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Design and Research of Low Temperature Plasma Soil Remediation System

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Abstract: The most basic resource on earth island, and soil accounts for about 29% of the earth's area. With the advancement of modern technology, the damage to soil is becoming more and more serious. Therefore, the protection of soil environment and the restoration of soil quality are not only a national policy of the country, but also a mission that everyone should keep in mind. In this paper, the contaminated soil is remediated based on low-temperature plasma technology. Following the concept of environmental protection and energy saving, dielectric barrier discharge is used as the remediation technology. The purpose of soil remediation is achieved by degrading the content of polycyclic aromatic hydrocarbons in the soil. The experimental results verify the feasibility of barrier discharge in soil remediation systems, and thus promote the application of low-temperature plasma technology in the field of soil remediation.

1. Preface

In recent years, the soil quality and nutrients in Northeast China have declined, causing serious soil erosion. The deterioration of soil mainly includes salinization, chemical pesticide pollution, oil and coal pollution, etc. The most harmful among them is oil pollution. The oil contains a large amount of polycyclic aromatic hydrocarbons, once the crops enter the human body, it will cause serious failure of the body. Soil pollution indirectly affects the yield of crops and causes the country to suffer huge economic losses. Therefore, soil remediation is an important policy [1-3]. The content of this design is based on the theory of low temperature plasma, and the dielectric barrier discharge technology is applied to the soil remediation of pyrene pollutants.

2. Basic Theory

2.1. Overview of Plasma

Plasma is a new condensed state of matter, followed by solids, liquids and gases in order, so it can also be called the fourth state of matter. Ions conduct electricity well and react with most substances because they are highly susceptible to magnetic fields.[4] Plasma can be obtained by artificial means. In the experiment, the plasma is generally obtained by gas discharge. Gas discharge is a convenient and safe method. By applying voltage to the discharge area, when the temperature is increased to the ignition point of the gas, the gas is ionized. Electrons and free radicals collide with each other and combine to generate plasma. The discharge forms include: corona discharge, spark discharge, glow discharge and dielectric barrier discharge [5].

2.2. Dielectric Barrier Discharge

Dielectric barrier discharge is a discharge form suitable for plasma reaction. Electrodes are placed at the upper and lower ends of the reactor to release a tiny current. When the generated plasma consists of multiple channels to form a discharge area, the discharge phenomenon is stable, and the current filaments are evenly distributed in the discharge area. In the region, the standard atmospheric pressure was used in the whole experiment, so the dielectric barrier discharge was also regarded as a form of non-equilibrium gas discharge. In addition, inserting an insulating medium in the discharge area prevents the generation of local sparks, which is more conducive to the reaction. [6,7] Dielectric barrier discharge has a good effect on the ability to generate plasma in various environmental governance fields.

2.3. Plasma Soil Remediation

Since the advent of plasma technology, it has been mostly used in the field of repair. For example, in air pollution, the United States, Germany and other developed countries use plasma technology to treat sulfur and nitrogen oxidation waste gas, and the air pollution after purification is significantly reduced. Plasma technology also has certain advantages in the treatment of water pollution. At this stage, the rapid increase of domestic wastewater and industrial wastewater has seriously endangered the drinking water resources used by people. The first time to use plasma technology to treat polluted water was published by Clements in 1987. He studied the phenomenon of electrode discharge breakdown in aqueous solution, and proved that there is ultraviolet light in the discharge system, and $Fe^{+}$was used to improve the degradation rate of sewage.[8] Due to the superiority of plasma technology, it is now widely used in the field of soil remediation.

3. Technical Route and System Construction

3.1. Technical Route

The technical route of this paper is shown in Figure 1. First, consult books and literature to find out the adverse effects caused by soil pollution in recent years, and understand the technical essentials and precautions of plasma technology. Secondly, investigate the records of farmland pollution in my country, collect information on the sources of pollutants, and economic losses caused by soil pollution. Establish an experimental plan again, conduct a large number of experiments, observe experimental phenomena, and collect experimental data, debug and organize. Finally, the data is summarized and analyzed.

