Degradation of 2,4,6-Trinitroresorcinol in Aqueous Solution by Cold Plasma Technology

Hoang Van Nguyen*, Khue Ngoc Do, Tuan Cao Nguyen

Institute of New Technology, 17 Hoang Sam Street, Hanoi, Vietnam

Received: 12 February 2021
Accepted: 15 April 2021

Abstract

The degradation of 2,4,6-Trinitroresorcinol (TNR) in aqueous solution by dielectric barrier discharge system was investigated and the effect of some factors that might affect the degradation process was also further examined. The results showed that TNR could be effectively removed from aqueous solution by cold plasma. Under the experimental conditions, the TNR removal efficiency was proportional to the input electric power and the circulating flow rate, but inversely proportional to the initial pH, initial concentration and electrode distance. Initial pH significantly influenced the TNR removal efficiency. Accordingly, in acidic medium, the TNR removal efficiency was higher than that in neutral and alkaline medium and is highest at pH = 3.2. The presence of some oxidizing agents in the solution such as H₂O₂, Na₂S₂O₈, O₃ greatly increased the TNR removal efficiency under the effect of cold plasma. The TNR removal efficiency increased gradually by the range of plasma/H₂O₂ > plasma/O₂ > plasma/Na₂S₂O₈ > plasma. The TNR degradation process in the presence and absence of the oxidizing agents all abided by the regulation of first order reaction kinetics.

Keywords: 2,4,6-Trinitroresorcinol, cold plasma, dielectric barrier discharge, kinetics

Introduction

2,4,6-Trinitroresorcinol (TNR) or styphnic acid with formula C₆H₃N₃O₈ is a nitrophenol compound that is widely used in the explosives industry. Wastewater containing nitrophenols has the characteristics of high chroma, high toxicity, and low biodegradability. Under natural conditions, it is difficult for nitrophenols to be removed because of their high stability and solubility, leading to a long-term retention and an accumulation in the environment, causing serious pollution to the environment and hazard to humans [1]. Like nitrophenol compounds, the TNR contaminated water could be treated by many methods such as adsorption, advanced oxidation processes (AOPs), chemical reduction or bioremediation. However, there was some issues about economics, equipment, or efficiency when applying these methods [2].

Nowadays, cold plasma technology such as dielectric barrier discharge (DBD) is promising in environmental pollution control. This is a new and advanced technology due to its many advantages compared to other traditional technologies, by forming a plasma that produces ultraviolet (UV), ozone (O₃), H₂O₂ and hydroxyl free radicals (•OH) in situ through electrical discharge at the surface of the electrode exposed to liquid or air [3-6] . Therefore, it can degrade the organic pollutants into CO₂, H₂O, and small-molecule compounds, the TNR contaminated water could be treated by many methods such as adsorption, advanced oxidation processes (AOPs), chemical reduction or bioremediation. However, there was some issues about economics, equipment, or efficiency when applying these methods [2].
carboxylic acid by the active particles produced during the discharge process [7]. The mechanism of the active species formation is described as follows [8, 9]:

(i) The process of ozone formation under the action of electric sparks:

\[ \text{O}_2 + h\nu \rightarrow \text{O} + \text{O} \]  

(1)

\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]  

(2)

(ii) The process of free hydroxyl formation when ozone is dissolved in water:

\[ \text{O}_3 + \text{OH} \rightarrow \text{O}_2 \dddot{\cdot} + \dddot{\cdot}\text{OH} \]  

(3)

\[ \text{O}_2 \dddot{\cdot} \rightarrow \dddot{\cdot}\text{O} + \dddot{\cdot}\text{O} \]  

(4)

\[ \dddot{\cdot}\text{OH} + \text{H}_2\text{O} \rightarrow \dddot{\cdot}\text{OH} + \dddot{\cdot}\text{OH} \]  

(5)

