Catalysis-assisted Decomposition of Aqueous 2, 4, 6-Trinitrotoluene by Pulsed High Voltage Discharge Process

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Abstract: TNT removal by the combination of high voltage pulsed discharge plasma and different catalysts with various concentration was investigated. In the case of 9.8 kV peak pulsed voltage and 120Hz pulsed frequency, the degradation rate of 30 mg/L TNT solution with pH value of 6.8 reached 66.1% after 60 min treatment. It was showed that Fe^{2+} had a remarkable catalytic effect on degradation of TNT. When the concentration of Fe^{2+} was 0.15 mmol/L, it promoted the TNT degradation, and 84.0% removal was obtained. However, addition of H_2O_2 into TNT solution inhibited the TNT removal, especially at the initial reaction. After 120min treatment, the degradation efficiency of 100mg/L TNT was 87%, and COD reduced 80%. The results indicated that TNT could be efficiently removed by high voltage pulsed discharge plasma.

Keywords: Pulsed high voltage discharge, Catalyzed oxidation, TNT, Degradation

1 INTRODUCTION

TNT (2, 4, 6-trinitrotoluene) is widely used in detonators, mines, rockets, and plastic explosives. All of these courses may cause serious harm to human health[1]. How to treat TNT wastewater has been a problem concerned by the world. Now, several methods of treating TNT contaminated water have been developed, among which ozone-active carbon absorption has often been used as the efficient treatment of TNT wastewater. However, because the solubility of O_3 in water is little, the O_3 treatment cost is high, there will be some other midway productions in treatment process, the active carbon is easy to become saturation adsorption and the regeneration cost is high too, this method is still need to do further researches[2]. Because the biology toxicity of TNT waste water can restrain the growth and propagation of kinds of bacterium, the TNT treatment by biochemistry method is not steady, and the cycle time is so long that it is hard to suffice the practice need[3].

Now the technique of high voltage pulsed discharge plasma in wastewater treatment has been aroused the interest of the researchers in the entire world, because there are ozone, hydrogen peroxide, hydroxyl radicals and others active species produced in discharge [4]. In 1996□Willberg[5] treated TNT by pulsed high voltage discharge in liquid, and the degradation rate reached 99% after about 200 times high energy discharge in 1 min. Many Chinese researchers [6, 7] also have done experiments about TNT treatment by pulsed high voltage discharge in liquid, but because of the long pulse discharge (pulsed width = several ms) power supply, the low energy using rate and the bad electrodes corrupted. Recently the researchers are focusing water treatment by narrow pulse discharge methods, because of the short pulse rise time, narrow pulse width and higher utilizing energy efficiency.

In this research, we present the results of TNT degradation by pulsed high voltage discharge process. The efforts of various parameters on the degradation efficiency, such as initial concentration of TNT, pH of the solution, adding $Fe^{2+}$and H_2O_2 were investigated to determine the optimum treatment conditions. The degradation rate of COD was also determined.

2 MATERIALS AND METHODS

2.1 The Reactor System

The experimental apparatus used in the research was illustrated in Fig. 1. Parameters of the pulsed high-voltage power supply (design and manufactured by ourselves) are as follows: peak pulsed voltage 0-30 kV, pulse rise time<60 ns, pulsed width<300 ns, pulsed frequency 0-200 Hz. The reactor vessel was made from a plexiglass cylinder (90 mm inner diameter and 92mm length). The multi-needle-to-plate electrode, which produced positive stream corona discharge at its needle tips, was located in the cylinder, and the distance between needle anodes and the ground plate electrode was adjustable. The ground plate electrode consisted of an 80 mm diameter stainless-steel disc of 1.5 mm thickness.

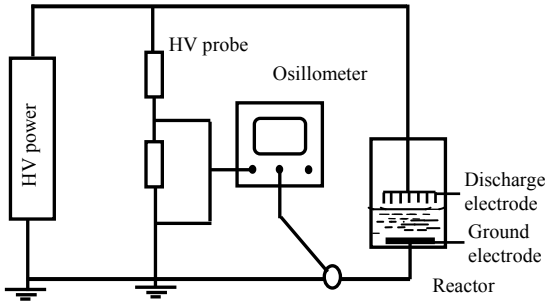

Fig. 1 The diagram of experimental device

2.2 Experimental Methods

100 mg/L TNT mother solution was made by dissolving TNT with distilled water, which was diluted in function of experiments need. The peak pulsed voltage, pulsed frequency and the distance of electrode were 9.8 kV, 125 Hz, 20 mm. The total volume of the treated TNT solution was 120mL, and its usual concentration was 30 mg/L at pH=6.8. Analysis of the degradation efficiency was performed by measuring TNT concentration every 10 min.

