Experimental research of pulsed discharge plasma and TiO$_2$/Zeolite coupling technology for formaldehyde removal

**Bingyan Dong*, Shuirong Lan**

College of Resources & Environmental Engineering, Jiangxi University of Science & Technology, Ganzhou 341000, Jiangxi, China

E-mail: dongbingyan1@sina.com

**Abstract.** The pulsed discharge plasma combining with catalyst to remove formaldehyde is a novel type of advanced oxidation technology. In the present work, taking wire-tube pulsed discharge plasma and TiO$_2$/Zeolite coupling technology for formaldehyde removal. The studies have investigated the wire-tube reactor with zeolite, TiO$_2$, TiO$_2$/Zeolite for formaldehyde removal respectively. Results show that in the optimal experimental conditions and the baking time is 120 min, the baking temperature is 450 $^\circ$C, that TiO$_2$/Zeolite catalyst which made by sol-gel shows higher photocatalytic activity and efficiency. The pulsed discharge with TiO$_2$/Zeolite catalyst for formaldehyde removal has higher removal efficiency than pulsed discharge with zeolite or TiO$_2$. Therefore, pulsed discharge plasma with TiO$_2$/Zeolite for the removal of formaldehyde can greatly increase the removal efficiency.

1. Introduction

Formaldehyde, a colourless volatile liquid with a pungent odour, is the main poisonous and harmful substance in the room. Formaldehyde is of great harm to human health, it ranks second in toxic chemicals list of China and it is identified as suspicious teratogenic carcinogen by the World Health Organization.

Long-term release of organic pollutants which volatilize from decorating materials and furniture can endanger people's health seriously, and formaldehyde is one of such pollutants. Nowadays, photocatalysis and low-temperature plasma are the most promising air purification techniques, their functions and advantages on degradation of formaldehyde have been gradually recognized by people with further development of their application and studies, therefore, they have become a hot spot in the field of environmental protection [1-7].

* To whom any correspondence should be addressed.
At present, compared with other traditional methods, pulsed discharge plasma and catalyst coupling technology for indoor toxic gas removal is promising [8-9], its advantage includes simple devices, oxidation to almost all pollutants, high efficiency, fast oxidation rate, less secondary pollution and catalyst recycling.

Taking TiO$_2$/Zeolite catalyst which made by sol-gel and wire-tube pulsed discharge plasma coupling technology for formaldehyde removal, the influence of various factors on the characters of such photocatalyst in the sol-gel preparation process and the influence of electrical parameters on the removal efficiency of formaldehyde were studied. In the optimal experimental conditions, further research of pulsed discharge plasma and TiO$_2$/Zeolite catalyst coupling technology for formaldehyde removal was carried on, that shows the synergy of ultraviolet light and pulsed discharge non-thermal plasma can improve formaldehyde removal efficiency.

2. Experimental Facility and Method

2.1. Experimental Facility

High-voltage pulsed power supply was provided by the Institute of Electrostatic and Special Power, Dalian University of Technology. The electrical parameters of high-voltage pulsed power supply are mainly involved with positive pulse, pulse width less than 500 ns, pulse rise lower than 100 ns, and pulse repetition rate of 0-200 Hz.

The wire-tube reactor is adopted in the experiment, tube is made of stainless steel cylinder, inner diameter is 58 mm, outer diameter is 60 mm and the length is 310 mm. The tube is used as ground electrode, and star wire which made of stainless steel is used as discharge electrode and its diameter of the wire is 4 mm. Wire electrode is fixed in the cyclinder circle and connected with high-voltage pulsed power supply.

The whole experimental system diagram as shown in figure 1, the system is composed of four parts including high-voltage pulsed power supply, gas supply system, reactor and detecting instrument.

![Figure 1. The Experimental System Diagram.](image)

2.2. Experimental Instruments and Reagents

(1) Instruments

XL30 Scanning Electron Microscope is supplied by Philips; Miniflex X-ray Diffractometer is supplied
by Rigaku; AR2130 Electronic Balance (0.001 g) is supplied by Ohaus Corp. Pine. Brook, NJ, USA; Muffle with the type of HZC4-LX-1; LZB-10 Glass Rotameter is supplied by Zhejiang Yuyao Zhenxing Flow Meter Factory; ACO-003 Electromagnetic Air Pump is supplied by Guangdong Risheng Group Company; SM95 PPM HTV, America.

(2) Reagents
Formaldehyde Solution (analytical reagent) is supplied by Beijing Wuxing Chemical Plant; Titanium Dioxide (anatase TiO₂): Particle size is about 10 nm, which BET specific surface area is about 130 m² g⁻¹, and supplied by Ganzhou Chengxin Direct Marketing Factory; Tetrabutyl Titanate (C₁₆H₃₆O₄Ti): Chemically pure, it is supplied by Shanghai Kefeng Chemical Reagent Co., Ltd; Anhydrous Ethanol (CH₂CH₂OH): Analytical reagent, it is supplied by Tianjin Damao Chemical Reagent Plant; Concentrated Nitric Acid (HNO₃), analytical reagent, it is supplied by Jiangxi Hongdu Biochemical Co., Ltd; Glacial Acetic Acid (C₂H₄O₂): Analytical reagent, it is supplied by Tianjin Chemical Reagent Plant; Zeolite is supplied by Sinopharm Chemical Reagent Co., Ltd; Deionized water which made in lab has the effect of Hydrolysis.