(iii) The process of free hydroxyl formation when energy electrons collide with water vapor molecules:

\[ \text{e}^- + \text{H}_2\text{O} \rightarrow \dddot{\cdot}\text{OH} + \dddot{\cdot}\text{H} + \text{e}^- \]  

(6)

(iv) The process of forming free hydroxyl when atomic oxides react with water vapor molecules:

\[ \text{O} + \text{H}_2\text{O} \rightarrow \dddot{\cdot}\text{OH} + \dddot{\cdot}\text{OH} \]  

(7)

The impact of the high energy electrons of plasma and ozone chemistry on water molecules will result in more \( \dddot{\cdot}\text{OH}, \dddot{\cdot}\text{H}, \dddot{\cdot}\text{O} \), especially free radicals \( \dddot{\cdot}\text{OH} \) - a very strong oxidizing agent (oxidation potential of \( \dddot{\cdot}\text{OH} \) is 2.8 eV [11], which is much higher than that of other oxidizing agents), which are capable of decomposing most organic compounds. In addition, the combination of these agents also results in AOPs, which are capable of handling a wide variety of recalcitrant organic compounds presented in wastewater.

The degradation of TNR in aqueous solution by cold plasma technology has not yet been studied. This is the reason why this study was conducted to investigate the possibility of TNR degradation from aqueous solution by cold plasma. Furthermore, the degradation processes of TNR in the presence of \( \text{O}_2, \text{H}_2\text{O}_2 \) and \( \text{Na}_2\text{S}_2\text{O}_8 \) were also examined.

Materials and Methods

Materials

Analytical purity grade of solvents, chemicals and 2,4,6-Trinitroresorcinol were obtained from Merck, U.S.A and used without further purification. All the solutions were prepared prior to carrying out experiments and kept at room temperature.

Experimental Setup

The schematic diagram of dielectric barrier discharge (DBD) system is shown in Fig. 1. It consists of a homemade high voltage power supply and a coaxial cylindrical reactor. The outer quartz glass tube has inner and outer diameters of 28 and 34 mm, respectively. The inner tube is a stainless steel (SUS 316) ground electrode with a diameter of 21 mm. The two coaxial tubes were fixed on a Teflon insulated base. The plastic base was drilled for removing water from the plasma reactor. The outer electrode is made of copper foil glued to the outside of the quartz tube with a length of 20 mm. The TNR solution was circulated by a diaphragm pump with a flow rate of 450 mL/min and was made to flow as a film on the outer surface of the inner tube. The voltage of insulating glass tubes was always high to obtain electrical sparks, which spread around the pipe evenly without pipe breakdown. A high voltage source (from 10 to 19 kV) was connected the electrodes. DBD-cold plasma was obtained between a water layer and the inner surface of tube, because of sparks discharged in air between the outer surface of water layer and inside quartz tube. An air blower (Quarium SB-348A, China) was employed to supply air (3 L/min) inside and outside the quartz tube of plasma chambers for enhancing ozone generation and ozone dissolution in water. For every experiment, 500 mL solutions were added into the reactor.

Sample Preparation

TNR solution at initial concentration of 150 mg/L and a volume of 500 mL was used to test the effect of input power, circulating flow, initial pH value, electrode distance and oxidizing agents on the degradation by cold plasma. The input power of 250 W and circulating flow of 450 mL/min was employed to investigate the effect of initial pH value, electrode distance and oxidizing agents on the degradation by cold plasma.

Analytical Methods

TNR concentration was measured via a high performance liquid chromatography (Agilent, USA, 1100 Series) with a Hypersil C18 (200 × 4 mm) column as stationary phase. The mobile phase consisted of 65% acetonitrile and 35% water, the flow rate was...
0.35 mL/min, and the injection volume was 5 µL. The column temperature was kept at 25°C and a UV detector was set at 420 nm. The solution pH value were measured using a pH meter (Oaklon, USA).

