Research Progress in Application of Low Temperature Plasma Technology for Wastewater Treatment

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Abstract. As a new advanced oxidation technology, low temperature plasma integrates strong oxidizing particles, ultraviolet light decomposition, wet oxidation and other technologies. Compared with other technologies, it has the advantages of no selectivity, no secondary pollution, and mild reaction conditions. At present, low temperature plasma technology has made some achievements, but there are some limitations in the actual scale water treatment application. The mechanism of low temperature plasma oxidation needs to be further studied. The reaction and active factors produced by low temperature plasma in the process of water treatment are very complicated, and there is no uniform conclusion on the reaction mechanism. The stability of plasma discharge depends not only on the parameters of power supply equipment and solution, but also on the design of reactor. How to design a reasonable, efficient and mass transfer reactor by combining various influencing factors is also the future research direction. The combination of low temperature plasma water treatment technology with various advanced oxidation technologies should be strengthened.

1. Introduction

Low temperature plasma water treatment technology means that a large number of active components (such as ·OH, O3, H2O2) are generated by discharge in the gas phase or gas-liquid mixed phase, accompanied by a variety of physical and chemical effects (such as ultraviolet irradiation, high-energy electrons, shock wave). These active components cause organic molecules in water to excite, ionize, or break chemical bond, thereby achieving degradation. As a new advanced oxidation technology, low temperature plasma integrates strong oxidizing particles, ultraviolet light decomposition, wet oxidation and other technologies. Compared with other technologies, it has the advantages of no selectivity, no secondary pollution, and mild reaction conditions. In recent years, some progress has been made in the treatment of dye wastewater, pesticide wastewater and pharmaceutical wastewater by low temperature plasma technology.

2. Water treatment mechanism

High-energy electrons generated during plasma discharge collide with water inelastically, resulting in a series of intricate processes such as excitation, dissociation and ionization. A large number of active materials such as active radicals and strong oxidizing molecules are produced. The most important of these are ·OH [1]. Its oxidation-reduction potential is second only to fluorine. It can destroy the C-C bond of organic matter and form the C-OH bond during the reaction with organic matter, so that the structure of organic matter is destroyed. Due to continuous recombination and redissociation of short-lived free radicals, a large number of stable and strongly oxidizing active molecules, such as O3 and...
H$_2$O$_2$, are formed during low temperature plasma discharge. All of them can directly react with organic matter, or interact with other molecules to form ·OH, and indirectly participate in the removal of organic matter. In addition, the irradiation of ultraviolet light can excite molecules of organic substances and induce the molecular bonds to break to form corresponding ions or radicals[2].

3. Influencing factors

The effect of low temperature plasma on wastewater treatment not only depends on discharge mode and reactor structure, but also depends on different process parameters. Common process parameters include discharge voltage, discharge gas, initial concentration of solution, pH value and other factors. Therefore, it is of great significance for the application of low temperature plasma technology to understand the influence of these process parameters on water treatment and optimize these parameters.

3.1 Voltage value

Different voltage value have a great influence on the plasma production and components. Only when applied voltage exceeds critical voltage, plasma can be released. Theoretically speaking, in the process of treating organic matter, the higher voltage applied between electrodes, the more plasma will be released, thus releasing more strong oxidizing substances such as ·OH, H$_2$O$_2$ and O$_3$. Meanwhile, ultraviolet radiation and other effects will be more obvious and degradation efficiency of organic matter will be higher[3]. Wang, T.[4] used plasma to treat humic acid wastewater. When peak electric pressure was 12kV, 16kV, 19.6kV and 23kV, removal rate of humic acid increased from 62.3% to 74.3%, 84.6% and 89.1% within 30 min. However, the higher voltage, the higher the demand for electrode. It is likely to cause electrode corrosion.

3.2 Discharge gas

In the process of plasma degradation of organics, in addition to physical and chemical effects such as electron bombardment, instantaneous high temperature and pressure, and ultraviolet radiation, the main degradation role is strong oxidizing active particles generated during plasma process. Gas-liquid two-phase plasma technology produces a variety of active particles at the gas or gas-liquid interface, which react with organic pollutants to degrade organic matter. Discharge gases such as air, oxygen, argon, nitrogen or two or more mixture gases are commonly used. Due to the different properties of these working gases, active particles generated by discharge are different[5].