2.3. Experimental Method
(1) Preparation of Load-Type Titanium Dioxide
Zeolite was rinsed by distilled water repeatedly till upper solution became clear, then sediment will be heated drying at 105 °C for 5 hours.

First, 30 ml C₁₆H₃₆O₄Ti was added into 115 ml CH₃CH₂OH, then 1 ml C₂H₄O₂ and zeolite were put into them. A solution was made up with them by stirring until smooth. 7.5 ml C₂H₄O₂ and 2.5 ml HNO₃ inhibitors were added into 52.5 ml distilled water under shaking, then pH was adjusted to 2, B solution was formed. A solution was dropwise put into B solution about 30 minutes, transparent sol with light yellow was made after stirring by magnetic stirrer for one day and hydrolyzing for three days. Then sol should be heated drying at 130 °C for 2 hours. After it was crushed down, it was calcined in muffle at 450 °C, at last, TiO₂/Zeolite catalyst was made.

(2) Formaldehyde Removal Efficiency
Experiment is focus on volatile formaldehyde, formaldehyde concentration within the reactor is controlled through intake flow which is regulated by precision flow meter. The removal efficiency could be obtained by this formula.

\[ \eta = \frac{C_0 - C}{C_0} \times 100\% \]  \hspace{1cm} (1)

Where \( \eta \) is removal efficiency, \( C_0 \) is formaldehyde concentration of reactor inlet, and \( C \) is formaldehyde concentration of reactor outlet.

3. Experimental Results and Analysis
3.1. Structural Characteristics of TiO₂/Zeolite
When bath temperature is 30 °C, volume ratio of C₂H₄O₂ and C₁₆H₃₆O₄Ti was 0.1, water to C₁₆H₃₆O₄Ti was 0.15, HNO₃ to C₁₆H₃₆O₄Ti is 0.1, CH₃CH₂OH to C₁₆H₃₆O₄Ti was 4.0, TiO₂/Zeolite photocatalyst was made under such conditions, and then TiO₂/Zeolite photocatalyst was calcinated in the muffle for 2 hours at 375 °C, 450 °C and 500 °C respectively. After that, photocatalyst was analyzed through
electron microscope scanning and X-ray Diffraction.

Structural characteristics of catalyst were observed by using XL30 scanning electron microscope at different calcination temperature. Figure 2 shows that there is white material on the surface of carrier. It means that TiO$_2$ has been loaded on carrier successfully. TiO$_2$ loaded on zeolite has larger surface area, so surface area and activity of TiO$_2$ catalyst increase. X-ray Diffraction shows that preparation temperature has great effect on crystal form and phase composition of TiO$_2$. When solvent is the same, pure anatase TiO$_2$ could be generated at calcination temperature of 450 °C for 2 hours. Figure 3 shows that crystalline state of anatase TiO$_2$ is in good order and intensity reaches the maximum at 25°.

![Figure 2. SEM pictures of TiO$_2$/Zeolite at 450°C.](image)

![Figure 3. TiO$_2$/Zeolite diffraction pattern at 450°C.](image)

3.2 Pulsed Discharge Plasma and TiO$_2$/Zeolite Coupling Technology for Formaldehyde Removal

3.2.1. The Effect of Pulse Voltage on Formaldehyde Removal Efficiency Figure 4 shows that formaldehyde removal efficiency increases with the increase of voltage, when voltage is 30 kV, removal efficiency is 43.32%, after voltage reaches 35 kV, efficiency arrives to 46.93%, while increase
rate gradually slows down when voltage increases from 35 kV to 37.5 kV. That is because when the pulse voltage increases, the average electric field strength in the discharge gap increases markedly, and led to discharge become stronger, which can lead to generate radicals and reactive substances by the increasing of pulsed energy in reactor. But when voltage reaches a certain value, increases the voltage will decreases energy utilization efficiency, and removal efficiency enhance is not obvious. So the optimal discharge voltage of the reactor is 35 kV.

![Figure 4. The effect of pulse voltage on formaldehyde removal efficiency.](image)

![Figure 5. The effects of pulse frequency on formaldehyde removal efficiency.](image)

3.2.2. The Effects of Pulse Frequency on Formaldehyde Removal Efficiency As figure 5 shows, formaldehyde removal efficiency increases first and then decreases as the increase of pulse frequency, when pulse frequency is 50 Hz, after 30 minutes of pulsed discharge treatment, the removal efficiency is 46.78%; when pulse frequency increases to 70 Hz, the efficiency arrives to 50.21% under the same condition. Increased pulse frequency means the increase of discharge rate and discharge number, the increase of pulse frequency will always increase high-energy electron per unit time, and also increase actives concentration, all of these will enhance removal efficiency. While pulse frequency is too high, discharge time shortens in unit pulse, which hinder energy from discharging rapidly, so energy efficiency and removal efficiency decreases. Under such experimental conditions, formaldehyde removal efficiency is best when pulse frequency is 70 Hz.

