Mathematical model simulation of the reaction process between 2,4,6-trinitrotoluen and hydroxyl radio in water environment

Minh Tien Nguyen¹*, Anh Kien Le¹, Anh Kiet Huynh¹ and Duc Trung Le²

¹Institute For Tropical Technology And Environmental Protection, Institute Of Science Technology And Military, Viet Nam.
²Institute Of Environmental And Natural Resources, Viet Nam National University HCMC, Viet Nam.

*Corresponding author’s e-mail: tien92.nb@gmail.com

Abstract: In this study, the author formulated the equation that describes the reaction rate (mathematical modelling) of 2,4,6-trinitrotoluen and hydroxyl radical (OH*) of \( v = 4.3 \times 10^8 x [C_{TNT}]^{1.1} x [C_{OH*}]^{3.2} \) and mathematical simulation for the reaction process of 2,4,6-trinitrotoluen and OH* radical. The simulation results showed a decrease in concentration \([C_{TNT}]\) and a reaction rate proportional to each other; during the first 0-30 minutes of the reaction, the reaction speed is very fast. From the experimental results, the authors also determined that the 2,4,6-trinitrotoluen treatment performance in wastewater of the nonthermal plasma model reached >99% when increasing the treatment time to 120 minutes.

1. Introduction

2,4,6-trinitrotoluene (TNT) is one of the chemicals widely used in the military field and has many applications in the mining industry. In nature, TNT is difficult to decompose and affects human and animal health when entering the body through the skin, respiratory tract, digestive tract. There have been many research works, using different methods for treating TNT in wastewater [1, 2, 4, 5, 6, 8, 10, 13, 14, 16] such as physical methods (absorption, extraction, combustion), chemical methods (Fenton, UV/H₂O₂, O₃/H₂O₂, TiO₂ photochemical catalyst, electrolytic oxidation), biological methods (microorganisms, enzymes, plants) and these methods still have some limitations such as unstable performance, which depends heavily on the structure of the substances and the initial concentration, generate by-products.

Nonthermal plasma is a new technology and has the ability to indirectly generate strong oxidizing agents such as OH* radical, so plasma technology has high potential for application in wastewater treatment [11, 12]. The mathematical simulation is based on assumptions that allow the process to be predicted under different conditions and can be optimized and controlled for specific purposes [9, 15]. Therefore, this study was carried out to simulate the reaction process of TNT compounds and OH* radical to be able to optimize the design and operation of practical application models with high efficiency.

2. Materials and research methods
2.1. Research materials
Preparation of simulated wastewater samples containing TNT compounds: using acetoneitrile (CH$_3$CN) and methanol (CH$_3$OH) solvents to dissolve 1 gram of TNT crystals (99.8% purity) at a ratio of 50:50 to produce a TNT solution of 1,000 mg/l. Depending on the experiment, the TNT solution will be diluted at the appropriate concentration, the diluted sample will be stored for analysis to obtain the input TNT concentration value.

2.2. Research models
The diagram and experimental model are shown as Figure 1.

Figure 1. Diagram and model of experimental nonthermal plasma
Specifications of the model:
- High voltage source: $P_{\text{max}} = 120W$, $U_{\text{max}} = 15kV$, $f = 31kHz$;
- Plasma chamber:
  + Quartz glass tube: Ø34mm, 3mm thick, 35cm high;
  + Internal electrode: inox 316 tube, Ø22mm, 1.5mm thick, 30cm high;
  + External electrode: copper leaf, area $S = 32 \text{ cm}^2$;
  + Distance of 2 electrodes: 3mm;
- Circulating pump: SMART pumps (China), Model: MP-6R;
- Air pump: ATMAN (China), Model: HP 4000;
- Volume of water tank: 20 liters (experimental volume: 5 liters/batch).

2.3. Research methods

2.3.1. Set up experimental model.
The experiment was conducted as alternate batches (5 liters each reaction batch). The wastewater containing TNT is pumped circulating from the container onto the plasma column in the direction from the bottom up inside the stainless steel electrode tube with a diameter of 22mm and overflowing outside the tube through the plasma area and back to the container, the solution flow is adjusted by the valve system and monitoring through the flowmeter. Natural air is supplied into the plasma chamber in a top-down direction by an air supply pump, controlled air flow, adjusted by the flowmeter. Nonthermal plasma is generated from a high-voltage source with a frequency of 31 kHz, the voltage adjustment range is from 10-15 kV through the stepless transformer LiOA SD 255.

2.3.2. Sample preservation method.
The sample must be stored in a black glass bottle, with a lid and refrigerated at a temperature of about 1-5°C (if analyzed for 24 hours) and or -18°C (if analyzed for 05 days), to ensure uniformity, less degeneration and reduce the error of the analysis results.