2.3 Sample Analysis

The TNT concentration was measured by the light absorption technique [8]. Determination of the chemical oxygen demand (COD) was dichromate method [9].

3 RESULTS AND DISCUSSION

3.1 Effect of Initial pH Value

The effort of initial pH value was shown in Fig. 2. With the pH=3 of solution, TNT removal rate was 25.3% after 30min treatment, and with pH=6.8 and 11, the TNT removal efficiencies were 46.5% and 39.2% respectively. The result was that the degradation rate of 30mg/L was the best in litmusless solution, decreased in alkalescence or week acidity solution, and was the least in strong acidity solution. This result was the identical to the literature [10]. In the experiment, it was found that there were acids formation in TNT degradation by discharge, and the pH value decreased slowly with the treatment time. The effect of initial pH value was not marked in the end of reaction process.

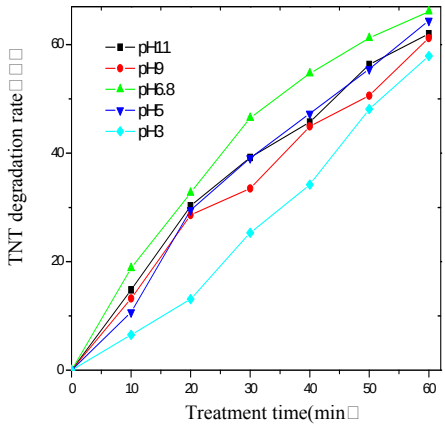

Fig. 2 Effect of initial pH on TNT removal efficiency

3.2 Effect of Different TNT Concentrations

The effect of different concentration solutions was shown in Fig. 3. The degradation efficiency of 30 mg/L, 50 mg/L, 70 mg/L and 100 mg/L TNT solution reached 66.1%, 60.2%, 59.7%, and 49.9% respectively after 60 min treatment. It was found that the degradation rate decreased with the increase of initial concentration, but in the same treatment time the TNT removal quantity increased with the increase of initial concentration. The reason was that with the increase of TNT concentration, the reaction probability between TNT and active species because of discharge (H_2O_2, O_3, •OH) in unit times increased, and so did the TNT removal quantity.

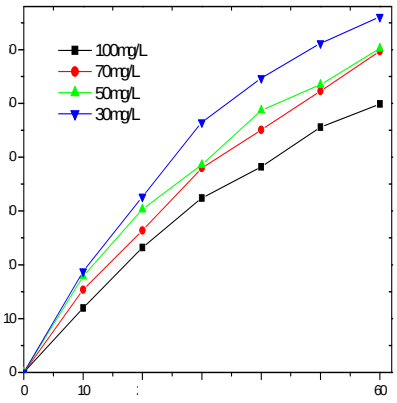

Fig. 3 Effect of initial concentration on TNT removal efficiency

3.3 Decomposition of TNT by Discharge with Catalysis

3.3.1 Effect of Fe^{2+} on TNT Removal

Fig. 4 presented the effect of Fe^{2+} on TNT removal. It was found that there was obvious accelerating effect to TNT degradation with addition of appropriate quantity of Fe^{2+} (0.05 mol/L -0.2 mol/L). The reason was that there was Feton reaction because of H_2O_2 produced in the reaction between Fe^{2+} and discharge, which increased the TNT degradation efficiency [11]. The main reaction equation was as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$$

However, when the Fe2+concentration was too high (>0.2 mol/L), the conductance of TNT solution increased with the result of restraining the discharge phenomena. So, with the increase of Fe^{2+}concentration, TNT removal rate firstly increased and then decreased. In the research, it was found that with the Fe^{2+} concentration was 0.15 mmol/L, TNT removal efficiency was 84.0% after 60 min treatment, which was higher than discharge alone by 17.9%.

