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A cold plasma plume with a highly conductive liquid electrode*

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A cold dielectric barrier discharge (DBD) plasma plume with one highly conductive liquid electrode has been developed to treat thermally sensitive materials, and its preliminary discharging characteristics have been studied. The averaged electron temperature and density is estimated to be 0.6 eV and $10^{11}/\mathrm{cm}^3$, respectively. The length of plasma plume can reach 5 cm with helium gas (He), and the conductivity of the outer electrode affects the plume length obviously. This plasma plume could be touched by bare hand without causing any burning or painful sensation, which may provide potential application for safe aseptic skin care. Moreover, the oxidative particles (e.g., OH, O*, O_3) in the downstream oxygen (O_2) gas of the plume have been applied to treat the landfill leachate. The results show that the activated O_2 gas can degrade the landfill leachate effectively, and the chemical oxygen demand (COD), conductivity, biochemical oxygen demand (BOD), and suspended solid (SS) can be decreased by 52%, 57%, 76% and 92%, respectively.

Keywords: plasma plume, liquid electrode, degradation, landfill leachate
PACC: 5250D, 5280H, 5220, 5225L

1. Introduction

Nonthermal atmospheric plasma has attracted much attention recently because they can provide a cheaper and more convenient alternative (e.g., for surface modification) in comparison with low-pressure plasmas.[1] Various configurations and applications of nonthermal atmospheric plasmas have been extensively investigated. These plasma sources can be used in many fields, such as preparing biomaterials,[2] fabricating plasma display panel,[3] treating the NO_x,[4] and killing germs.[5,6] More recently, much attention has been absorbed in creating cold plasma sources.[1,7−11] Particularly, Laroussi and Lu[7] developed a room-temperature atmospheric pressure plasma source, so-called plasma plume, which can lead to cell inactivation and even cell lysis. However, the common defects of these plasma sources include the small diameter of the plasma plume (< 5 mm) as well as the high gas speed at nozzle (> 100 m/s). These defects may limit the industrial application of these sources. Therefore, the cold plasma plume with a bigger area and a lower gas speed is very desirable.

In recent years, the treatment of contaminated water by nonthermal atmospheric plasma has become one of the hot research topics,[12−14] because there are many active particles (e.g., OH, O*, O_3) in the plasma which can degrade the contaminants effectively. However, most researchers just let the contaminated solution pass the discharge region where the plasma reacted with contaminants directly. When the contaminated solution flowed through the plasma, the discharge became less stable, less effective and more difficult to occur. On the other hand, some suspended materials with high density in the contaminated water deposited on the surface of the electrode and dielectric layer, which shortened the lifetime of the discharge system and increased the breakdown voltage. However, passing the reactive gases in the plasma through the contaminated water may avoid these defects. At-

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mospheric pressure glow discharge (APGD) plasma is widely used in printing and textile industries, where the downstream gas contains many active species unfriendly to the environment. Therefore, it is quite significant to pay attention to the application of plasma downstream gas. To date, few results in regard to the degradation of the contaminated water by plasma downstream gas, especially the landfill leachate, are presented in the literature.

As mentioned above, a cold plasma plume (with a diameter of 1 cm) that generated a bigger area than those found in Refs.[1, 7, 10] along with its preliminary discharging characteristics were presented. Moreover, to explore the potential applications of downstream gas generated by the plasma plume, the landfill leachate served as a probe for wastewater was treated by using the downstream He and O_2 plasma gas.

2. Experimental

Figure 1(a) shows a novel APGD apparatus with one liquid electrode. The copper tube (diameter: 4 mm), which was centred inside the quartz tube by Teflon and ceramic fittings, acted as one electrode, and the solution of potassium chloride (KCl) having a conductivity of $0.12\,\mathrm{S\cdot cm^{-1}}$ remained in the outer layer as the other electrode. A quartz tube (inner diameter: 10 mm, thickness: 1.2 mm) acted as the dielectric layer, and the gas velocity was controlled by the flowmeter, while the two electrodes were connected to an AC power with a maximum peak voltage of 30 kV and an adjustable frequency from 8 to 20 kHz. The highly conductive solution was in a tighter contact with the dielectric layer than the metal electrode.