The degradation efficiently for each sample was calculated from the following Eq:

$$\eta = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\%$$  \hspace{1cm} (13)

...where \( \eta \) was TNR degradation efficiency (%); \( C_t \) was TNR residual concentration at a given time \( t \) (mg/L); \( C_0 \) was TNR initial concentration (mg/L).

**Results and Discussion**

**Effect of the Input Power on Degradation of TNR**

Fig. 2 showed the degradation efficiency of TNR with different input powers using cold plasma. It was indicated that TNR could be effectively removed from aqueous solution by cold plasma and increasing input power favored the degradation process. With initial TNR concentrations of 135 mg/L, the discharge time of 120 min, 52.8%, 90.3% and 100% of TNR was removed when the input powers were 130, 250 and 370 W, respectively. However, regarding the strength of quartz tube, at the input power of 370 W, there is an appeared phenomenon of puncture of quartz tube by electric sparks. Therefore, the input power of 250 W was chosen for the next experiments.

**Effect of the Initial Concentrations on Degradation of TNR**

The results in Fig. 3 show that, when the initial TNR concentration increases, the discharge time also increases. With the initial TNR concentration of 61.7 mg/L, after 120 minutes of discharge, the removal efficiency of TNR reached 100%. Meanwhile, with the initial concentration of 115.6 mg/L and 175 mg/L, the removal efficiency of TNR after 120 minutes was only 93.32% and 69.63%, respectively. In addition, an increase in the initial TNR concentration also enhanced the degradation rate due to the increased contact between the pollutant molecule and the oxidizing agents formed from the cold plasma.
Effect of the Initial pH on Degradation of TNR

The process of discharging electric sparks in the air not only forms oxidizing agents such as ozone, \( \text{H}_2\text{O}_2 \), UV light ... and \( \cdot \text{OH} \) radicals, but also produces nitrogen compounds such as nitrates (\( \text{NO}_3^- \)), nitrites (\( \text{NO}_2^- \)) that make reduce the pH of the solution during discharge \([3, 4, 6, 9, 10, 12, 13]\). Therefore, in order to study the effect of initial pH on the removal efficiency of TNR, Borat buffer solution was used. The initial pH values of the TNR solution were selected as 3.2, 7.0 and 11.

The results in Fig. 4 show that TNR degradation efficiency in acidic medium is much higher than that in neutral and alkaline medium. This can be explained by the fact that an acidic medium is more conducive to the formation of \( \text{O}_3 \) and \( \cdot \text{OH} \) than an alkaline medium due to the oxidation potential of oxidizing agents such as \( \text{O}_3 \), \( \text{H}_2\text{O}_2 \) and radical \( \cdot \text{OH} \) in an acid medium lower in alkaline medium \([5, 14]\). Moreover, in acidic medium, \( \text{H}_2\text{O}_2 \) compounds can be decomposed into two \( \cdot \text{OH} \) radicals by cold plasma (Eq. 14). In addition, in alkaline medium, there is an increase in reaction between \( \text{H}_2\text{O}_2 \) with OH radicals (Eq. 15) \([15-18]\).

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow \cdot \text{OH} + \cdot \text{OH} \quad (14)
\]

\[
\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (15)
\]

In addition, Grabowski (2006) \([7]\) reported that the amount of \( \text{O}_3 \) generated in the plasma region is the highest at low pH (pH = 3.27). This is also one of the reasons why the TNR degradation efficiency in acidic medium is higher than that of neutral and alkaline medium.

Effect of Circulating Flow on Degradation of TNR

Research on the effect of the solution circulation on the TNR removal performance was performed in three circulation modes: 176, 450 and 833 mL/min. In which, the circulating flow of 176 mL/min is the smallest one that meets the amount of water creating a thin film of water evenly around the stainless steel tube electrode (Fig. 1). The results of the decomposition efficiency of TNR are presented in Fig. 5.

