ion, which makes the benzene ring more susceptible to hydroxyl radical attack, owing to the electrophilic nature of the hydroxyl radicals and the electron-donating properties of phenolate ions. As a result, the hydroxylation reaction prevailed, and the hydroquinone and pyrocatechol were the major intermediate products. In acidic medium, phenol was present in its undissociated form, making the hydrogen abstraction of the phenolic group by the hydroxyl radical prevail, producing 1,4-benzoquinone.

Table 3

Hydroxylation products of different benzenic derivatives.

| No. | Substrates | Products | Ref. |
|-----|------------|----------|--------|
| 1 | | | [9,11] |
| 2 | | | [54] |
| 3 | | | [55] |
| 4 | | | [62] |
| 5 | | | [63] |

Others also investigated the degradation of nitrophenol [67,75] and chlorophenols [30,53,59–61] induced by GDP. Most abundant intermediate products were formed by attacking the ortho- or para-position of $-\text{OH}$ due to the high electrophilic nature of the hydroxyl radicals. Other intermediate products were similar to those of phenol. Chlorine atoms in the organics were liberated as chloride ions. COD and TOC sharply decreased in the presence of Fe^{2+} and Fe^{3+} . In addition, Fe^{3+} showed a better catalytic effect than Fe^{2+} .

4.1.3. Other benzenic and heteroaromatic derivatives

Other benzenic and heteroaromatic derivatives are also investigated by GDP treatment with different reactors. For benzenic derivatives, carboxylic acids during ring cleavage are similar to that of phenol. Oxalic, formic and malonic acids are also found among the product mixture. The difference results from the hydroxylation of benzene ring. The hydroxylation products of different benzenic derivatives are listed in Table 3.

As shown in Table 3, the hydroxylation products of phenol are catechol and hydroquinone [9,11]. However, when aniline is subject to GDP, *p*-aminophenol is predominant product, while the minor isomers, *o*-aminophenol and *m*-aminophenols are yielded in comparable amounts [55]. For benzoic acid, both *m*-hydroxybenzoic acid and *p*-hydroxybenzoic acid are yielded in comparable amounts, while *o*-hydroxybenzoic acid cannot be detected [54]. With nitrobenzene as substrate, the distribution of the intermediates of nitrophenol during GDP treatment follows the order of *o*-nitrophenol > *p*-nitrophenol > *m*-nitrophenol and with the ratio of 1.0:0.85:0.70 at 40 min [63]. When chlorobenzene is underwent GDP treatment, the chlorophenol intermediates are found to be in the following order: *p*-chlorophenol > *o*-chlorophenol > *m*-chlorophenol [62]. Steric hindrance, conjugating effect accounts for the discrepancy of the isomeric ratio caused by hydroxyl radicals. Since hydroxyl radical has the electrophilic

reactivity, with phenol as substrate, the hydroxyl group is smaller in size and ortho, para-directing rather than meta-directing are favorable in the hydroxylation of phenol. However, for benzoic acid, the size of carboxyl group is large enough to cause steric hindrance to the ortho position, so para- and meta-directing properties are almost equal. For aniline and nitrobenzene, the steric hindrance of ortho-position can be ignored compared with carboxyl group and this will increase the chance of hydroxyl radical to attack on ortho- and para-position of nitro group and amino group. Since nitro group has the electron-withdrawing effect on the benzene ring, *o*-nitrophenol is more stable than the *p*- or *m*-nitrophenol. As a consequence, the *o*-nitrophenol is the major hydroxylating products in the degradation of nitrobenzene. However, amino-group has the electron-donating effect on benzene ring and *p*-aminophenol is more stable than *o*- or *m*-aminophenols. Therefore, *p*-aminophenol is predominant product, with aniline as substrate. For chlorobenzene, although Cl group has electron-withdrawing effect on benzene ring, it is also the donor of lone pair of electrons to the ortho- and para-positions of the benzene ring by conjugation. Therefore, *p*-chlorophenol is more predominant in the intermediate products.