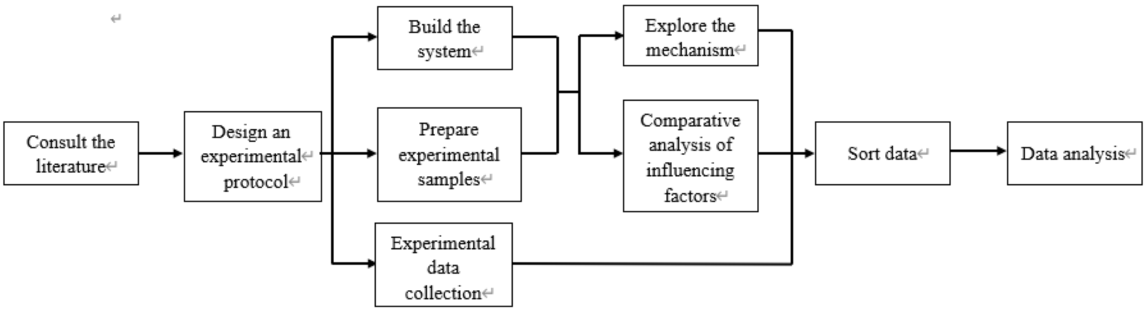

Figure 1: Technical route

3.2. System Construction

In order to meet the soil remediation environment, a DBD plasma reaction system was built. It is composed of power supply device-electrical control device-DBD plasma reactor. Among them, the high-voltage power supply system is composed of a high-voltage power supply and a voltage regulator, and the components of the electrical control system include: an oscilloscope, a current probe, and a high-voltage probe.[9] As an important part of this experiment, the DBD reactor not only provided the carrier gas required for the experiment, but also the reaction place of the experiment. The instrument materials used in the experiment include barrier medium, electrode, flow meter, and air pump.

3.3. DBD Plasma Reactor

The actual DBD plasma reactor is shown in Figure 2, and the experiment uses a flat-plate plasma reactor. Two metal steel plates are selected as electrodes, and there is a hollow glass tube on the top side of the electrode, which serves as the air inlet and the circular air outlet. The meter measures the volume of gas. A closed gas bottle is used to collect the product at the gas outlet. After the reaction is collected, a certain amount of product is collected, and its components are measured. The upper end of the high-voltage electrode is connected to the high-voltage power supply, and the low-voltage electrode is grounded to improve safety. In the experiment, the target pollutant soil was placed on the low-voltage electrode, and the ceramic medium was attached to the high-voltage electrode. The process of degrading polycyclic aromatic hydrocarbons in polluted soil is carried out by the plasma generated by gas discharge. The discharge time lasted for one hour, and after the experiment, the amount of polycyclic aromatic hydrocarbons in the soil was measured.

Figure 2: DBD plasma reactor

4. Experiment and Result Analysis

4.1. Experimental Subjects

As the most common pollution species, PAHs are also relatively harmful to soil. Therefore, pyrene (molecular formula:C_6H_{10}), the most typical representative of polycyclic aromatic hydrocarbons, was used in this experiment as the experimental object. Pyrene is stable in structure, insoluble in water and difficult to separate in crystalline form, but it is close to electricity, has excellent reaction and good effect, and is suitable for this experiment. Therefore, a plasma remediation system experiment with pyrene as the pollutant object was established in the experiment, and the degree of soil remediation was observed by degrading pyrene, so as to verify the feasibility of low-temperature plasma technology in the field of soil remediation and further verify the effectiveness of the experiment.

4.2. Selection and Preparation of Experimental Soil

This experiment uses soil from farmland in Northeast China, which should be taken from the soil about 10cm below the surface. The soil brought back must be air-dried in a cool place. The air-drying process is carried out in a fume hood. The air-dried soil is ground and sieved before it can be recovered. Save for backup. An appropriate amount of air-dried soil was weighed into a beaker, and a pyrene-dichloromethane solution was used as the raw material for pollutants. Pour in an appropriate volume and mix with air-dried soil. When the soil is thick paste, put it into a constant temperature oscillator and shake for 4 hours. When the time is up, put it in a ventilated place. After the ventilation is completed, remove the large soil particles and sieve them. Grind and store the sieved soil particles in a brown glass jar, sealed and kept out of the sun.

4.3. Extraction Method of Pyrene in Soil

The extraction of pyrene in the soil uses methanol as the extractant, and the pyrene-contaminated soil prepared is used for the extraction of pyrene. Part of the pyrene-contaminated soil is poured into a beaker, and an appropriate volume of methanol liquid is dropped into the beaker, and it is allowed to stand for fusion. After a period of time, put the experimental soil into the constant temperature oscillator, and take it out after shaking for 30 minutes. It was filtered into a liquid with a filter membrane, and the pyrene content of the filtrate was measured by high performance liquid chromatography. The recorded experimental data is shown in Table 1, and the analysis shows that the method can extract pyrene pollution to the greatest extent, and the practical effect is good.