The results in Fig. 5 show that the higher the circulating flow, the greater the TNR removal efficiency. The result can be explained by the fact that when the circulating pump flow is large, the high level of fluid disturbance leads to uniform distribution of contaminants in the system, improving treatment efficiency. Moreover, when the circulating flow increases, combined with increasing the contact surface between the liquid and gas phases, the phase contact surface is always refreshed, leading to the mass transfer rate of oxidizing particles such as \( \text{O}_3 \), \( \text{H}_2\text{O}_2 \), \( \cdot \text{OH} \) is enhanced, therefore the organic compounds treatment efficiency is improved \([7]\).

Effect of Electrode Distance on Degradation of TNR

The electrode distance has a great effect on the discharge to form cold plasma. Under the same conditions, when the distance between the two electrodes decreases, the potential (U) of plasma is reduced, which means reducing the power of the generator, saving electrical energy. The studies of H. Krause et al. \([19]\) and Y. Zhang et al. \([20]\) both stated that the voltage decreases when narrowing the gap between the two electrodes. However, a too narrow
Degradation of 2,4,6-Trinitroresorcinol in Aqueous...

Effect of Some Oxidizing Agents on Degradation of TNR

The purpose of this study is to evaluate the ability to activate some oxidants in the cold plasma reaction system to improve the removal rate of TNR. The factors selected to study include:

(i) H2O2: Adding H2O2 (with molar ratio TNR/H2O2 = 10) to the plasma reaction system to increase the original concentration *OH in the solution based on the reaction:

\[
\text{H}_2\text{O}_2 + 2\text{O}_3 \rightarrow 2\text{*OH} + 3\text{O}_2 \quad (16)
\]

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{*OH} \quad (17)
\]

\[
\text{H}_2\text{O}_2 + \text{O}_3 + \text{H}_2\text{O} + \text{hv} \rightarrow 4\text{*OH} + \text{O}_2 \quad (18)
\]

(ii) Na2S2O8: Adding Na2S2O8 (with molar ratio TNR/Na2S2O8 = 10) to the plasma reaction system to activate persulfate ions to create SO4⁻* radicals. SO4⁻* radical has very strong oxidizing properties with reduction potential \( E_\circ = 2.6 \text{ V} \) [6]. Non-selective reactivity of SO4⁻* radical with organic compounds similar to *OH radical (\( E_\circ = 2.8 \text{ V} \)) [11, 21]. The general reaction that activates persulfate to form sulfate SO4⁻* free radicals can be described as follows:

\[
\text{S}_2\text{O}_8^{2-} + \text{activating agent} \rightarrow 2\text{SO}_4^{-\bullet} \quad (19)
\]

Activating agents here can be temperature, UV light, transition metal, microwave, magnetite, etc.

(iii) O2: The pure oxygen gas is introduced into the cold plasma reaction system at a flow rate of 3 L/min (redundancy) to enhance the ozone generation (O3) according to the reactions (1) and (2).

The results in Fig. 7 show that all 3 chemicals added to the plasma reaction system have the ability to improve the TNR removal efficiency of the cold plasma. In particular, H2O2 gives the highest removal efficiency, many times higher than that of other reaction systems. Specifically, within the first 15 minutes of treatment, the TNR removal efficiency of the plasma/H2O2 system has reached 90%. It is higher 1.7 times of the plasma/O2 system.
system, 2.1 times the plasma/Na$_2$S$_2$O$_8$ system and 2.9 times of the plasma/air system. And in just 60 minutes, the entire amount of TNR in the solution was removed. Meanwhile, for plasma/O$_2$ and plasma/Na$_2$S$_2$O$_8$, it takes 90 to 120 minutes to remove all pollutants. The reason may be that the addition of H$_2$O$_2$ will create more reactions based on advanced oxidation AOPs such as UV/H$_2$O$_2$; UV/H$_2$O$_2$/O$_3$; H$_2$O$_2$/O$_3$ compared with the addition of Na 2S2O8 and O 2. In addition, unlike the plasma/O$_2$ reaction system, which is a heterogeneous (gas/liquid) reaction, the reaction efficiency depends much on the mass transition of O$_3$ from the gas phase to the liquid phase, the reaction of the plasma/H$_2$O$_2$ system is a homogeneous reaction (liquid/liquid), it is capable of creating more direct oxidizing agents of pollutants.