On the other hand, the hydroxylation of benzene ring also results in the formation of phenol and inorganic ions [62]. With benzenic derivatives containing Cl group as substrate, the concentration of Cl^- increases with the treatment time. With benzenic derivatives containing NO_2 as substrate, nitrate ion increases at a much higher rate during the whole process, whereas nitrite ion decreases slowly from the beginning of GDP treatment [63]. This maybe the fact that the nitrite produced is not stable and is rapidly oxidized to nitrate by hydrogen peroxide or hydroxyl radical in GDP. Similarly, benzenesulfonates are exhaustively destroyed by GDP to liberate sulfo group as sulfate ion [12,56].

In most cases, many researchers believe that most of intermediate products results from the attack of $\bullet\text{OH}$. However, appreciable amount of aniline produced in the degradation of azobenzene [84] verifies the role of $\bullet\text{H}$ in GDP. Therefore, combined effect of active species in GDP should be considered in the mechanism of degradation.

For heteroaromatic derivatives [72,82,84], intermediate products are more complex than those of benzenic derivatives. GDP can make cleavage of compounds occur at aromatic ring and other bond such as C–C, C–N and N=N. For example, 2-naphthylamine solution is subjected to GDP treatment with reactor (b) and three major intermediate products are *o*-phthalic acid, *o*-hydroxylbenzoic acid and catechol. The attack of $\bullet\text{OH}$ occurs at aromatic ring and leads to the cleavage of aromatic ring [82]. For azobenzene, it seems that GDP leads to the cleavage of N=N bond and aniline is the major product [84].

4.1.4. Reduction of Cr(VI)

Initially, the application of GDP focuses on the utilization of oxidative species in GDP such as $\bullet\text{OH}$ and H_2O_2 . And it seems that the existence of $\bullet\text{H}$ would be insignificant. Wang lei et al. utilized $\bullet\text{H}$ in GDP for the reduction of hexavalent chromium [Cr(VI)] for the first time [43]. Experimental results showed that Cr(VI) could be smoothly reduced to Cr(III) by reactor (a) with 500 V as the optimum operating voltage. The reduction rate of Cr(VI) was enhanced by either decreasing the solution pH or adding radical scavengers to the solution such as ethanol and phenol. At initial pH 2.0, 100 mg/L Cr(VI) was completely reduced within 10 min treatment in the presence of 100 mg/L phenol. Therefore, simultaneous oxidation of phenol and reduction of Cr(VI) could be achieved in GDP treatment [44]. Experimental results also showed that the phenol oxidation increased evidently in the presence of Cr(VI) and the Cr(VI) reduction increased with the addition of phenol. The possible mechanism can be explained as follows.

When GDP occurred, water molecules near the plasma/solution interface dissociated to $\bullet\text{OH}$, $\bullet\text{H}$ and H_2O_2 . $\bullet\text{H}$ was captured by Cr(VI) according to the following reaction.



Since $\bullet\text{OH}$ in GDP can combine with $\bullet\text{H}$ to form water, therefore, the addition of phenol reduced the concentration of $\bullet\text{OH}$ and more $\bullet\text{H}$ radicals were available for reduction of Cr(VI). On the other hand, the addition of phenol inhibited the oxidation of Cr(III), since $\bullet\text{OH}$ can oxidize Cr(III) and Cr(V) to Cr(IV) and Cr(VI), respectively. Based on the above reasons, both the reduction of Cr(VI) and oxidation of phenol were efficiently accelerated in GDP treatment. The findings would be helpful for the removal of organic and inorganic pollutants simultaneously in the complex wastewater.

4.1.5. Algae

Recently, GDP has been utilized for the inactivation of algae in the aqueous solution. The inactivation of *Microcystis aeruginosa* (MA) was investigated with reactor (a) [46]. The results showed that relatively higher applied voltage, current and treatment time benefited MA removal and the inactivation ratio reached 90% within 5 days after 20 min treatment under optimal conditions (voltage: 530 V; current: 30 mA). Furthermore, the concentration of Chlorophyll-a and dehydrogenase decreased after 20 min treatment, which demonstrated GDP treatment could effectively inhibit the growth of MA and cause the decrease of MA activity and deteriorating of cell integrity. Although the underlying mechanism of inactivation of algae with GDP remained unclear, this study still provided a kind of possible application of GDP for the inactivation of algae.