Table 1: The change of the shaking time and the extraction rate of pyrene.

Oscillation time (min)	Pyrene content (mg/L)	Extraction rate (%)
10	17.53	92.7
15	18.59	93.3
25	18.86	93.8

4.4. Experimental Method of Low Temperature Plasma Soil Remediation

The input voltage peak of the supply voltage is 10-20kV and the output rate is 5.2kHz. The plasma used in the experiment was divided into gradients. Each group of experiments used 5g of sample soil, spread it on the metal plate used for the experiment, adjusted the distance of the high-voltage electrode to 2cm, and started the dielectric barrier discharge experiment. The discharge time was After 60 minutes, the soil was filtered after discharge, and the residual amount of pyrene was determined by phase analysis.

The formula for calculating the pyrene concentration is:

$$Ln\left(\frac{C_0}{C_1}\right) = kt \qquad (1)$$

Among them, C_0 is the initial concentration of pyrene, and C_1 is the concentration of pyrene at time t.

4.5. The effect of Soil Particle Size

The size of soil particles is a part of soil properties, and the particle size is related to soil permeability.[10] In this barrier discharge plasma soil remediation, the size of soil particles will affect the flow of active particles generated during the discharge process. In the experiment, we selected soils with different particle sizes for testing. It can be seen from Figure 3 that 1mm particles The degradation rate of pyrene in polluted soil with a diameter of 2 mm is higher than that of pyrene with a particle size of 2 mm. Smaller soil particle size can promote the combination of active substances and organic chemicals in soil, thereby increasing the degradation rate of pyrene in soil. Soil with particle size can reduce the contact time between active particles and pyrene pollutants, and achieve higher degradation efficiency.

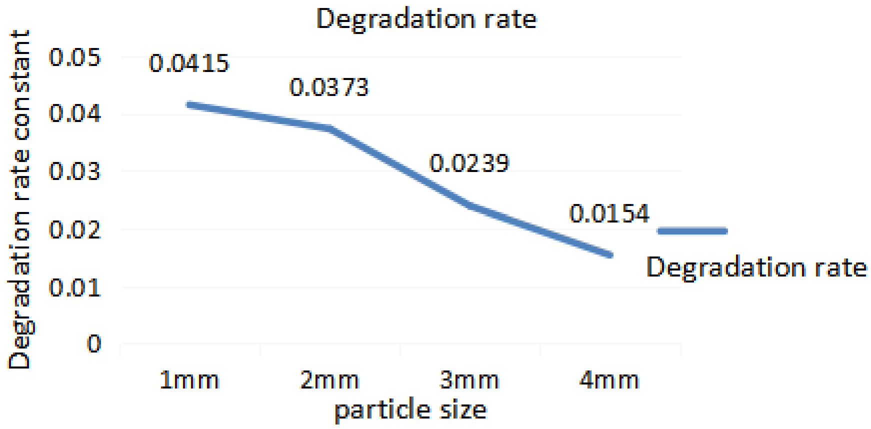

Figure 3: Degradation rate of contaminated soil by soil particle size.

4.6. Influence of Soil Initial Ph Value

In the study of plasma treatment for sewage remediation, it is shown that the PH of the solution is a factor affecting the remediation effect. In the study of plasma soil remediation, when the organic matter is in an alkaline environment, the removal rate of pollutants is higher. The remediation effect of soil with high PH is better than that of neutral soil under the same conditions, while the degradation efficiency of pyrene in polluted soil in acidic environment is poor. In this experiment, when the PH are 4 (acidic), 6 (neutral), and 9 (acidic), the results of the degradation rate of pyrene pollution are shown in Figure 4. When the discharge time is ten minutes, the degradation rate of the three environments The rate of degradation is 30%-40%, the discharge time continues to increase, the degradation rate of the acidic environment does not change much, and the degradation rate of the alkaline environment increases greatly. The main reason is that when the soil is alkaline and acidic, the environment is conducive to the formation of oxidative substances such as $\cdot H$,$\cdot OH$, O_3.These oxidizing substances can effectively degrade pyrene pollution in the soil, while in the acidic environment with low PH, reducing substances will be produced. And these reducing substances reduce the rate of pyrene degradation.