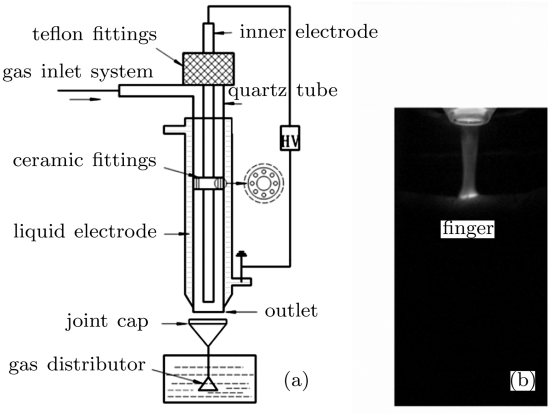


Fig.1. (a) Schematic presentation of a cold He plasma plume device at one atmospheric pressure. (b) Photograph of the He plasma plume in contact with human skin.

Therefore, the distribution of the electrical field became more uniform, which was a desirable feature for generating homogeneous plasma. On the other hand, the liquid electrode served as the coolant of the system. Figure 1(b) exhibits a photograph of the helium plasma plume in contact with a bare finger without establishing any conductive pathway.

A digital camera (Olympus, G: 1024×768 pixels, shutter speed: 1 s) was used to record the discharges, and the optical emission spectrum (OES) was measured by a UV–visible emission spectrometer (Stellarnet, EPP-2000). The plasma gas temperature was measured by an infrared thermometer (Fluke, Fluke62). In the degradation experiment, the joint cap was closed to cover the reactor outlet, and the O_2 gas was transported to the discharging area through the inner electrode. Subsequently, the activated O_2 and He gases were bubbled in the landfill leachate tank. It should be noted that the distance between the reactor outlet and the leachate tank was 15 cm. The COD and BOD measurements were performed by using the COD meter (ET99718, Germany) and BOD meter (ET99724A-6, Germany), respectively. The SS is analysed by weight method according to the GB/T 11901–1989 standard procedure of China.

3. Results and discussion

From the application point of view, gas temperature is one of the most important parameters for atmospheric plasmas. Figure 2(a) is the gas temperature along the axis of the He plasma plume obtained by an infrared thermometer. It is well known that the infrared thermometer is only suitable to measure surface temperature of the thermal sources which are optically thick, but the plasma gas is transparent. Therefore, it is difficult to measure the plasma gas temperature by the infrared thermometer directly. We thus used an insulative epoxy plate (2 cm×1 cm×0.15 cm, $L\times W\times T$) to stay in contact with the plasma plume, and then measured the contacting point by the infrared thermometer to indicate the temperature of the plasma gas. In order to reduce the effect of the absorbed energy on the plate temperature, the measuring time was 3s. Although the method could not measure the plasma gas temperature directly, the surfaces of the epoxy plate contacted the plasma gas directly, and the measured data may indicate the temperature of the plasma gas. The result exhibited a linear relationship

between the temperature of the plasma plume and the plume length. The highest gas temperature of the He plasma plume was not higher than 310 K when the applied power was lower than 15 W. The plasma gas temperature was nearly equal to the room temperature. This may be the reason that there was no burning or painful sensation when a bare finger was in direct contact with the plasma plume. Therefore, the He plasma plume is very suitable for treating thermally sensitive materials, polymerizing organic materials or sterilizing human skin. The plasma gas temperature was usually estimated by employing an optical spectroscopy technique.[15] Hong and Uhm [1] and Kong group[16] have found a good agreement between the simulated gas temperature and the measured data by this method. However, the higher spectral resolution (i.e., higher cost) of the optical spectrometer is needed to obtain accurate data. Compared with the optical spectroscopy method to measure the gas temperature, infrared thermometer is more convenient and less expensive, and therefore, more popular for most of the factories.