4.1.6. Polymer

GDP was also used for the degradation of polymers. 0.1 g poly(acrylamide) was dissolved in 50 mL of 1.7×10^{-3} M NaCl solution and underwent GDP treatment with reactor (a). The voltage was 700 ± 10 V and the current varied from 60 to 120 mA. The analytical results of the degradation products showed that the degradation took place stepwise caused by the cleavages of the main and also the side chains of the polymer [85].

Recently, GDP has been explored to enhance the adsorption properties of chitosan for dye removal. The results showed that the GDP treatment changed the morphology and crystallinity of chitosan particles, and that the number of $-\text{CH}_2$ and $-\text{CH}_3$ group in chitosan samples increased. Various pretreatment parameters, including discharge current and pretreatment time, played significant roles on the chitosan modification. Dye uptake in GDP modified chitosan was faster than adsorption in untreated chitosan. Thus, GDP is an attractive pretreatment method for environmental adsorption materials [86].

4.2. Comparison with other AOPs

As a kind of AOPs, it is instructive to assess GDP by comparing with other AOPs. Although there are not systematical experimental results for each reactor, some results available in literatures are enough to demonstrate the advantage of GDP. Removal efficiency, energy efficiency and formation rate constants of active species in GDP have been compared with other AOPs in some papers.

With regard to the removal of either substrate or TOC in the degradation of benzenesulfonate and *p*-toluenesulfonate, experimental results show that GDP with reactor (a) are comparable to those with UV/TiO₂ and ozone [12], which is listed in Table 4. In case of pentachlorophenolate, GDP seems somewhat superior to UV/TiO₂.

Table 4

Comparison of substrate and TOC removal efficiency of GDP with other AOPs.

| Substrate | C ₀ (mM) | Method | (1) | (2) | Ref. |
|----------------------------|---------------------|--|---------|--------|------|
| Pentachlorophenolate | 2.1 | GDP 35 W with reactor (a) | 100/120 | 90/240 | [61] |
| | 0.65 | UV/TiO ₂ (0.1 g/L) 125 W | 97/360 | 91/360 | |
| Benzenesulfonate | 1.00 | GDP 45 W with reactor (a) | 100/150 | 89/240 | [12] |
| | | UV/TiO ₂ (500 W) | 100/120 | 90/300 | |
| <i>p</i> -Toluenesulfonate | 1.00 | GDP 45 W with reactor (a) | 100/150 | 91/240 | [12] |
| | | Ozone 24 mg O ₃ /min pH = 3 | 100/180 | 28/180 | |

Note: (1) denotes substrate removal/reaction time (%/min); (2) denotes TOC removal/reaction time (%/min).

Besides the removal of substrate and TOC, energy efficiency is another important parameter. Generally, the energy efficiency is calculated using the following equation:

$$\eta = \frac{(1/2)C_0V}{UIt_{1/2}} \quad (27)$$

where C₀ is the initial substrate concentration, V is the liquid volume, U is the applied voltage, I is the current, and t_{1/2} is the reaction time required for decomposing half of initial substrate.

Previous study has reported energy efficiency of GDP with different pollutants as substrate. As shown in Table 5, with phenol as substrate, all values of energy efficiency are in the magnitude of 10^{−9} mol/J, which is comparable to those in pulsed corona streamer discharge (PCD) and spark discharge [29,65]. Similarly, the degradation of MTBE and bisphenol A (BPA) induced by GDP confirms that energy efficiency in GDP treatment with reactor (a) is in the similar order of magnitude to those in high-density plasma and ultrasonic degradation [15,66]. With MTBE, Cr(VI) and BPA as substrate, energy efficiency of GDP is higher than that with UV/TiO₂, especially in GDP combined with Fenton process [15,43,66]. Recently, Malik calculates energy yields (G₅₀) and relative energy efficiency (REE) with different GDP reactors with dyes as substrate, some of which is shown in Table 6. With methyl orange as substrate, G₅₀ with reactor (a) is 0.024 g/kWh, and REE is 1. It also demonstrates that GDP in contact with liquid is comparable to that in PCD, which is consistent with that with phenol as substrate aforementioned. At the same time, it was found that GDP reactor is less efficient comparing with other plasma reactors such as dielectric barrier discharges (DBD) and microwave discharges (MWD) according to the value of REE [37].