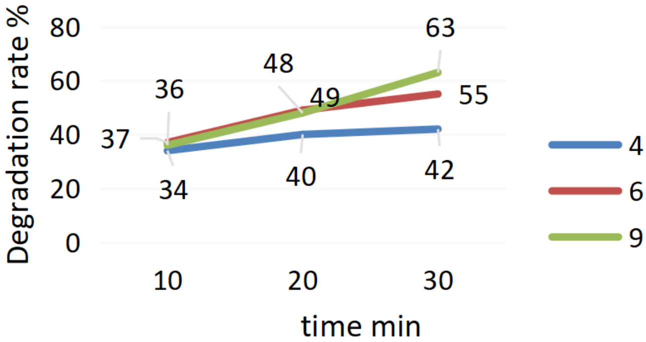

Figure 4: Effect of soil initial pH value on degradation rate.

4.7. Effect of Initial Soil Moisture Content

Moisture content is one of the important factors affecting soil remediation.[11] When the moisture content is too high, soil pollutants are easily lost. Therefore, in the design experiment, the initial moisture content of the soil we selected should be controlled below 15%. As shown in Figure 5, when the water content is 5%, the reduction rate coefficient is 0.037, when the water content is 10%, the coefficient is 0.023, and when the water content is 15%, the coefficient is 0.015. And this ratio will increase proportionally with the increase of discharge time. The lower the water content, the higher the degradation rate of pyrene pollutants, and the best soil remediation effect. The lower the water content, the stronger the soil permeability, the air flow can fully flow through the soil layer, and the active particles generated by the barrier discharge are fully in contact with the soil, so that the removal efficiency of pyrene is the highest.

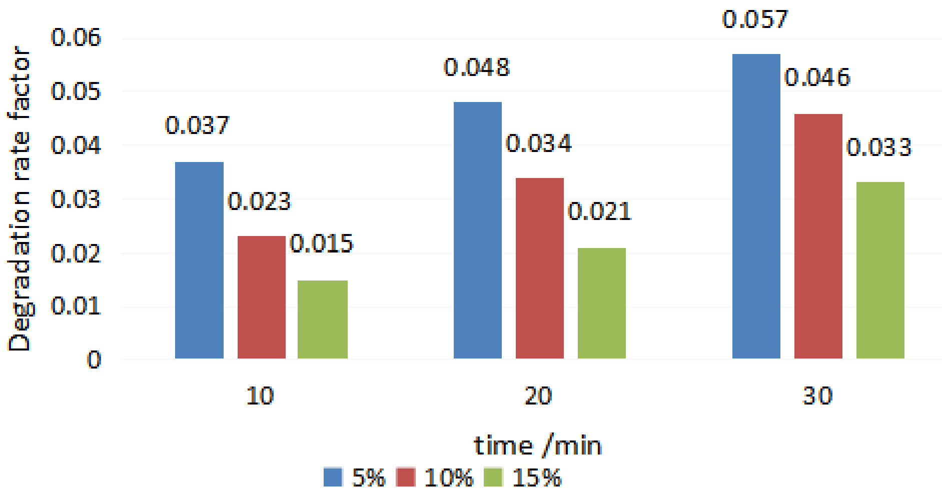

Figure 5: Effect of initial soil moisture content on rate.

5. Discharge Parameter Test and Analysis

5.1. Variation of Discharge Current with Different Applied Voltages

The plasma system built in this experiment is based on the dielectric barrier discharge reactor as the main plate, and the commonly used technical means is dielectric barrier discharge. The energy to maintain the entire plasma system is the applied voltage. The content of this section is the change of the applied voltage and the effect of the plasma system on the remediation of pyrene-contaminated soil. The applied voltage is an important parameter that affects the dielectric barrier discharge process. During the discharge process, the effect of the dielectric barrier discharge phenomenon will be different due to the applied voltage. Therefore, before the experiment, the initial applied voltage variation range is 10-20kV. The experiment uses a voltage regulator to make the initial applied voltage 12kV, 15kV, 18kV, and 20kV, respectively. The discharge time continues to increase, and the output discharge current changes in amplitude from the density of the current filaments observed in the oscilloscope is shown in Figure 6, and these data are used to discuss and study the impact. The other operating conditions of the experiment were set as follows: frequency 50 Hz, electrode spacing 15 mm, and carrier gas flow rate 1 L/min.