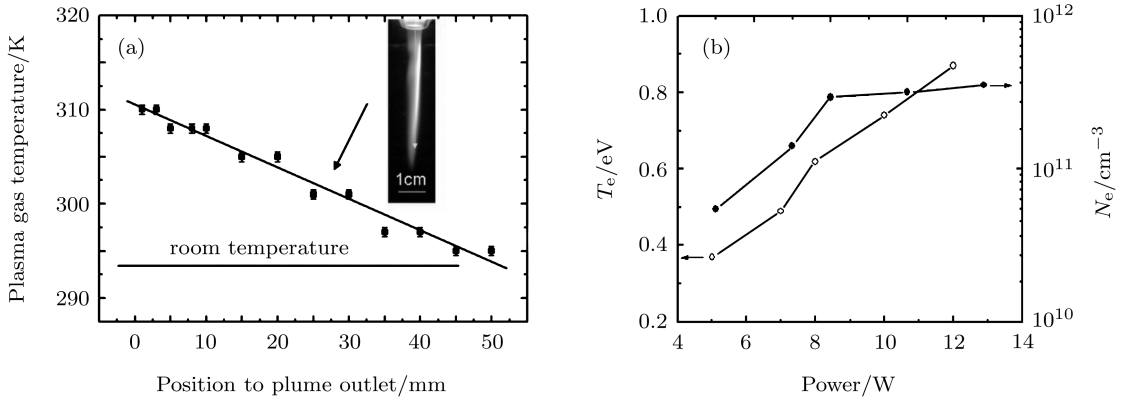


Fig.2. (a) The plasma gas temperature along the plume axis with a He velocity of $3\,\mathrm{m\cdot s^{-1}}$, an outer electrode conductivity of $0.12\,\mathrm{S\cdot cm^{-1}}$ and applied power of 15 W. (b) The effect of power on the electron temperature and density.

The electron temperature (T_e) and electron density (N_e) are two important parameters of the atmospheric plasmas. Dong *et al*[17] and Li *et al*[18] have carried out some works on this field. However, there is still not an accurate method to measure these plasma parameters under an atmospheric condition. Recently, Hong and Uhm [1] used a relatively simple method to estimate the T_e and N_e. They believed that the averaged electron density can be estimated from the electrical parameters of the discharge, such as the current density J, the electric field E, and the electron mobility μ_e. The electron density is defined as $n_e = J/(E\mu_e e)$.[1] The same analysing method was taken in our work for the similar discharging conditions with these in Ref.[1]. For example, if the He plasma works with a power of 8 W at 1 atmospheric pressure, the reduced electric field (E/P) is estimated to $0.028(\mathrm{V\cdot cm^{-1}\cdot Pa})$, which meets a value of $\mu_e P$ for He gas as $1.14\times10^8\,\mathrm{cm^2\cdot Pa/(V\cdot s)}$.[19] The current density obtained from the voltage–current curve obtained with the discharge structure in Fig.1(a) is about $0.15\,\mathrm{A/cm^2}$. Consequently, the electron density is estimated to be $2.94\times10^{11}/\mathrm{cm^3}$ in the discharging tube. This is similar to the N_e density generated in a helium rf plasma at one atmospheric pressure.[18] In our study, the averaged electron temperature is estimated to be 0.62 eV based on the Einstein thermodynamic equation $D_e/\mu_e \approx k_B T_e/e$, where D_e $(1.5\times10^3/p[\mathrm{Pa}]\,\mathrm{cm^2/s})$[19] and k_B are diffusion coefficient and Boltzmann constant, respectively. The influence of power on N_e and T_e is illustrated in Fig.2(b).