Gao et al. also compared the formation rate constants of active species in GDP with those in PCD, which was shown in Table 7 [77]. It can be seen that the formation rate of H₂O₂ and •OH with reactor (d) was higher than that in PCD. What's more, the experimental equipment in GDP is much simpler than that of PCD. Furthermore, the PCD process seems to perform best in water with lower

Table 5

Comparison of energy efficiency of GDP with other AOPs.

| Substrate | C ₀ | Method | Energy input | η | Ref. |
|-----------|----------------|---|--------------|--------------------------------|------|
| Phenol | 100 mg/L | GDP with reactor (a) | 50 W | 0.6 × 10 ^{−9} mol/J | [65] |
| | | GDP with reactor (a) + Fe ²⁺ 37 mg/L | 50 W | 7.4 × 10 ^{−9} mol/J | |
| | | GDP with reactor (a) + Fe ³⁺ 37 mg/L | 50 W | 9.5 × 10 ^{−9} mol/J | |
| | | GDP with reactor (c) | 99 W | 3.1 × 10 ^{−9} mol/J | |
| MTBE | 489 μM | PCD | 40 kW | 1.04 × 10 ^{−9} mol/J | [29] |
| | 532 μM | Spark discharge | 2 MW | 2.28 × 10 ^{−9} mol/J | |
| | 50 mg/L | GDP with reactor (a) | 53 W | 0.76 × 10 ^{−9} mol/J | |
| | 50 mg/L | High-density plasma | 200 W | 2.65 × 10 ^{−9} mol/J | |
| | 200 mg/L | GDP with reactor (a) | 53 W | 3.00 × 10 ^{−9} mol/J | |
| Cr(VI) | 200 mg/L | UV/TiO ₂ | 1 kW | 1.89 × 10 ^{−11} mol/J | [15] |
| | 50 mg/L | GDP with reactor (a) pH = 2 | 50 W | 5.0 × 10 ^{−4} mg/J | |
| | 36 mg/L | UV/TiO ₂ (0.5 g/L) pH = 1 | 125 W | 1.0 × 10 ^{−5} mg/J | |
| BPA | 100 mg/L | GDP with reactor (a) Na ₂ SO ₄ | 50 W | 6.1 × 10 ^{−5} mg/J | [43] |
| | 100 mg/L | GDP with reactor (a) NaCl | 50 W | 43.8 × 10 ^{−5} mg/J | |
| | 100 mg/L | GDP with reactor (a) Na ₂ SO ₄ + 0.33 mM Fe ³⁺ | 50 W | 207 × 10 ^{−5} mg/J | |
| | 40 mg/L | UV/TiO ₂ (1.0 g/L) | 200 W | 5.0 × 10 ^{−7} mg/J | |
| | 26.9 mg/L | Ultrasonic degradation | 80 W | 4.2 × 10 ^{−5} mg/J | |

Table 6Comparison of energy yields (G₅₀) and relative energy efficiencies (REE) of GDP reactors with other plasma reactors [37].

| Name of dye | C ₀ (mg/L) | Reactor | G ₅₀ (g/kWh) | REE |
|----------------|-----------------------|------------|-------------------------|------|
| Eosin | 12 | b | 0.029 | 0.07 |
| Methylene blue | 12 | c | 0.042 | 0.7 |
| Methyl orange | 13 | a | 0.024 | 1 |
| Eosin | 12 | c | 0.307 | 0.7 |
| Methyl orange | 10 | Pulsed-DBD | 9.38 | 400 |
| Methylene blue | 10 | MWD | 0.155 | 3 |

Note: REE = (REER)_{G₅₀}/G_{50r}, where 'G_{50r}' and 'REER' are energy yield and relative energy efficiency of the reference reactor. REE is being calculated pulsed corona discharge (PCD) in water without bubbling gas, which is taken as the reference reactor and assigned REE value 1.

conductivity, which is not suitable for real wastewater that contains salts. However, GDP seems to have advantage in this respect.