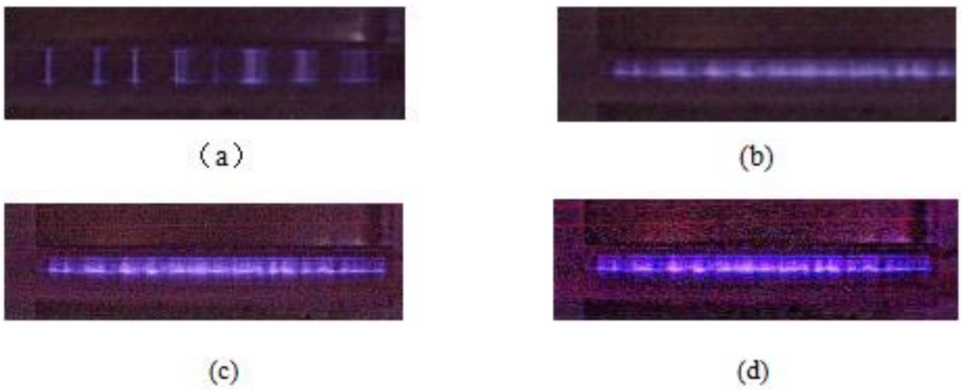

Figure 6: The density of current filaments under different applied voltages.

Among them, figure (a) is the initial applied voltage of 12kV, figure (b) is the initial applied voltage of 15kV, figure (c) is the initial applied voltage of 18kV, and (d) is the initial applied voltage of 20kV. Record in Table 2 the amplitude of output discharge current change under these four initial applied voltages.

Table 2: Discharge current and current filament density at different voltages.

Applied voltage amplitude (kV)	Discharge current amplitude (mA)	Current filament density
12	1.3	very sparse
15	1.6	gradually dense
18	27.6	denser
20	35.3	very dense

It can be seen from the experimental data that when the applied voltage gradually increases, the amplitude of the discharge current also increases gradually, and the current filaments gradually become denser. It can be seen that the applied voltage is one of the important parameters affecting the dielectric barrier discharge. The key point is that when the applied voltage is less than or equal to

15kV, the amplitude of the discharge current increases slightly, and when the applied voltage is greater than or equal to 15kV, the amplitude of the discharge current changes greatly.

5.2. Changes in the Degree of Pyrene Degradation with Different Applied Voltages

With the increase of the applied voltage, the degradation rate of pyrene also increases, and the change of the applied voltage on the degradation rate of pyrene is shown in Figure 7. It can be seen from the figure that the discharge voltage and the degradation rate of pyrene increase proportionally, but the degradation effect is completely different. The discharge time of the experiment was set at 10-60 minutes, and when the voltage was below 15kV, the rate of pyrene degradation increased slowly. When the applied voltage is above 15kV and the discharge time is in the first 30 minutes, the rate increases proportionally, and the growth rate is the fastest. Finally, with the passage of time, the final degradation rate is between 60% and 70%. This experimental result shows that the increase of the applied voltage is helpful for the degradation of pyrene in the reaction, and it also shows that the applied voltage has a promoting effect on the soil remediation system. This is because the increase of the applied voltage provides more energy to the system and produces There are more highly active particles that can promote specific degradation, so that pollutant molecules can be effectively removed. At the same time, in the process of pyrene decomposition, the generated oxygen can also inhibit the diffusion of pollutant molecules into the deep soil.

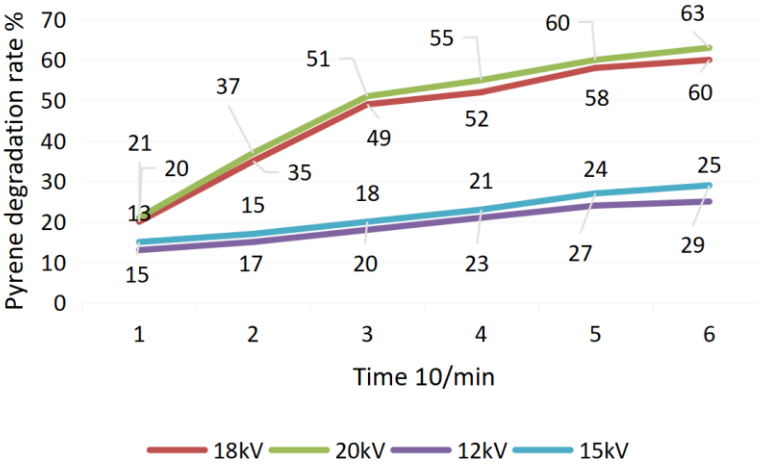

Figure 7: Changes of pyrene degradation by applied voltage.