Metal materials, such as sliver[20] and copper,[21] are generally used as electrodes in DBD system. The influence of metal electrodes on discharge is usually not considered due to the low resistance of the metal materials. Compared with the metal electrode, the conductivity of the liquid electrode is lower by several orders of magnitude. Therefore, it is very necessary to study the influence of the liquid conductivity on the discharge characteristics. Figure 3 shows the effect of the liquid conductivity on the plume length. It is clear that the electrode conductivity will affect the discharge. The plume generated when using KCl solution as the electrode is about two times longer than

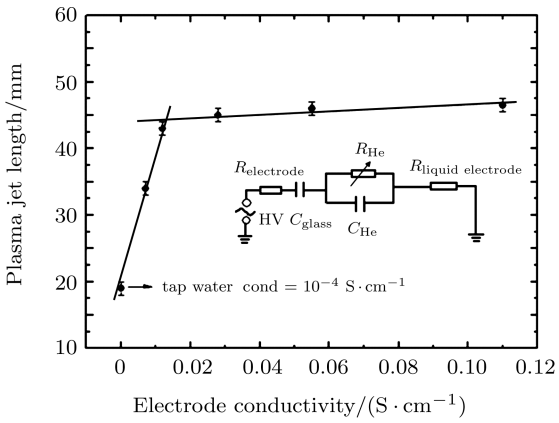


Fig.3. The influence of the liquid conductivity on the plume length for a He velocity of $3\,\mathrm{m\cdot s^{-1}}$ and a power of 10 W. The inset is the equivalent circuit of the discharge system.

when using tap water. As the conductivity decreases, the consumed power of the outer liquid electrode increases. Therefore, less power would be used for the plasma generation, and the plume length became shorter with the same input power. However, a nonlinear relationship between the plasma plume and the electrode conductivity was observed. Instead, there was a critical conductivity point ($0.014\,\mathrm{S\cdot cm^{-1}}$) above which the plume length changed little when the other conditions remained the same. The inset in the figure shows the equivalent circuit of the discharge system according to Ref.[22]. The phenomenon indicates that the influence of the power consumed by the liquid electrode ($R_{\rm liquid}$) on the plume length can be neglected when $R_{\rm liquid}$ is smaller than the critical point. Therefore, it is very necessary for the discharge system to use the highly conductive liquid as the electrode in the production process. As a result, the liquid temperature at the outer electrode will decrease and it will also reduce the operating cost effectively.

Figure 4 presents the effects of the power and the discharge volume (DV) on the plume length. From Fig.4(a), it can be seen that plume length becomes longer after the power value reaches a critical point (5 W), and a near-linear relationship is established between them. According to Brown diffusion theory,[23] we speculate that the plasma volume ionization in the device is far lower than the electron loss when the power is lower than the critical point (the minimum power to sustain plasma is 3 W). Therefore, no superfluous plasma is taken out by He gas. With increasing power, the discharge becomes stronger, and more electron avalanches can be generated in the He gas which is in favour of forming longer plume. Figure 4(b) shows the influence of the discharge volume (DV) on the plume length and the plume light emission intensity, and the DV is adjusted by the length of the outer liquid electrode. At the same input power, the power density would decrease with increasing DV, which will cause the decrease of plasma density in the quartz tube as well. Thus, the plume length becomes longer and its light emission intensity will be improved greatly when DV is decreased. It should be noted that there is a buffering scope (8–18 cm^3) of the discharge volume where the plume length is barely changed. Compared with the argon (Ar) gas used in another plasma system,[2] the He plasma plume needs lower discharge power and gas velocity for generating the same plume length. The reason for the easier plasma operation in He is the smaller electron–atom collision cross section, which allows of the existence of more fast electrons.