5. Conclusion and outlook

This manuscript provided a holistic view on the progress of GDP in wastewater treatment, as well as mechanisms of GDP generation and the removal of hazardous pollutants, with the aim of drawing more attention to this emerging technique, which exhibit unique characteristic such as simpler equipment, easier operation, higher energy efficiency and environmental compatibility. What's more, GDP was suitable for the degradation of effluents containing salts. This review also summarizes reactors commonly used for the generation of GDP, covering various kinds of experimental parameters, electrode materials.

As GDP enables the generation of numerous high energy particles integrated with light, electricity and chemical oxidation, functioning as a multiple energy field, there exist the conditions for the combination of catalysis and GDP. The synergistic combination of GDP and catalysis such as TiO₂ and Fenton process can more efficiently utilize active species and energies generated in GDP, which

Table 7Comparison of formation rate constants of H_2O_2 and $\cdot\text{OH}$ in GDP with PCD.

| Method | Applied voltage | Power input (W) | $k_{\cdot\text{OH}} [(\text{Ms})^{-1}]$ | Applied voltage | Power input (W) | $k_{\text{H}_2\text{O}_2} [(\text{Ms})^{-1}]$ |
|--------|-----------------|-----------------|---|-----------------|-----------------|---|
| PCD | 30 kV | 75 ^a | 4.1×10^{-10} | 35 kV | 85 ^a | 1.02×10^{-7} |
| GDP | 600 V | 75.6 | 1.66×10^{-6} | 560 V | 75.6 | 4.06×10^{-6} |

^a Average power input per 550 mL.

has shown the enhanced results. The application of Ti anode and stainless steel anode must be emphasized because they realize the process of electrode catalysis, as well as electrolyte catalysis. The search for other coupled process is a natural development for GDP.

Like other AOPs, the current reactors were designed to treat small volumes of aqueous solution containing hazardous pollutants. Although many efforts have been made to develop reactors for efficient degradation of pollutants, it is still limited in lab and far from satisfactory for actual wastewater treatment. The next major commitment is to address the successful development of pilot plants capable of treating larger volumes, allowing thereafter the use of this technique at an industrial level. Therefore, the reactors suitable for industrial application should be developed in the future. In addition, the cost should also be considered, since wastewater treatment induced by GDP is achieved at the expense of electrical energy. It is impractical to utilize GDP as the only technique for wastewater treatment, which can make the cost relatively higher. Coupling with other processes such as biological treatment perhaps will be a cost-effective and feasible means to utilize GDP. In such cases, GDP can degrade the target pollutants into byproducts in short time, and then byproducts can be decomposed by other biological treatment with less-energy. Therefore, the combined process calls for further study.

The understanding of GDP continues with the increasing interests for its application. As we exposed in this review, currently the theoretical fundamentals related to this technology are not well established. There are still many theoretical fundamentals about its onset, kinetics and mechanism of the removal of pollutants not available for us. Therefore, more studies should be undertaken to confirm these preliminary results to develop this technology. More attention should be paid to the great contribution of analytical techniques such as HPLC–MS, GC–MS or toxicity testing, which can help researcher to establish an integrated wastewater treatment considering both the optimized experimental setup and the elucidation of the reaction pathways and biodegradability enhancement. Furthermore, energy efficiency of different reactors and its combined process should be systematically investigated in order to improve the energy yields of GDP. All of the above could then be used to predict the behavior and performance of such treatments in different reactors and select the best procedures for their real application.