5.3. Effects of Different Power Frequencies on the Degradation of Pyrene

The power frequency is one of the factors affecting the electric field energy in the dielectric barrier discharge plasma system. Under the condition of the same applied voltage, the power frequency output is 25Hz, 50Hz, 75Hz, respectively, the degree of pyrene degradation rate changes. Other experimental conditions were set as follows: the applied voltage was 20kV, the electrode spacing was 15mm, and the carrier gas flow was 1L/min. The density of the current filaments observed from the oscilloscope is shown in Figure 8.

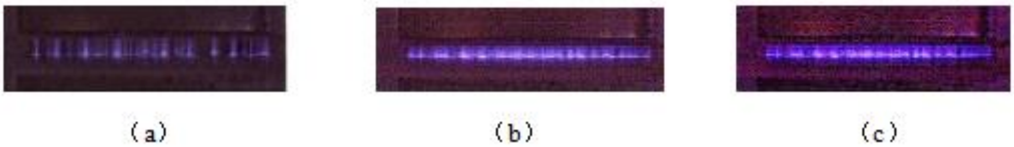

Figure 8: Current filament density at different power frequencies.

Where (a) is the power frequency of 25Hz, (b) is the power frequency of 50Hz, and (c) is the power frequency of 75Hz. Under these three power frequencies, the output discharge current changes as shown in Table 3:

Table 3: Discharge current and current filament density at different power frequencies.

Power frequency (Hz)	Discharge current amplitude (mA)	Current filament density
20	14.8	very sparse
50	26.1	denser
75	56.3	very dense

With the increase of discharge time, the effect of pyrene degradation rate is shown in Fig. 9.

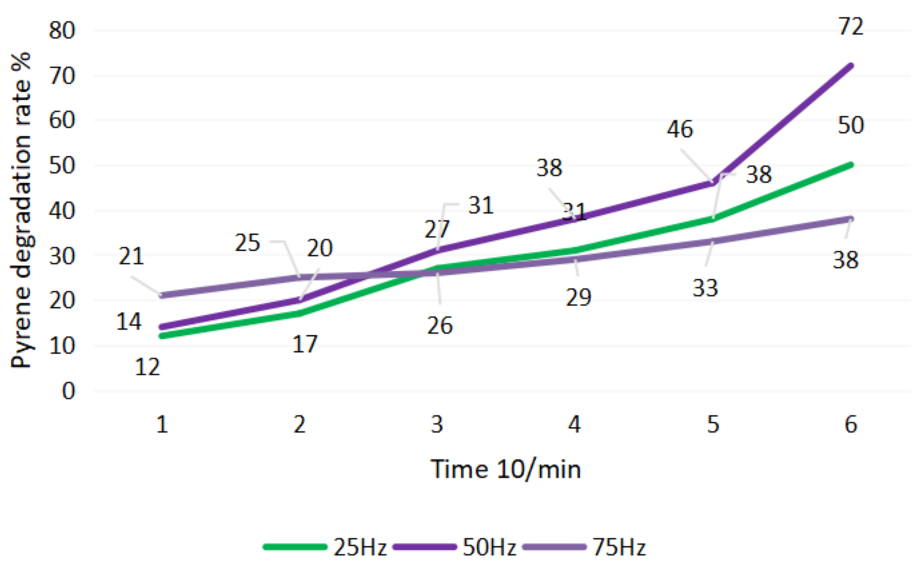

Figure 9: Variation of power frequency on pyrene degradation.

Within the same discharge time of 10-60 minutes, the initial degradation rate of the 75Hz power frequency is the highest, but as the discharge time increases, the degradation rate of the high power frequency increases slowly, while the degradation rate of the low and medium power frequencies increases high. This is because the increase of frequency provides more energy for the whole repair system, which is more conducive to the generation of active substances for pyrene degradation, but the higher the energy, the more energy is lost, which is not conducive to the degradation of pyrene. From the perspective of energy saving and environmental protection, a moderate power frequency can provide the electric field energy to maintain the entire reaction, and the utilization rate of energy is also the highest. In remediation systems, it is not advisable to use high power frequencies to increase the efficiency of reactive remediation systems.

5.4. Effect of Different Electrode Gaps on Pyrene Degradation

In the DBD plasma system, the distance between the high-voltage electrode and the ground electrode will affect the discharge form, that is, the electrode distance will affect the energy accumulation on the surface of the medium. In order to verify that the electrode distance will affect the soil remediation effect, different electrode distances are used as the medium. Barrier discharge in the experiment, the electrode spacing was set to 15mm, 20mm, and other factors affecting the experiment were excluded. The other operating conditions of the experiment were set as: applied voltage 20kv, frequency 50Hz, and carrier gas flow rate of 1L/min. The experimental phenomenon is shown in Figure 10.