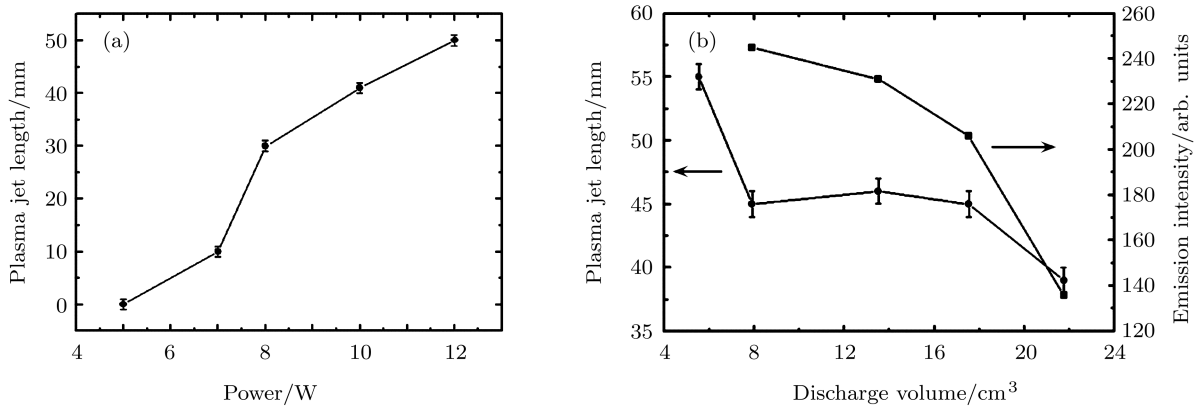


Fig.4. Effects of the power and discharge volume on the plume length with an outer electrode conductivity of $0.12\,\mathrm{S\cdot cm^{-1}}$: (a) with He velocity of $2\,\mathrm{m\cdot s^{-1}}$, (b) at a power of 10 W, with He velocity of $3\,\mathrm{m\cdot s^{-1}}$.

To identify various excited plasma species generated by the plume device, optical emission spectroscopy has been applied in a wide wavelength range of 190–850 nm. Figure 5 is a typical UV–visible emission spectrum of the atmospheric plasma plume (L = 5 cm) of O_2 and He. Although the spectrum is very rich in emission features, most of the atomic lines or molecular systems can be unambiguously identified by referring to Refs.[16, 20]. The emission spectrum is dominated by the presence of excited nitrogen (N_2: 337 and 357 nm; N_2^+: 309 and 470 nm) and helium species (3^1P–2^1S at 501 nm; 2^3P–3^3D at 587 nm; 2^1P–3^1D at 667 nm; 2^1P–3^1S at 706 and 728 nm).[21,24] In addition, highly reactive radicals such as hydroxyl (OH) at 309 nm, O_2^+ at 427 nm and atomic oxygen at 777 nm are also detected due to the opening to the ambient air and introducing O_2 in the He gas. The O_2^+ particle in He gas is probably formed by the electron-impact ionization ($e^- + O_2 \rightarrow 2e^- + O_2^+$) and Penning ionization (He (2^1S)+He(2^3S)+$O_2 \rightarrow$ He + O_2^++e^-).[25] The emission from the polar molecule of OH at 309 nm may result from the reaction of excited O with water vapour ($H_2O+O^* \rightarrow 2OH$) or from the electronic impact dissociation ($H_2O+e^{-1} \rightarrow H+OH+e^{-1}$).[20] The appearance of N_2 and H_2O molecules may indicate that the air in the discharge system was not removed entirely or air leak at some joints of the device occurred.

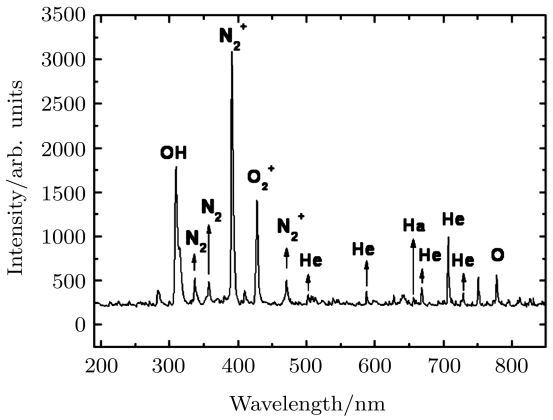


Fig.5. Emission spectrum of the cold plasma plume (L : 40 mm) about 10 mm downstream of the reactor outlet at a power of 15W with a He velocity of 0.7m $\cdot$ s^{-1} and an O_2 velocity of 1.5 m $\cdot$ s^{-1}.