Finally, we think that this review constitutes a reference document in the field and will help those inquiring about different aspects of this environmentally friendly water treatment technology as well as helping researchers launch new ideas and technological devices and applications.

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References

- [1] T. Mizuno, T. Akimoto, K. Azumi, T. Ohmori, Y. Aoki, A. Takahashi, *Japanese Journal of Applied Physics* 44 (2005) 396.

- [2] Z. Yan, L. Chen, H. Wang, *International Journal of Hydrogen Energy* 34 (2009) 48.
- [3] K. Harada, S. Suzuki, *Nature* 266 (1977) 275.
- [4] S.K. Sengupta, U. Sandhir, N. Misra, *Journal of Polymer Science: Part A: Polymer Chemistry* 39 (2001) 1584.
- [5] M. Tezuk, M. Iwasaki, *Thin Solid Films* 407 (2002) 169.
- [6] Y. Liu, X. Jiang, L. Wang, *Plasma Chemistry and Plasma Processing* 27 (2007) 496.
- [7] X. He, W. Yang, L. Yuan, X. Pei, J. Gao, *Materials Letters* 63 (2009) 1138.
- [8] Q. Lu, J. Yu, J. Gao, W. Yang, Y. Li, *Plasma Processes and Polymers* 8 (2011) 803.
- [9] M. Tezuk, M. Iwasaki, *Denki Kagaku, Electrochemistry* 65 (1997) 1057.
- [10] J. Gao, X. Wang, Z. Hu, H. Deng, J. Hou, X. Lu, J. Kang, *Water Research* 37 (2003) 267.
- [11] J. Gao, Y. Liu, W. Yang, L. Pu, J. Yu, Q. Lu, *Plasma Sources Science & Technology* 12 (2003) 533.
- [12] R. Amano, M. Tezuka, *Water Research* 40 (2006) 1857.
- [13] Z. Yan, Y. Liu, W. Ren, Z. Yuan, *Journal of Electrostatics* 70 (2012) 48.
- [14] X. Jin, H. Zhang, X. Wang, M. Zhou, *Electrochimica Acta* 59 (2012) 474.
- [15] S. Tong, Y. Ni, C. Shen, Y. Wen, X. Jiang, *Water Science and Technology* 63 (2011) 2814.
- [16] H.H. Kellogg, *Journal of the Electrochemical Society* 97 (1950) 133.
- [17] J. Garbarz-Olivier, C. Guilpin, *Journal of the Electrochemical Society* 91 (1978) 79.
- [18] H. Vogt, *Electrochimica Acta* 42 (1997) 2691.
- [19] A. Hickling, M.D. Ingram, *Journal of Electroanalytical Chemistry* 8 (1964) 65.
- [20] A.R. Denaro, K.O. Hough, *Electrochimica Acta* 17 (1972) 549.
- [21] S.K. Sengupta, *Journal of Electroanalytical Chemistry* 127 (1981) 263.
- [22] A. Hickling, M.D. Ingram, *Transactions of the Faraday Society* 60 (1964) 783.
- [23] S.K. Sengupta, O.P. Singh, *Journal of Electroanalytical Chemistry* 301 (1991) 189.
- [24] S.K. Sengupta, O.P. Singh, *Journal of Electroanalytical Chemistry* 369 (1994) 113.
- [25] S.K. Sengupta, R. Singh, A.K. Srivastava, *Indian Journal of Chemistry* 34A (1995) 459.
- [26] S.K. Sengupta, R. Singh, A.K. Srivastava, *Journal of Electroanalytical Chemistry* 427 (1997) 23.