As the degradation curves in Fig. 7 appeared to be exponential, an attempt was made to apply the data to the integral rate equation for the pseudo-first-order reaction Eq. (19).

$$\ln\left(\frac{C}{C_0}\right) = -kt$$

...where $k$ denoted the rate constant (min$^{-1}$). Calculation results are shown in Fig. 8 below.

Fig. 8 shows that the linear correlation coefficient ($R^2$) of the degradation rate constant was quite high. It was 0.9904, 0.9949, 0.9943 and 0.9904 for plasma, plasma/Na$_2$S$_2$O$_8$, plasma/O$_2$ and plasma/H$_2$O$_2$ systems, respectively. This means that the degradation process abided by the regulation of first order reaction kinetics.

### Conclusions

A DBD plasma reactor was used for the degradation of TNR in aqueous solution. The results show that TNR could be effectively removed from aqueous solution by cold plasma. Under the experimental conditions, the TNR removal efficiency was proportional to the input electric power and the circulating flow rate, but inversely proportional to the initial pH, initial concentration and electrode distance. When the input power was 370W, the TNR removal efficiency was the highest, however due to the strength factor of quartz tube, the input power of 250W was chosen. Initial pH significantly influenced on the TNR removal efficiency. Accordingly, in acidic medium, the TNR removal efficiency was higher than that in neutral and alkaline medium and is highest at pH = 3.2. The presence of some oxidizing agents in the solution such as H$_2$O$_2$, Na$_3$S$_2$O$_8$, O$_2$ greatly increased the TNR removal efficiency under the effect of cold plasma. The TNR removal efficiency increased gradually by the range of plasma/H$_2$O$_2$>plasma/O$_2$>plasma/Na$_2$S$_2$O$_8$>plasma. The TNR degradation process in the presence and absence of the oxidizing agents all abided by the regulation of first order reaction kinetics.

**Acknowledgement**

The authors gratefully acknowledge Prof. Dang Kim Chi, Hanoi University of Science and Technology and Assoc. Prof. Tran Van Chung, Institute of Chemistry and Materials, Hanoi, Vietnam for their assistance with particular technique and methodology.

**Conflict of Interest**

The authors declare that there is no conflict of interests regarding the publication of this article.

**References**

1. LIU L.H., LIN Y., HE Q. Pretreatment of lead 2, 4, 6-trinitroresorcinol wastewater by Fe-C internal electrolysis process. Advanced Materials Research, 955–959, 1955, 2014.
2. RODGERS J.D., BUNC E.N.J. Treatment methods for the remediation of nitroaromatic explosives. Water Research, 35 (9), 2101, 2001.
3. RONG S.P., SUN Y. B., ZHAO Z.H. Degradation of sulfadiazine antibiotics by water falling film dielectric barrier discharge. Chinese Chemical Letters, 25 (1), 187, 2014.
4. JIANG B., ZHENG J., QIU S., WU M., ZHANG Q., YAN Z., XUE Q. Review on electrical discharge plasma technology for wastewater remediation. Chemical Engineering Journal, 236, 348, 2014.
5. LI S., WANG X., LIU L., GUO Y., MU Q., MELLOUKI A. Enhanced degradation of perfluorooctanoic acid using dielectric barrier discharge with La/Ce-doped TiO$_2$. Environmental Science and Pollution Research, 24 (18), 15794, 2017.
6. CHEN, J., FENG J., LU S., SHEN Z., DU Y., PENG L., ZHANG A. Non-thermal plasma and Fe$^{2+}$ activated persulfate ignited degradation of aqueous crystal violet:
Degradation mechanism and artificial neural network modeling. Separation and Purification Technology, 191, 75, 2018.