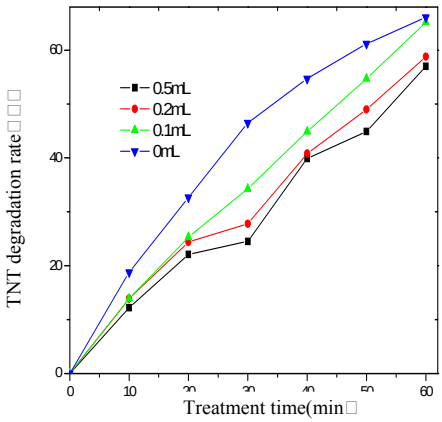

Fig. 4 Effect of Fe^{2+} concentration on TNT removal efficiency

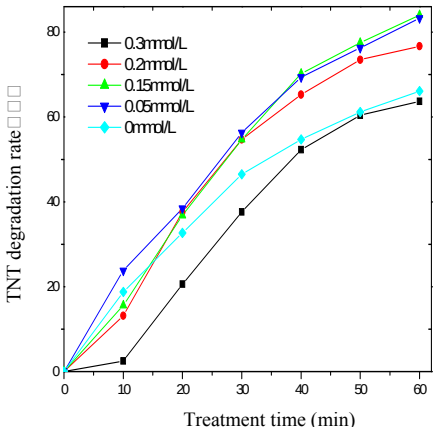

Fig. 5 Effect of H_2O_2 concentration on TNT removal efficiency

3.3.2 Effect of H_2O_2 Addition

Fig. 5 presented the effect of H_2O_2 addition on TNT removal by discharge. It was found that TNT degradation efficiencies were 46.5%, 34.3%, 27.8% and 24.5% respectively with addition of 0 mL, 0.1, 0.2 and 0.5 mL H_2O_2 in solution after 30 min treatment. It could be concluded by these results that H_2O_2 restrained TNT degradation, which was identical to the research of Ralf[12].

When the pulsed discharge voltage was high enough, the plasma channels could be formed between high voltage electrode and grand electrode, and there were high speed electrons, UV light and active species obtained in the gas-discharge process in split second, which could be transported into the solution nearby the grand electrode. There were kinds of chemical reactions on the water surface, and after O_3 obtained in discharge entered the solution, kinds of active species and H_2O_2 could be gotten, and the high energy electrons also react with H_2O to produce certain active particles. These active species could react with and degraded organic compounds [13]. The H_2O_2 obtained in discharge could accelerate to produce lots of ·OH, but when the H_2O_2 concertain raised to a certain volue, H_2O_2 would become an eliminate reagent for·OH free radicals.

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2\cdot$$

$$H_2O\cdot + \cdot OH \rightarrow H_2O + O_2$$

It was found that because the excessive H_2O_2 added in the TNT initial solution eliminated parts of ·OH, the TNT degradetion rate decreased.

3.4 Connection with TNT and COD Degradation Efficiency

According to the former researches[14,15], in TNT degradation process there may be 2, 4, 6-trinitrobenzene carboxylic acid, 2, 4, 6-trinitrophenol and 1, 3, 5-trinitro-benzene midway reaction productions obtained, and TNT would not degraded completely. In the experiment, the TNT and COD removal rates were compared in Fig. 6. It was found that the TNT concentration of 100 mg/L TNT solution decrease evidently with treatment time, and the removal efficiency was 87% after 2 hours treatment; but the slope of COD concentration decreased, and the removal rate was 80% after 2 hours treatment. It was concluded that TNT of solution could be degraded effectively by pulsed high voltage discharge.

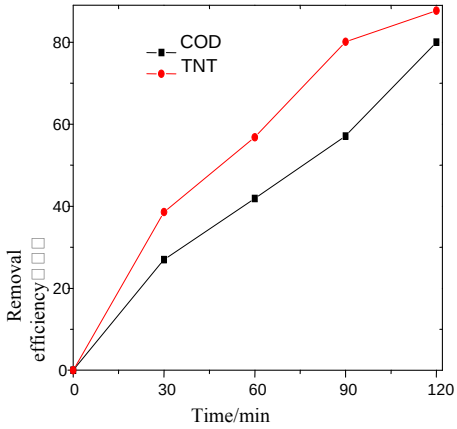

Fig. 6 TNT and COD removal efficiency changing with time

4 CONCLUSIONS

TNT in water could be degraded effectively by narrow pulse high voltage discharge in air. In the case of the 20 mm space between electrodes, 9.8 kV peak pulsed voltage and 120 Hz pulsed frequency, the degradation rate of 30 mg/L TNT solution with pH value of 6.8 reached 66.1% after 60 min treatment. It was showed that Fe^{2+} had a remarkable catalytic effect on degradation of TNT. In the case of the concentration of Fe^{2+} was 0.15 mmol/L, it promoted the TNT degradation, and 84.0% removal was obtained. However, addition of H2O2 into TNT solution restrained the TNT removal. After 2 hours treatment, the degradation efficiency of 100 mg/L TNT was 87%, and COD reduced 80%. It was showed that TNT could be degraded completely into small molecule substances at last with enough treatment time.

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