When oxygen is used as working gas, it can not only be stimulated to produce more O$_3$[6], but also can generate a large number of active oxygen-containing free radicals, and cooperate with ·OH to accelerate the degradation of organic matter. As a strong oxidizer, the degradation of pollutants by ozone can be divided into direct oxidation and indirect oxidation. Direct oxidation means that ozone molecules directly react with organic substances. Indirect oxidation refers to the decomposition of ozone molecules and the generation of other active substances to achieve the degradation of organic compounds, as shown in formula (1) - (3)[7].

$$O_3 + M(\text{Organic matter}) \rightarrow M + O_3 \quad (1)$$

$$\text{OH}^- + O_3 \rightarrow \text{O}_2 + \text{HO}_2 \quad (2)$$

$$O_3 + 3\text{HO}_2 \rightarrow 3\cdot\text{OH} + 3\text{O}_2 \quad (3)$$

When nitrogen is used as a working gas, nitrogen molecules are excited to produce large amounts of reactive nitrogen (RNS). In particular, in the presence of oxygen molecules, reactive groups such as N$\cdot$, H$\cdot$, O$\cdot$, and ·OH are produced in the two gas atmosphere or react with original materials (N$_2$, O$_2$, H$_2$O, etc.) to produce substances such as NO$_2$, HNO$_2$, and HNO$_3$, thus bringing about changes in conductivity and pH in the system[8].

When Ar is used as working gas, argon atoms and metastable particles generated in the gas phase are dissolved in water. This produces a higher density of ·OH, ·O, and ·H than O$_3$ discharge without generation of ozone and oxygen atoms. When Takemura et al.[9] used gas-phase discharge plasma technology to treat methylene blue wastewater, they found that when Ar, N$_2$ and O$_2$ were used as
working gas, degradation efficiency of methylene blue was basically the same, but higher than that of air as working gas. Zhao, Y. et al. [10] used DBD low temperature plasma to degrade oxadiazon industrial wastewater, using a mixed gas of Ar and O₂ gas and using top-inlet discharge after 10h (discharge power 72W). The COD degradation rate in wastewater can reach 89.97%.

3.3 Initial concentration of solution
Initial concentration has an important effect on decolorization rate and mineralization rate of organic wastewater treated by low temperature plasma. In a specific plasma discharge device, under the same experimental conditions, the amount of plasma generated and the intensity of physical action are basically constant. When the concentration of the target pollutant is lower than a certain value, the number of pollutant molecules per unit volume is relatively small, which results in a relatively small chance of collision with the active particles, causing a certain waste of relatively sufficient active particles and reducing the energy utilization efficiency. When the concentration of target pollution increases gradually, the number of pollutant molecules per unit solution volume will increase, and the probability of collision with active particles such as hydroxyl radical will increase with the increase of solution conductivity, thus improving utilization efficiency of active particles. However, when the concentration reaches a certain value, the oxidation load of active particles tends to saturation. The intermediates generated in the degradation process also compete with the target pollutant, resulting in the phenomenon that the removal rate decreases gradually but the absolute removal amount increases with the increase of pollutant concentration. Magureanu et al. [11] proved this by experiment.

3.4 PH value of solution
On the one hand, pH value affects the existence state of organic matter, and different existence states show different reaction constants with the hydroxyl radical reaction. On the other hand, a large amount of ozone will be generated during plasma discharge process, and pH value is the key factor affecting ozone oxidation efficiency. Furthermore, there is an acid-base balance between different active particles, and the oxidation capacity of ·OH under acidic conditions is stronger than that under alkaline conditions [12]. Sun, G.Y. et al. [13] used a self-made line barrel-type dielectric barrier discharge plasma device to degrade methyl orange. It was found that under strong and weak acid conditions, decolorization efficiency of methyl orange was better than alkaline and neutral conditions. The experimental results are shown in Figure 1 and Figure 2. Wu, H.X. et al. [14] also obtained similar result.