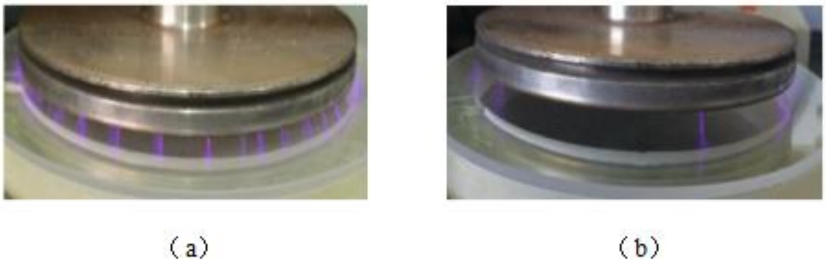

Figure 10: The density of current filaments under different electrode spacing.

Among them, (a) is the electrode gap of 15mm, and (b) is the electrode gap of 20mm. It can be seen from this that when the electrode is closer to the medium, the current filaments on the surface of the medium are denser, the sparser the current filaments on the surface of the medium. When two different electrode spacings are used, the effect of pyrene degradation rate is shown in Figure 11.

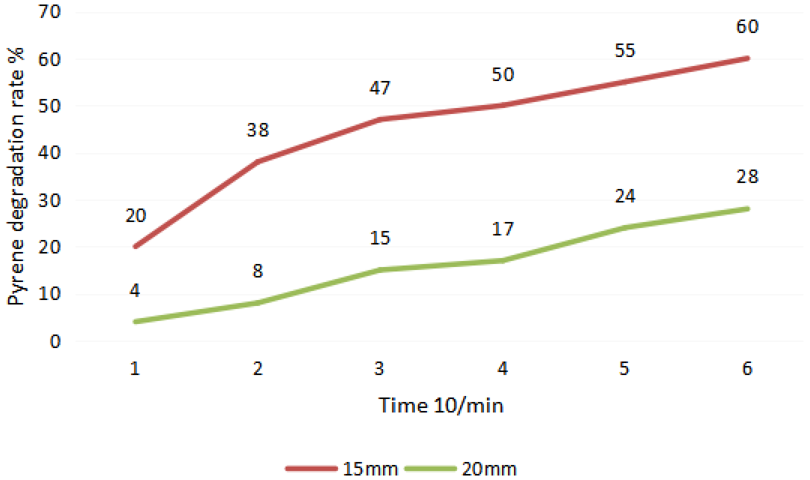

Figure 11: Variation of pyrene degradation rate with different electrode spacings.

When the same discharge time is 10-60 minutes, the degradation efficiency of the electrode spacing of 15mm is much better than that of the electrode spacing of 20mm. This is because when the electrode spacing becomes smaller, the electric field strength increases, and the gas molecules move more violently, which is related to the active the more active particles produced by the collision between the two substances, the higher the pyrene degradation rate.

5.5. Effects of Different Carrier Gas Flow Rates on Pyrene Degradation

In the plasma reaction, the flow rate of the carrier gas directly affects the generation of active substances and affects the discharge phenomenon. It was investigated whether the flow rate of carrier gas would affect the remediation effect of pyrene-contaminated soil. We conduct experiments at 0L/min, 1L/min, and 2L/min respectively. The other operating conditions of the experiment were set as follows: the applied voltage was 20kv, the frequency was 50Hz, and the electrode spacing was 15mm.

Under the same discharge time, the degradation rates of the three carrier gas flow rates are shown in Figure 12: in the first 30 minutes, the degradation rate is the fastest, and then the degradation rate gradually decreases, and the carrier gas flow rate of 1L/min has the best effect, almost twice that of 2L/min. The flow rate of carrier gas can affect the degradation efficiency of pyrene and play a role in promoting it, but the flow rate of carrier gas will also be interfered by the degradation. The contact rate with the target pollutants, which in turn leads to a decrease in the degradation rate of pyrene.