3.2.3. Pulsed Discharge Plasma Coupling with Zeolite and TiO₂ for Formaldehyde Removal A certain amount of anatase TiO₂ or zeolite were put into discharge reactor respectively, then formaldehyde removal efficiency of pulsed discharge plasma coupling with zeolite and TiO₂ were tested at different time and analyzed.

As figure 6 shows, in the condition of different additives, formaldehyde removal efficiency improves along with the increase of treatment time, when time lasts 40 minutes, formaldehyde removal efficiency of pulsed discharge plasma coupling with zeolite catalyst is 57.87%, efficiency of pulsed discharge plasma coupling with TiO₂ catalyst is 65.34%, the latter is higher than the former obviously. Because photocatalyst is motivated by discharge UV-light, in the process, photogenerated
electrons and holes are produced, then they form a redox system, and a mass of highly reactive radicals are generated after a series of reactions. In the meantime, catalyst activity would also be motivated by pulsed discharge plasma. Zeolite additions only play a part of adsorption, which will gather formaldehyde on the surface of zeolite and strengthen oxidation of pulsed discharge plasma, but pulsed discharge plasma coupling with zeolite do not have real synergy, so pulsed discharge plasma coupling with zeolite has less function than pulsed discharge plasma with TiO$_2$ photocatalyst. At last, through the experimental research shows that pulsed discharge plasma coupling with TiO$_2$ photocatalyst do have synergy, discharge plasma and UV-light will motivate photocatalyst activity to improve formaldehyde removal efficiency.

![Figure 6. Pulsed discharge plasma coupling with Zeolite or TiO$_2$ for formaldehyde removal.](image)

3.2.4. Pulsed Discharge Plasma Coupling with TiO$_2$ and TiO$_2$/Zeolite for Formaldehyde Removal

A certain amount of anatase TiO$_2$ or TiO$_2$/zeolite were put into discharge reactor respectively, then formaldehyde removal efficiency of pulsed discharge plasma coupling with TiO$_2$ and TiO$_2$/zeolite were tested at different time and analyzed.

Figure 7 shows that the pulsed discharge with TiO$_2$/Zeolite catalyst for formaldehyde removal has higher efficiency than pulsed discharge with TiO$_2$. Because discharged UV-light contacts with TiO$_2$/Zeolite catalyst directly, which has photocatalytic function. Moreover, active radicals which produced from pulsed discharge plasma have synergistic effect with TiO$_2$/Zeolite catalyst, thus increasing formaldehyde removal efficiency. Furthermore, pulsed discharge could prevent electron-hole from recombining and enhance catalyst efficiency. Electron-hole pairs will be motivated more easily in light for changing catalyst bandwidth and shape and accelerating electron speed on the band by pulsed discharge. Besides, using zeolite as carrier, carrier could provide photocatalytic reaction environment for high concentration formaldehyde and accelerate the rate of photocatalytic degradation on formaldehyde by adsorption and surface gathering. Formaldehyde adsorbed by carrier
will move to TiO$_2$ surface through diffusion, then TiO$_2$ can resolve formaldehyde on the carrier, carrier will be regenerated in situ. So pulsed discharge plasma coupling with TiO$_2$/Zeolite catalyst for formaldehyde removal can bring the coupled effect of discharge plasma, UV-light and photocatalyst to improve formaldehyde removal efficiency.

![Graph](image_url)

**Figure 7.** Pulsed discharge plasma coupling with TiO$_2$ or TiO$_2$/Zeolite for formaldehyde removal

4. Conclusions
(1) TiO$_2$/Zeolite catalyst was made by sol-gel method. The volume ratio of CH$_2$CH$_2$OH to C$_{16}$H$_{36}$O$_4$Ti is 4.0, C$_2$H$_4$O$_2$ to C$_{16}$H$_{36}$O$_4$Ti is 0.1, water to C$_{16}$H$_{36}$O$_4$Ti is 0.15, HNO$_3$ to C$_{16}$H$_{36}$O$_4$Ti is 0.1, when the baking temperature is 450 $^\circ$C and the baking time is 120min, TiO$_2$/Zeolite catalyst shows higher photocatalytic activity.
(2) Pulse voltage and frequency do have great effect on formaldehyde removal efficiency, within a certain scope, removal efficiency increases with the increase of pulse voltage and frequency, when pulse voltage and frequency exceed a certain value, increase rate of the efficiency will slow down.
(3) The pulsed discharge plasma coupling with TiO$_2$ photocatalyst do have synergy, discharged plasma and UV-light will motivate catalyst activity, which could improve formaldehyde removal efficiency.
(4) The pulsed discharge with TiO$_2$/Zeolite catalyst for formaldehyde removal has higher photocatalytic activity and efficiency than pulsed discharge with TiO$_2$.

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