CHEMICAL ENGINEERING TRANSACTIONS

VOL. 55, 2016

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Tichun Wang, Hongyang Zhang, Lei Tian

ISBN 978-88-95608-46-4; **ISSN** 2283-9216

DOI: 10.3303/CET1655045

Advances in Catalysis Non-thermal Plasma Reactor in the Field of Air Conditioning

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Because the water quality in the central air conditioning cooling water circulation system exists a lot of sediment, widely breeding of microorganism and equipment corrosion problems, Serious damage to people's health and affect the service life of the air conditioning itself. In this paper, the use of high voltage pulsed discharge in water to produce a high-density non-thermal plasma bonding of the catalyst method to solve the problem, the paper introduces the technology of non-thermal plasma and catalyst separate disinfection sterilization mechanism and the mechanism of synergy respectively, the reactor configuration, and points out the research direction in the future.

1. Introduction

With the rapid development of economy and improvement of people’s livelihood in China, central air conditioning (CAC) has been widely used in industrial and civil buildings. While enjoying the comfort of air conditioning, people often ignore the water pollution in the cooling water circulation system. Normally, the CAC features an open cooling water circulation system in which the circulating cooling water is in direct contact with the air. Due to the direct exposure to the dusts in air and the sunlight, a large number of bacteria and algae are bred in the cooling tower and cooling water. As time goes, the water impurities continue to concentrate, resulting in a variety of problems such as equipment corrosion, pipe and heat exchanger scaling, and public health damages brought by bacteria and viruses.
A good air conditioning system creates a clean, healthy indoor environment characterized by appropriate wind, temperature, humidity and biological cleanliness. Unfortunately, there are some problems of existing air conditioning systems that endangers people’s health. In 2003, the SARS virus makes China to realize the virus floating in the air indoor. Bacteria and viruses not only pose threats to people’s health, but also put forward new challenges to indoor biological pollution control. Against this backdrop, the catalytic low-temperature plasma technology stands out and become a promising tool of air purification and sterilization.
As the low-temperature plasma contains a large number of active particles, and the chemical reaction caused by high-energy electrons can be completed in femtosecond level, so low-temperature plasma technology can be used for water pollution control. low-temperature plasma technology carries high energy electrons, low-temperature plasma technology carries energetic electrons, O_3 oxidation, and UV photolysis, so it can effectively solve the water quality problem of central air-conditioning cooling water circulation system. However, low-temperature plasma has many disadvantages, such as low energy efficiency, CO_2 poor selectivity and side products, which limits its further application in environmental management. Photocatalytic technology is widely used because of its low energy consumption, simple operation and complete catalytic reaction, However, there are some defects in using alone, such as unstable UV light source, difficult to deal with high concentrations of pollutants, catalyst easy poisoning and inactivation, etc. In order to overcome these shortcomings, a combination of low-temperature plasma and catalyst was proposed, as the catalytic low-temperature plasma technology combines the advantages of both low-temperature plasma and catalysis, With the characteristics of (1) easy to use, convenient design; (2) high energy efficiency, mild reaction conditions; (3) $CO_2$with high selectivity, less amount of by-products generated; (4) applicable to the central air-conditioning cooling water circulation system of water quality problems etc, so that the technology has a great competitive advantage and a broad space for development.

Please cite this article as: Mo M., Zhao L.Z., 2016, Advances in catalysis non-thermal plasma reactor in the field of air conditioning, Chemical Engineering Transactions, 55, 265-270 DOI:10.3303/CET1655045

Despite its recent emergency, catalytic low-temperature plasma technology has already attracted wide attention in the world. So far, much research has been done on the sterilization and disinfection with low-temperature plasma, which is clean, safe and efficient (Kalla et al., 2015; Kutasi et al, 2006; Gadri et al, 2000; Su et al., 2016). The catalytic low-temperature plasma technology mainly refers to catalysing the chemical reaction of low-temperature plasma by placing catalysts in the electrode material, low-temperature plasma area and inter-electrode area and on the walls of discharge reactors. Featuring low energy consumption, high efficiency and few by-products, the catalytic low-temperature plasma reactor is a key study object in the fields of harmful gases purification, chemical synthesis, sterilization and disinfection, etc (Zeng et al, 2016; McAdams et al, 2008).