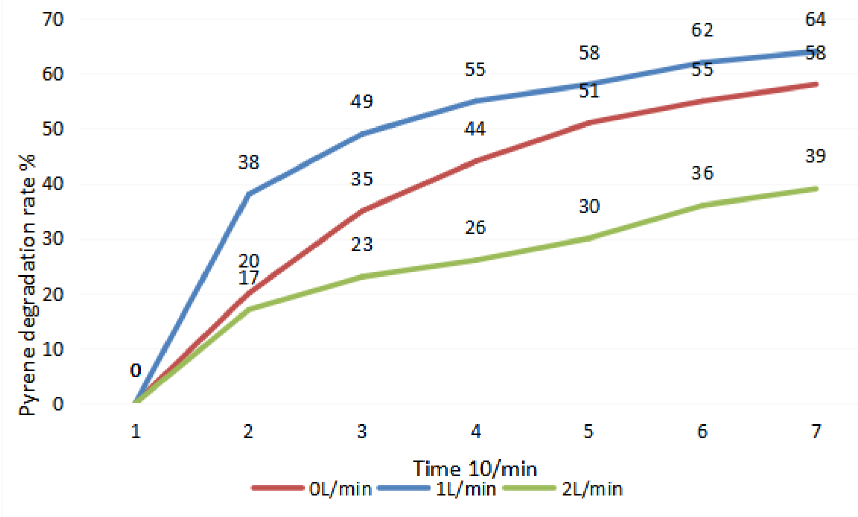

Figure 12: Variation of pyrene degradation rate under different carrier gas flow rates.

6. Epilogue

This paper focuses on the low-temperature plasma technology, and uses the dielectric barrier discharge mechanism to build a plasma soil remediation equipment. The soil in Northeast China is used as the basic experimental soil to collect and measure the basic properties of the soil. After calculating the data, mix it with pyrene-dichloromethane solution, put into the shaker, oscillate for the corresponding time, obtain the experimental soil, calculate the pyrene concentration, and analyze the pyrene hue peak. The optimal soil parameters of the experiment were soil particle size of 1 mm, PH is alkaline, and moisture content of 5%-10%. Under the same reaction time, the pyrene degradation rate was between 65% and 75%, which basically achieved the expected effect. In addition to pyrene pollution, plasma can also conduct research on other refractory pollutants, and follow-up research can expand the application of plasma technology in the field of soil remediation.

Acknowledgements

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References

[1] Yan Qing, Wang Linjie. Current situation and main control strategies of soil pollution in China. Rural Science and Technology,2021,12(30):94-96.

[2] Lei Pengcheng. Research progress in remediation of organically polluted soil by low temperature plasma technology. Petrochemical Construction,2020(4):95-99.

[3] Zhan Jiaxun, Zhang Ai, Li Zhenyu, Liu Yanan. Study on the degradation of petroleum pollutants in soil by low temperature plasma 2018.

[4] Zhang Yinghua. An overview of plasma and its engineering application. World Products and Technology,1995(1):18-20.

[5] Technology - Plasma Research; Studies from Research and Development Center Have Provided New Information about Plasma Research (Plasma Diagnosis and Biomedical Application Using Linear Microwave Atmosnheric-Pressure Plasma Generator IournaL of Technoloev 2020.
[6] Chen Changwen, Wang Shaoning, Xu Hengtong. Experimental research on dielectric barrier discharge phenomenon in high frequency transformers. New Technology of Electrical Engineering,2020,39(11):18-24.
[7] Zhuang Hongchun, Sun Yaohong, Peng Yanchang, Zhang Wei, Yan Ping. Research on plasma generation technology by dielectric barrier discharge. High Voltage Technology,2021(S1):57-58.
[8] Teng Qing, Wang Chun, Lin Xuanjie, Xie Meibing, Cheng Lusi. Research progress in soil polycyclic aromatic hydrocarbon pollution remediation technology. China Agricultural Science Bulletin, 2021, 37(23): 138-143.
[9] Wang Qibin, Li Jun. Development of high-frequency high-voltage power supply for generating cold plasma. Electric Transmission, 2017, 47(1): 78-80.
[10] Lei Ye, Chen Yukun, Hu Rong, Wang Xingyu, Li Su, Huang Wenwen. Effects of soil types on oxidative remediation of benzo[a]pyrene contaminated soils. Petroleum and Natural Gas Chemical Industry, 2021, 50(4) :135-139.
[11] Peng Wei; Shazhou An; Mei Ke; Chao Li; Yurong Hou; Jiyong Lan; Shuai Kang; Junpeng Jin Effects of Enclosure on Plant and Soil Restoration in the Junggar Desert. Journal of Resources and Ecology Volume 12, Issue 6. 2021. PP 840-848.