7. GRABOWSKI L.R., VAN VELDHUIZEN E.M., PEMEN A.J.M., RUTGERS W.R. Corona above water reactor for systematic study of aqueous phenol degradation. Plasma Chemistry and Plasma Processing, 26 (1), 3, 2006.

8. DORS M. Plasma for water treatment. Lecture. 1, 2013. Available online: https://www.yumpu.com/en/document/read/8848153/plasma-water-treatment-plastep

9. BRUGGEMAN P.J., KUSHNER M.J., LOCKE B.R., GARDENIERS J.G.E., GRAHAM W.G., GRAVES D.B., ZVEREVA G. Plasma-liquid interactions: A review and roadmap. Plasma Sources Science and Technology, 25 (5), 053002, 2016.

10. MAGUREANU M., BRADU C., PARVULESCU V I. Plasma processes for the treatment of water contaminated with harmful organic compounds. Journal of Physics D: Applied Physics, 51, 313002, 2018.

11. RADHA K.V., SIRISHA K. Electrochemical Oxidation Processes. Advanced Oxidation Processes for Wastewater Treatment: Emerging Green Chemical Technology, 359, 2018.

12. LUKES P., DOLEZALOVA E., SISROVA I., CLUPEK M. Aqueous-phase chemistry and bactericidal effects from an air discharge plasma in contact with water: Evidence for the formation of peroxynitrite through a pseudo-second-order post-discharge reaction of H₂O₂ and HNO². Plasma Sources Science and Technology, 23 (1), 2014.

13. CREMA A.P.S., PIAZZA BORGES L.D., MICKE G.A., DEBACHER N.A. Degradation of indigo carmine in water induced by non-thermal plasma, ozone and hydrogen peroxide: A comparative study and by-product identification. Chemosphere, 244, 125502, 2020.

14. CHEN X.H., BIAN W.J., SONG X.H., LIU D.Q., Z.J. Degradation of 4- chlorophenol in a dielectric barrier discharge system. Sep Purif Technol, 120, 102, 2013.

15. ANH THU N., JUANG R.-S. Photocatalytic degradation of chlorophenol by hybrid H₂O₂ and TiO₂ in aqueous suspensions under UV irradiation. J Environ Manag, 147, 271, 2014.

16. ZHANG J.B., ZHENG Z., ZHANG Y.N., FENG J.W., L. J. Low-temperature plasma-induced degradation of aqueous 2,4-dinitrophenol. J Hazard Mater, 154, 506, 2008.

17. FAHMY A., EL-ZOMRAWY A., SAEED A.M., SAYED A.Z., EZZ EL-ARAB M.A., SHEHATA H.A. Modeling and optimizing Acid Orange 142 degradation in aqueous solution by non-thermal plasma. Chemosphere, 210, 102, 2018.

18. ASGHAR A., RAMAN A.A.A., DAUD W.M.A.W. Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: A review. Journal of Cleaner Production, 87 (1), 826, 2015.

19. KRAUSE H., SCHWEIGER B., PRINZ E., KIM J., STEINFELD U. Degradation of persistent pharmaceuticals in aqueous solutions by a positive dielectric barrier discharge treatment. Journal of Electrostatics, 69 (4), 333, 2011.

20. ZHANG Y., ZHENG J., QU X., CHEN H. Design of a novel non-equilibrium plasma-based water treatment reactor. Chemosphere, 70 (8), 1518, 2008.

21. GLIGOROVSKI S., STREKOWSKI R., BARBATI S., VIONE D., UNIVERSITE A., UMR L.C.E. Environmental Implications of Hydroxyl Radicals (•OH ). Chem. Rev, 115 (24), 13501, 2015.