2. Overview of low-temperature plasma

2.1 Plasma generation mechanism

For the universe, as a whole, almost 99% of the material is present in the plasma state. Nature's brilliant lightning, hot flashes of flame, as well as a brilliant inquiry of the auroras are the results of the role of plasma. The plasma was discovered by Crookes in 1879, In 1928 the United States scientist Erwin Langmuir and Tonks first introduced the term "plasma" to physics, used to describe the gas discharge tube in the form of substance. The difference between plasma and gas is reflected in: (1) the gas is usually non-conductive, while the plasma is a conductive fluid, and in the whole while maintaining electrical neutrality; (2) the interaction force between particles is different. There exists Coulomb force between charged particles in the plasma, but there is no net magnetic force between the gas molecules; (3) as a charged particle system, the motion behavior of plasma is influenced and restricted by obvious electromagnetic field. The biggest difference between a plasma and an ordinary gas is that it is an ionized gas, the existence of a large number of negatively charged electrons and positively charged ions. If the gas is continuously heated, the molecules are broken down into atoms and ionized, formed by ions, electrons and neutral particles of gas, this state is called plasma.

The plasma exists as the fourth state in addition to the three common states of solid, liquid and gas. It contains a mass of ions, molecules, excited atoms and electrons, free radicals, etc. Plasma is both found in nature and produced by artificial methods. It is usually generated by applying a strong electric field to gas, which causes charged particles to accelerate. Because electron is lighter than ion, the accelerated particles are all electrons. The accelerated electrons collide intensely with a large number of particles, leading to ionization and the formation of plasma (Laroussi et al, 2015). When the temperature of the ions and neutral particles in the system is as low as 300K-500K and the temperature of the electrons is above 10^4K, the resulting plasma is called low-temperature plasma.

2.2 The principle of using high-voltage pulse discharge to produce low-temperature plasma

Low-temperature plasma can be obtained by pulsed discharge in water with a high-voltage pulse power supply. The process is accompanied by chemical and physical effects (Sun et al, 2000). When a high-voltage pulse is applied between the two electrodes, a strong electric field can be formed and high-energy electrons (5~20 eV) can be generated between the electrodes. As the high-energy electrons collide with discharge medium in elastically, the electric field energy carried by the electrons are rapidly transformed into the internal energy of the ground state molecules, triggering a series of complicated physical and chemical reactions, such as excitation, dissociation and ionization. In terms of chemical effect, a lot of active free radicals like ·OH, ·O, ·H, and O_3 would come into being. In terms of physical effect, ultraviolet light and shock waves would take shape (Joshi et al, 1995).

The high-voltage pulse power supply and the voltage pulse used to treat the water quality of the CAC cooling water circulation system should fall in the nanosecond range. A steep, narrow pulse power supply system satisfies the requirement and fulfils the purpose of continuous production of low-temperature plasma, generation of a strong electric field, and conservation of energy. In general, the discharge pulse width of high-voltage pulse in water is <700ns, and the voltage rise time is <100ns. In this case, the relatively light electrons in the electric field are accelerated to form high-energy free electrons while the relatively heavy ions are not accelerated. The high-energy free electrons would excite, crack or ionize the organic matter in the water. Hence, the high-voltage pulse discharge in water boasts a very high energy utilization rate.

The collision between free high-energy electrons and medium particles plays a leading role in the whole process of high-voltage pulse discharge in the water of CAC cooling water circulation system. The inelastic collision between free high-energy electrons and water molecules leads to water molecule excitation, ionization and dissociation. The reaction is expressed in the following equation:

$$H_2O \rightarrow \cdot OH + H\cdot \quad (1)$$

$$2H_2O \rightarrow H_2O_2 + H_2 \quad (2)$$

$H_2O \rightarrow H_3O^+ + e^-_{aq}$ (3)

These active particles are characterized by high density, high pressure in the plasma channel, high temperature and an abundance of free radicals. In ionic conditions, the organic molecules in the water of CAC cooling water circulation system are fully pyrolyzed under high temperature and subject to reaction under the action of free radicals. Besides, the formation of high-pressure and high-temperature plasma channels are accompanied by intense emission of ultraviolet light and super shock waves, which further cause ultraviolet photolysis, electrohydraulic cavitation and supercritical water oxidation of the water of the CAC cooling water circulation system.

3. The principle of sterilization and disinfection of low-temperature plasma

The formation of low- temperature plasma is a very complex physical and chemical reaction process, low-temperature plasma is partially ionized gas, including charged particles, high-energy electrons and neutral particles of electricity, such as free radicals, excited atoms and molecules etc. Excited atoms and molecules produce various optical radiations during electron transitions. The plasma generated by high voltage discharge, accompanied by the chemical effect and strong electromagnetic field, thermal effect, shock wave and other physical effects. These physical and chemical effects have enough energy to break chemical bonds and initiate a series of chemical reactions, with the role of microorganisms reflect the rapid and efficient sterilization, as shown in Figure 1. Due to the considerable complexity of both low- temperature plasma and biological cells, the specific process and the exact lethal mechanism of microorganisms are not clear.