3.5 Electrical conductivity
Industrial wastewater, especially dye wastewater, not only contains a wide variety of organic matter, but also a variety of inorganic ions, such as HCO₃⁻, CO₃²⁻, Cl⁻, PO₄³⁻, SO₄²⁻ and other metal ions, so that solutions present different conductivity. When the conductivity of the solution is too high, the concentration of ions in the solution is too high. The high-energy electrons generated by plasma are difficult to enter the aqueous solution and affect the degradation of organic matter in water. Jin, X.L. et al. [15] used Na₂SO₄ and NaCl to regulate different conductivity solutions to explore the relationship
between conductivity, discharge intermediate potential and hydrogen peroxide yield in contact glow discharge. It was concluded that intermediate potential of discharge decreased gradually with the increase of conductivity, and electrolyte decreased in different ranges. The concentration of hydrogen peroxide increased linearly with the increase of conductivity and remained stable. Moreover, many inorganic salt ionization ratios, such as HCO$_3^-$, CO$_3^{2-}$, Cl$, have quenching effect on ꞏOH and affect the degradation of organic compounds, and reaction process is shown in formula (4) - (9).

\[
\cdot\text{OH} + \text{Cl}^- \rightarrow \cdot\text{Cl} + \text{OH}^- \quad (4)
\]

\[
\text{Cl}^- + \cdot\text{Cl} \rightarrow \text{Cl}_2 \quad (5)
\]

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO} \quad (6)
\]

\[
2\text{HClO} + \text{H}_2\text{O}_2 \rightarrow 2\text{Cl}^- + \text{O}_2 + 2\text{H}^+ \quad (7)
\]

\[
\text{HCO}_3^- + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \cdot\text{CO}_3^{2-} \quad (8)
\]

\[
\text{CO}_3^{2-} + \cdot\text{OH} \rightarrow \text{OH}^- + \text{HCO}_3^- \quad (9)
\]

### 3.6 Treatment time
In the process of plasma treating organic wastewater, the length of treatment time often determines the amount of energy consumption. Wang, H.T. et al. [16] used dielectric barrier discharge plasma / micro-aeration to treat phenol wastewater. With the extension of discharge time, the removal rate of phenol gradually increased, but the degradation growth rate began to decrease after 25 minutes, and at the same time there was a pungent odor production.

### 3.7 Plasma catalysis technology
Plasma water treatment technology has disadvantages such as long treatment time, low utilization efficiency of active components and ultraviolet radiation, and low energy utilization efficiency in practical applications. In view of these limiting factors, the combination of catalytic oxidation and plasma technology has become future development trend. At present, more researches have been made on the addition of particles such as Mn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, TiO$_2$.

The addition of iron ions can cause Fenton or Fenton-like reactions in the system. In the presence of ultraviolet radiation, ferric ions can react with hydrogen peroxide to produce ferric ions and hydroxyl radicals, which can effectively alleviate the accumulation of ferric ions or iron mud in the traditional Fenton reaction. Gao, J. et al. [17] investigated the effects of different metal ions such as Mn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$ on the decolorization rate of dyes in their studies on the treatment of weakly sour red B and weakly acid bright yellow G by glow discharge technology. The results showed that ferric ions showed the best catalytic activity, and weak acid bright red B and weak acid bright yellow G were almost completely decomposed. The study showed that ferric ion had the best catalytic activity, and weakly sour red B and weakly acid bright yellow G were almost completely decomposed.

The addition of photocatalytic material TiO$_2$ further utilizes ultraviolet radiation released during discharge process. Excited by ultraviolet light, TiO$_2$ generates strong redox ability holes (h$^+$) -electron (e$^-$) pairs on its surface, thus generating ·OH to achieve pollution degradation [18]. Li, S. et al. [19] studied the degradation of 2,4-dichlorophenol by dielectric barrier discharge. Compared with blank group, degradation rate of 2,4-dichlorophenol was increased by 13.43% and 7.5%. Sun, Y. et al. [20] used TiO$_2$ and Fe-TiO$_2$ as catalysts in the degradation of active brilliant blue by dielectric barrier discharge. The addition of the catalyst not only improved removal rate of active brilliant blue, but also significantly improved mineralization rate.

### 4. Conclusion
At present, low temperature plasma technology has made some achievements, but there are some limitations in the actual scale water treatment application. In view of the shortcomings of this technology, the following aspects of research should be strengthened.

- The mechanism of low temperature plasma oxidation needs to be further studied. The reaction and active factors produced by low temperature plasma in the process of water treatment are very
complicated, and there is no uniform conclusion on the reaction mechanism. Only by clarifying its reaction mechanism can it help the promotion of this emerging technology.

- The stability of low temperature plasma during oxidation is poor. The stability of plasma discharge depends not only on the parameters of power supply equipment and solution, but also on the design of reactor. How to design a reasonable, efficient and mass transfer reactor by combining various influencing factors is also the future research direction.
- The combination of low temperature plasma water treatment technology with various advanced oxidation technologies should be strengthened. We should make full use of the advantages of various advanced oxidation technologies and optimize the operation conditions of the combined process to obtain the best combined process.