- [27] S.K. Sengupta, R. Singh, A.K. Srivastava, *Indian Journal of Chemistry* 37A (1998) 558.
- [28] S.K. Sengupta, R. Singh, A.K. Srivastava, *Journal of the Electrochemical Society* 145 (1998) 2209.
- [29] Y. Liu, X. Jiang, *Environmental Science & Technology* 39 (2005) 8512.
- [30] L. Wang, *Plasma Chemistry and Plasma Processing* 29 (2009) 241.
- [31] Z. Stará, F. Krčma, M. Nejezchleb, J.D. Skalný, *Desalination* 239 (2009) 283.
- [32] Z. Kozáková, M. Nejezchleb, F. Krčma, I. Halamová, J. Čáslavský, J. Dolinová, *Desalination* 258 (2010) 93.
- [33] A.T. Bullock, D.L. Gavin, M.D. Ingram, *Journal of the Chemical Society, Faraday Transactions* 76 (1980) 648.
- [34] H. Hiroto, H. Kaoru, *Viva Origino* 29 (2001) 61.
- [35] Y. Liu, B. Sun, L. Wang, D. Wang, *Plasma Chemistry and Plasma Processing* (2012), <http://dx.doi.org/10.1007/s11090-011-9347-7>.
- [36] P. Bruggeman, C. Leys, *Journal of Physics D – Applied Physics* 42 (2009) 1.
- [37] M.A. Malik, *Plasma Chemistry and Plasma Processing* 30 (2010) 21.
- [38] B.R. Locke, M. Sato, P. Sunka, M.R. Hoffmann, J. Chang, *Industrial & Engineering Chemistry Research* 45 (2006) 882.
- [39] J. Zhang, J. Chen, X. Li, *Journal of Water Resource and Protection* 2 (2009) 99.
- [40] M.A. Malik, A. Ghaffar, S.A. Malik, *Plasma Sources Science & Technology* 10 (2001) 82.
- [41] J. Gao, X. Wang, Z. Hu, *Plasma Science & Technology* 3 (2001) 765.
- [42] Q. Lu, J. Lu, *Technology of Water Treatment (Chinese)* 33 (2007) 9.
- [43] L. Wang, X. Jiang, *Environmental Science & Technology* 42 (2008) 8492.
- [44] Y. Liu, *Journal of Hazardous Materials* 168 (2009) 992.
- [45] L. Wang, Y. Liu, *Plasma Chemistry and Plasma Processing* (2012), <http://dx.doi.org/10.1007/s11090-012-9375-y>.
- [46] X. Jin, Q. Xia, X. Wang, J. Yue, D. Wei, *Plasma Chemistry and Plasma Processing* 31 (2011) 697.
- [47] U. Gangal, M. Srivastava, S.K. SenGupta, *Journal of the Electrochemical Society* 156 (2009) F131.
- [48] X. Jin, X. Wang, H. Zhang, Q. Xia, D. Wei, J. Yue, *Plasma Chemistry and Plasma Processing* 30 (2010) 429.
- [49] X. Jin, X. Wang, J. Yue, Y. Cai, H. Zhang, *Electrochimica Acta* 56 (2010) 925.
- [50] J. Gao, J. Yu, Y. Li, X. He, L. Bo, L. Pu, W. Yang, Q. Lu, Z. Yang, *Journal of Hazardous Materials* B137 (2006) 431.
- [51] J. Gao, J. Yu, Q. Lu, X. He, W. Yang, Y. Li, L. Pu, Z. Yang, *Dyes and Pigments* 76 (2008) 47.
- [52] U. Gangal, M. Srivastava, S.K. SenGupta, *Plasma Chemistry and Plasma Processing* 30 (2010) 299.
- [53] M. Tezuk, M. Iwasaki, *Thin Solid Film* 316 (1998) 123.
- [54] M. Tezuk, M. Iwasaki, *Plasma & Ions* 1 (1999) 23.