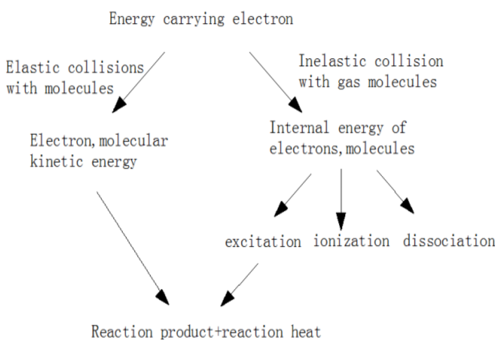

Figure 1: Technical principle of low- temperature plasma treatment of pollutants

Although there is no satisfactory explanation to the sterilization and disinfection of low-temperature plasma, several basic hypotheses have been proposed from physical and chemical perspectives by researchers through repeated experiments and exploration: (Sullivan et al, 2007; Moisan et al, 2001)

(1) When the plasma is generated, a lot of ultraviolet light is emitted which directly damages the genetic material of micro-organisms;

(2) The bacteria are killed by the chemical reaction between the active substances in the plasma and the nucleic acids and proteins of micro-organisms;

(3) The plasma device continues to produce high concentrations of negative and positive ions. The ions bring about strong shear force on the surfaces of micro-organisms, which is far greater than the surface tension of cell membranes. Thus, the cell walls of micro-organisms are severely damaged and more positive ions penetrate the cell walls into the cells, causing damages to the cell electrolyte and leading to the eventual death of cells.

4. The mechanism of nano-TiO_2 photocatalytic microbe killing

With reaction energy of 120 Kcal/mol, the active hydroxyl radicals produced by TiO_2 photocatalytic reaction can decompose the organic matter of bacteria effectively and quickly. The sterilization effect is more obvious when coupled with other active oxides (H_2O_2, ·OOH and·O_2^-). Hydrogen peroxide, active hydroxyl, superoxide ions and per hydroxyl radicals destroy the biological cell structure either through the directly reaction with biological macromolecules (proteins, nucleic acid macromolecules, enzymes, lipids) or through a series of oxidative chain reactions, promote lipolysis and protein variation of bacteria, then destroy the RNA in the virus particles, and ultimately achieve the purpose of killing bacteria. In the TiO_2 photocatalytic reaction, TiO_2 acts as a catalyst and does not participate in the chemical reaction (Gumy et al, 2006; Rizzo et al., 2009; Nikos et al., 2010).

5. The mechanism of synergistic effect between low-temperature plasma and catalyst

In the process of producing low- temperature plasma, the pollutants by high energy electron bombardment can be decomposed into elemental or transformed into harmless substances. In addition, the bombardment of high energy electrons causes ionization, dissociation and excitation of pollutants, resulting in a large number of plasma. The ions, electrons, excited atoms, molecules and free radicals in the plasma are very active reactive species, it is possible to accelerate the reaction which is difficult to proceed or which is very slow, they further react with pollutant molecules, ions, so that pollutants are degraded, in particular, is conducive to the treatment of refractory pollutants. On the other hand, when the active ion and free radical gas discharge, some high-energy excitation particles downward transition can produce ultraviolet light, when the photon or electron energy is greater than the semiconductor band gap, it will stimulate the semiconductor electronic from the valence band transition to the conduction band, formation of electron hole pairs with strong activity and further induction of a series of redox reactions. Photo generated hole has a strong ability to obtain electrons, which can react with OH^- and H_2O adsorbed on the catalyst surface to generate hydroxyl radicals, thus further oxidizing pollutants. In addition, the photo catalyst can selectively react with the intermediate by-product produced by the plasma to obtain an ideal degradation substance, such as H_2O and CO_2. Therefore, the synergistic effect of low- temperature plasma and light catalyst than using single plasma or light catalyst has better removal effect, can effectively reduce the formation of the intermediate products, further reducing energy consumption of reaction.

In low-temperature plasma, high active substances like ions, molecules, excited atoms, high-energy electrons and free radicals can participate in degradation reactions that are difficult to achieve under normal circumstances. In particular, the high-energy electrons can significantly reduce the activation energy of the synergistic catalyst of low-temperature plasma, making it possible to use the catalyst, which only works under high temperature or special conditions, at room temperature. In the meantime, proper catalyst can selectively react with the intermediate by-products of low-temperature plasma so that the pollutants are fully transformed and the harm is reduced to a minimum (Lu et al, 2014).

At present, little research has been done by Chinese and foreign scholars on the mechanism of synergistic effect between low-temperature plasma and catalyst. That is because the synergistic action of low-temperature plasma and catalyst involves extremely complex chemical and physical reactions, which are easily affected by various self-induced fields and external fields. To make matters worse, the mechanism maps of the reaction process can not accurately describe the process and results because they are mostly deducted based on the spectral analysis of the reaction products and process. Because of the complexity of the reaction mechanism, the systematic study is still in the exploratory stage (Van et al, 2008; Ayrault et al, 2004).