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References
[1] Yang, Y, Kim, K.H. (2017) Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants. Science of the Total Environment, 596:303-320.
[2] Kim, S.D., Cho, J. (2007) Occurrence and removal of pharmaceuticals and endocrine disruptors in South Koreans surface drinking water. High Water Research, 41:1013-1021.
[3] Tang, S., Lu, N., Li, J. (2012) Design and application of an up-scaled dielectric barrier discharge plasma reactor for re-generation of phenol-saturated granular activated carbon. Separation & Purification Technology, 95:73-79.
[4] Wang, T., Qu, G., Ren, J. (2016) Evaluation of the potentials of humic acid removal in water by gas phase surface discharge plasma. Water Research, 89:28-38.
[5] Rosario, L.M.D., Lee, H.V. (2017) Characterization of a microwave-induced atmospheric pressure Ar-N2 plasma pencil. IEEE Transactions on Plasma Science, 99:1-9.
[6] Lukes, P. (2005) Generation of ozone by pulsed corona discharge over water surface in hybrid gas-liquid electrical discharge reactor. Journal of Physics D Applied Physics, 38:409-416.
[7] Wu, J., Ma, L., Chen, Y. (2016) Catalytic ozonation of organocipollutants from bio-treated dyeing and finishing wastewater using recycled waste iron shavings as a catalyst: Removal and pathways. Water Research, 92:140-148.
[8] Chen, G.L., Zhou, M.Y., Chen, S.H. (2009) The different effects of oxygen and air DBD plasma byproduct on the degradation of methyl violet 5BN. Journal of Hazardous Materials, 172:786-792.
[9] Takemura, Y., Yamaguchi, N., Hara, T. (2013) Decomposition of methylene blue by using an atmospheric plasma jet with Ar, N2, O2, or air. Japanese Journal of Applied Physics, 52:492-494.
[10] Zhao, Y., Chen, L.W., Yao, R.S. (2015) Research on the degradation of industrial wastewater containing oxadiazon by DBD cryogenic plasma technique. Industrial Water Treatment, 35:60-64.
[11] Magureanu, M., Piroi, D., Mandache, N.B. (2010) Degradation of pharmaceutical compound pentoxifylline in water by non-thermal plasma treatment. Water Research, 44:3445-3453.
[12] Cheng, H., Ye, Q.Z. (2007) Influential factors on degradation rate of organic contamination in water treatment by discharge plasma. High Voltage Engineering, 33:150-153.
[13] Sun, G.Y., Song, M. (2016) Degradation of methyl orange dye wastewater by non-thermal plasma technology. China Water & Wasterwater, 21:96-99.
[14] Wu, H.X., Xu, Y.H. (2012) Treatment of azo dye wastewater by high-voltage arc discharge nonthermal plasma. Chinese Journal of Environmental Engineering, 6:4327-4288.
[15] Jin, X.L., Wang, X.Y., Zhang, H.M. (2010) Influence of solution conductivity on contact glow discharge electrolysis. Plasma Chemistry & Plasma Processing, 30:429-436.

[16] Wang, H.T., Lv, Y.K. (2015) Treatment of phenol-bearing wastewater by the combination of dielectric barrier discharge plasma/micro-aeration process. Industrial Water Treatment, 35:67-70.

[17] Gao, J., Wang, X., Hu, Z. (2003) Plasma degradation of dyes in water with contact glow discharge electrolysis. Water Research, 37:267-272.

[18] Ghodbane, H., Hamdaoui, O., Vandamme, J. (2014) Degradation of AB25 dye in liquid medium by atmospheric pressure non-thermal plasma and plasma combination with photocatalyst TiO$_2$. Open Chemistry, 13:325-331.

[19] Li, S., Ma, X., Liu, L. (2014) Degradation of 2,4-dichlorophenol in wastewater by low temperature plasma coupled with TiO$_2$ photocatalysis. Rsc Advances, 5:1902-1909.

[20] Sun, Y., Liu, Y., Li, R. (2015) Reactive blue degradation in aqueous medium by Fe-doping TiO$_2$ catalytic nonthermalplasma. IEEE Transactions on Plasma Science, 43:3234-3241.