- [55] M. Tezuka, M. Iwasaki, *Thin Solid Films* 386 (2001) 204.
- [56] R. Amano, S. Tomizawa, M. Tezuka, *Electrochemistry* 72 (2004) 836.
- [57] S. Tomizawa, M. Tezuka, *Plasma Chemistry and Plasma Processing* 26 (2006) 43.
- [58] S. Tomizawa, M. Tezuka, *Plasma Chemistry and Plasma Processing* 27 (2007) 486.
- [59] H. Yang, Y. Matsumoto, M. Tezuka, *Journal of Environmental Sciences Supplement* (2009) 142.
- [60] H. Yang, M. Tezuka, *Journal of Physics D – Applied Physics* 44 (2011) 1.
- [61] H. Yang, M. Tezuka, *Journal of Environmental Sciences* 23 (2011) 1044.
- [62] Y. Liu, X. Jiang, *Plasma Chemistry and Plasma Processing* 28 (2008) 15.
- [63] L. Wang, X. Jiang, Y. Liu, *Plasma Chemistry and Plasma Processing* 27 (2007) 504.
- [64] L. Wang, *Journal of Hazardous Materials* 171 (2009) 577.
- [65] L. Wang, X. Jiang, *Journal of Hazardous Materials* 161 (2009) 926.
- [66] L. Wang, X. Jiang, Y. Liu, *Journal of Hazardous Materials* 154 (2008) 1106.
- [67] Y. Liu, D. Wang, B. Sun, X. Zhu, *Journal of Hazardous Materials* 181 (2010) 1010.
- [68] X. Jin, X. Wang, Q. Wang, J. Yue, Y. Cai, *Water Science and Technology* 62 (2010) 1457.
- [69] X. Jin, H. Bai, F. Wang, X. Wang, X. Wang, H. Ren, *IEEE Transactions on Plasma Science* 39 (2011) 1099.
- [70] X. Jin, Q. Xia, H. Zhang, X. Wang, *IEEE Transactions on Plasma Science* 39 (2011) 3218.
- [71] J. Gao, Z. Hu, X. Wang, J. Hou, X. Lu, J. Kang, *Thin Solid Films* 390 (2001) 154.
- [72] J. Gao, Z. Hu, X. Wang, J. Hou, X. Lu, J. Kang, *Plasma Science & Technology* 3 (2001) 641.
- [73] J. Gong, W. Cai, *Plasma Science & Technology* 9 (2007) 190.
- [74] J. Gao, Y. Liu, W. Yang, L. Pu, J. Yu, Q. Lu, *Central European Journal of Chemistry* 3 (2005) 377.
- [75] J. Gao, L. Pu, W. Yang, J. Yu, Y. Li, *Plasma Processes and Polymers* 1 (2004) 171.
- [76] J. Gao, D. Ma, X. Guo, A. Wang, Y. Fu, J. Wu, W. Yang, *Plasma Science & Technology* 10 (2008) 422.
- [77] J. Gao, A. Wang, Y. Fu, J. Wu, D. Ma, X. Guo, Y. Li, W. Yang, *Plasma Science & Technology* 10 (2008) 30.
- [78] J. Gao, Y. Li, W. Yang, L. Bo, J. Yu, L. Pu, *Plasma Science & Technology* 8 (2006) 198.
- [79] J. Gao, D. Ma, X. Guo, Y. Li, W. Yang, *Chinese Journal of Applied Chemistry* 24 (2007) 534.
- [80] Z. Stará, F. Krčma, P. Slavíček, V. Aubrecht, 28th ICPIG, Prague, Czech Republic, July 15–20, 2007, p. 1082.
- [81] S.N. Ramjaun, R. Yuan, Z. Wang, J. Liu, *Electrochimica Acta* 58 (2011) 364.
- [82] Q. Lu, J. Yu, J. Gao, W. Yang, *Plasma Science & Technology* 7 (2005) 2856.
- [83] W. Zhang, W. Yang, X. Guo, J. Gao, *Chemical Engineer (Chinese)* 140 (2007) 1.
- [84] K. Gai, Y. Dong, *Journal of the Chinese Chemical Society* 52 (2005) 273.
- [85] E. Kokufuta, S. Fujii, H. Ishibashi, H. Yokoi, K. Harada, I. Nakamura, *Polymer Bulletin* 3 (1980) 173.
- [86] Y. Wen, C. Shen, Y. Ni, S. Tong, F. Yu, *Journal of Hazardous Materials* 201–202 (2012) 162.