Probing into the treatment of volatile organic compounds, Roland et al (Roland et al, 2002). find that the synergistic effect between plasma and catalyst is attributable to the full utilization of the strong oxidizing short-lived active particles generated inside the catalyst (e.g. the ground state atomic oxygen and excited state atomic oxygen produced in ozone photolysis). If the volatile organic compounds pass through the plasma before the catalyst, only the long-lived particles O_3 are functioning. In the event where the concentration of organic matter is lower than that of nitrogen and oxygen, the catalyst chooses to react with the organic matter first.

Through the discussion of the mechanism of the synergistic effect between low-temperature plasma and Mn catalyst on removal of toluene from the air, Delagrange et al (Delagrange et al, 2006). point out that the oxidation of toluene in plasma is resulted from the combined actions of long-lived and short-lived species, and put forward two dynamic models: X=1-0.24$e^{-99.5\ (27.9\sqrt{C_0})}$ (plasma catalytic reactor) and X=1-$e^{-Ed(27.9\sqrt{C_0})}$ (plasma reactor).

6. Catalytic low-temperature plasma reactor

Depending on the combination form of the catalyst and the reactor, catalytic low-temperature plasma reactors can be divided into one-stage reactor and two-stage reactor. In one-stage reactor, the catalyst, in the form of particles, is filled in the area of discharge electrode or placed in the low-temperature plasma generation area as deposition on the inner walls of the reactor or on the discharge electrode. If one-stage reactor is adopted, high energy active particles are more easily coupled with the catalyst. However, it is much more difficult to explore the coupling between low-temperature plasma and the catalyst due to secondary discharge phenomenon on particle surfaces and the uncertain quantification of short-lived active particles. In two-stage

reactor, a catalytic reaction zone is placed in the downstream of the low-temperature plasma reaction zone. Usually, there is a certain distance between the two reaction zones so that short-lived high energy particles cannot reach the catalytic area, making it easier to study the active particles acting on the catalyst. Of course, if the distance is set improperly, it might be impossible to observe the synergistic effect between the low-temperature plasma and the catalyst (Subrahmanyam et al, 2006).
There are many types of reactors for the synergistic effect between the low-temperature plasma and the catalyst. From the perspective of the mechanical structure, the reactors are divided into: plate-type, packed bed-type, composite-type, flat-type, etc. This paper mainly introduces the packed bed-type catalytic low-temperature plasma reactor which uses nano-TiO_2 photo catalyst. See Figure 2 for the sketch map. The reactor uses a cylindrical organic glass reaction vessel, the grounding electrode is a stainless-steel plate on the inner wall of the vessel, the high voltage pole is coaxial stainless steel wire, and the media particles inside the reactor are nano-TiO_2 photo catalyst (Bystritskii et al, 1999; Zhu et al, 2007).

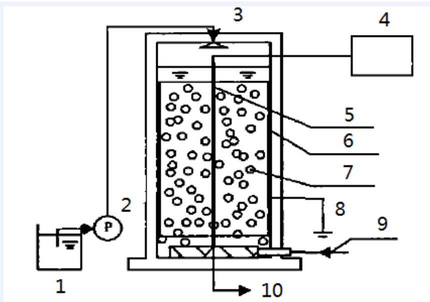

Figure 2: Packed bed-type reactor (1-the water of the CAC cooling water circulation system; 2-water pump; 3-water spray device 4-high-voltage pulse power supply; 5-wire electrode; 6-cylindrical electrode; 7- TiO_2 particles; 8- grounding electrode; 10 -to the next device)

The water of CAC cooling water circulation system goes through the following purification procedures: use the water pump to extract the water from the CAC cooling water circulation system, and spray the water evenly in the reactor. Pulse an electric discharge in water with high-voltage pulse power supply to form the low-temperature plasma. The strings of chemical reactions between the numerous strong oxidizing particles of the plasma and the micro-organisms in water, coupled with the active hydroxyl radicals produced by TiO_2 photocatalytic reaction, can eliminate and decompose viruses and bacteria very soon. Simple in structure and easy to implement, the device is very suitable for purifying the water of CAC cooling water circulation system.

7. Conclusion

On the treatment of the water from CAC cooling water circulation system, catalytic low-temperature plasma reactor greatly outperforms low-temperature plasma reactor or TiO_2 photo catalyst reactor. Suffice it to say that the reactor has a wide application prospects. However, due to the lack of research at home and abroad, great efforts must be made in the following aspects:
(1) Further optimize the structure design of catalytic low-temperature plasma reactor, explore the effect of catalyst shape and particle size on the performance of the reactor, and improve the energy efficiency of the reactor.
(2) Dig deep into the mechanism of synergistic effect of catalytic low-temperature plasma on the purification of the water of the CAC cooling water circulation system.
(3) Carry out reliability and stability analysis of the catalytic low-temperature plasma on treating the water of the CAC cooling water circulation system in the long run.

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