Landfill leachate contains quantities of polluted organic compounds, ammonia and heavy metals and is identified as a potential source of ground and surface water contamination.[14] Today, landfill leachate is generally treated by the reverse osmosis technology used in developed countries. However, the reverse osmosis systems cannot function normally when the conductivity and COD of the leachate is very high (e.g., in China). Facing the worsening environmental conditions, therefore, it is very urgent and important to find an alternative technology to pretreat or degrade the leachate. Figure 6 reveals the effect of contact time of the plasmas downstream gas on the treatment of leachate solution. The landfill leachate has a green-dark colour. When it is in contact with the downstream O_2 gas for 45 minutes, the colour changes from green-dark to aqua. After 60 minutes, leachate solution turns nearly colourless and its unpleasant odour also disappears. After 120 minutes, the landfill leachate becomes transparent entirely. This phenomenon indicates that some dissolved materials and suspended solid particles in the solution are degraded by the activated O_2 particles.

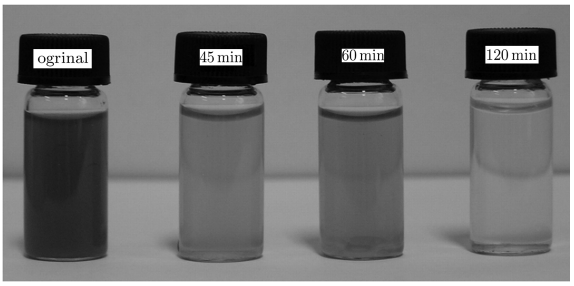


Fig.6. The effect of treating time on the leachate colour change for a power of 30 W with a He velocity of 0.7 m $\cdot$ s^{-1} and an O_2 velocity of 1.5 m $\cdot$ s^{-1}.

Table 1 shows the improvement of typical solution quality parameters when the leachate solution is treated by the activated O_2 gas for 60 minutes. Compared to the original solution, the conductivity, COD, BOD and SS in the treated solution are reduced by 52%, 57%, 76% and 92%, respectively. Thus, utilizing the downstream O_2 gas in the plasma plume is an effective approach to degrade the landfill leachate. The reduced quantities of substances in the leachate will create a friendly environment in decreasing pressure of the membrane in the reverse osmosis system and make the system work normally. The cost of pretreating leachate (per ton) for 60 minutes is about 10 dollars, therefore, the downstream gases generated in the surface modification can be used in the industry. It is very difficult to analyse the degradation kinetics occurring in the treatment process, because the

landfill leachate contains a variety of unknown components. According to Refs.[26–28], some radicals (e.g., OH, O_3) having strong oxidizing properties play the major roles in degrading the compounds in leachate, and oxidized the organic molecules to mineral species such as NH_4^+, NO_3^-, SO_4^{2-}, CO_2, and H_2O.

Table 1. The change of solution quality parameters after treating the landfill leachate with the downstream O_2 gas for 60 minutes. Applied power is 30 W, O_2 velocity is $1.5\,\mathrm{m\cdot s^{-1}}$ and He velocity is $0.7\,\mathrm{m\cdot s^{-1}}$.

	conductivity/(μS/cm)	COD/(mg/L)	BOD/(mg/L)	SS/(mg/L)
original	34600	15820	7100	1800
treating 60 minutes	16570	6880	1686	148
degrading ratio/%	52	57	76	92

4. Conclusion

In summary, we have developed a cold atmospheric-pressure plasma plume with high conductive liquid electrode, and its preliminary discharge characteristics are presented. The length of the plasma plume is longer than 5 cm by using He gas, and its gas temperature is not higher than 310 K when the applied power is lower than 15 W. From the characteristics of the cold plasma plume, it is expected that the cold plasma plume device is applicable to delicate objects, vulnerable biological materials, and human skins. The downstream O_2 gas in the plasma plume can generate strongly oxidative particles, which can degrade the leachate solution effectively. The properties of the treated leachate ensure the reverse osmosis system to work normally. Therefore, using the activated O_2 generated by the plasma plume may be an effective approach to pretreat the landfill leachate.

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