2.3.3. Method for determination of TNT concentration.
Determine the concentration of TNT by high performance liquid chromatography coupled to mass spectrometry (HPLC/MS) according to Method 8330B and refer to methods EPA 3510C, EPA 3535A, EPA 3540C. The main equipment for the method:
- HPLC Agilent Technologies 1200 Series and LC/MS probes: using Agilent Technologies 6130 system
- Chromatographic column: The reverse phase chromatography column C-18 is 5 μm in size, 4.6 mm in diameter, 150 mm in length.
- Drying column - Use a tube containing about 5-7gram of Na$_2$SO$_4$ to remove water from the extract (do not let Na$_2$SO$_4$ go into the extract).
- Vacuum System - Capable of maintaining a vacuum pressure of about 13 cmHg and can reach up to 66 cmHg.

2.3.4. Determination of processing efficiency ($H$, %).

$$H = \frac{C_0 - C_t}{C_0} \times 100$$

$H$ is processing efficiency (%); $C_0$ is Initial concentration of substance A (mg/L); $C_t$ is concentration of substance A at time t (mg/L).
2.3.5. Determine the initial rate of the reaction (M/s).

\[ v = \frac{M_0 - M_t}{\Delta t} \]

\( v \) is the initial rate of the reaction (mol/s); \( M_0 \) is initial molar concentration of substance A; \( M_t \) is molar concentration of substance A at time t.

3. Results and Discussion

3.1. Construct a mathematical description for the reaction between the 2,4,6-trinitrotoluene compound and the \( \text{OH}^* \) radical

The reaction equation of the TNT compound and \( \text{OH}^* \) radical is written in a shortened form as follows:

\[ \text{C}_7\text{H}_5\text{N}_3\text{O}_6 + 39 \text{OH}^* \rightarrow 7 \text{CO}_2 + 22 \text{H}_2\text{O} + 3 \text{NO}_3^-(\text{PT}) \]

The rate of the PT-1 reaction is written as: \( v = k [\text{C}_{\text{TNT}}]^m [\text{C}_{\text{OH}^*}]^n \). In which: \( k \) is the reaction rate constant, \( k = 4.3 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1} \) [3]; \( m, n \) is the order of the reaction and determined experimentally; \([\text{C}_{\text{TNT}}]\) and \([\text{C}_{\text{OH}^*}]\) are respectively the molar concentrations of TNT and \( \text{OH}^* \) radical.

3.1.1. Determine the reaction tier \( m \).

To determine the \( m \) reaction tier according to the TNT compound, we choose constant \([\text{C}_{\text{OH}^*}]\) concentration \(([\text{C}_{\text{OH}^*}] = a \text{ (M)})\) and \([\text{C}_{\text{TNT}}] > [\text{C}_{\text{OH}^*}]\). According to the experimental results, we have:

| Table 1. The molar concentration (M) of the TNT participating in the reaction |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| [\text{C}_{\text{TNT}}]_o [mg/L] | [\text{C}_{\text{TNT}}] [mg/L] | [\text{C}_{\text{TNT}}]_{\text{react}} [mol/L] | Initial rate of reaction (M/s) |
| Experiment 1 | 3.9 | 1.72x10^{-5} | 1.270 | 2.630 | 1.16x10^{-5} | 1.29x10^{-8} |
| Experiment 2 | 8.7 | 3.83x10^{-5} | 2.175 | 6.525 | 2.87x10^{-5} | 3.19x10^{-8} |

Note: \([\text{C}_{\text{TNT}}]\) remaining after the first \( t = 15 \text{ min} \) of the reaction.

According to the reaction rate equation \( v = k [\text{A}]^m [\text{B}]^n \), we have:

\[ 1.29x10^{-8} = k [1.72x10^{-5}]^m [a]^n \]
\[ 3.19x10^{-8} = k [3.83x10^{-5}]^m [a]^n \]
\[ \Rightarrow 3.19x10^{-8} = k [3.83x10^{-5}]^m [a]^n \]
\[ \Rightarrow m \times \log(2.23) = \log(2.47) \]
\[ \Rightarrow m = 1.1 \]

Thus, the \( m \)-reaction tier determined by the TNT compound is \( m = 1.1 \).

3.1.2. Determine the reaction tier \( n \)

To determine the \( n \) reaction tier according to the \( \text{OH}^* \) radical, we choose constant \([\text{C}_{\text{TNT}}]\) concentration \(([\text{C}_{\text{TNT}}] = b \text{ (M)})\) and \([\text{C}_{\text{TNT}}] > [\text{C}_{\text{OH}^*}]\), we have:

| Table 2. The initial rate of the reaction is determined by \( \text{OH}^* \) concentration |
|-----------------|-----------------|-----------------|-----------------|
| [\text{C}_{\text{OH}^*}]_o [cm^3] | [\text{C}_{\text{TNT}}] [cm^3] | [\text{C}_{\text{TNT}}]_{\text{react}} [cm^3] | Initial rate of reaction (M/s) |
| Experiment 3 | 2.01x10^{-12} | b | 4.52x10^{-4} | 5.03x10^{-7} |
| Experiment 4 | 2.68x10^{-12} | b | 1.12x10^{-3} | 1.24x10^{-6} |

\( ^* \text{Determined based on the molar ratio of TNT and } \text{OH}^* \text{ radical in PT-1 reaction is } \frac{n_{\text{TNT}}}{n_{\text{OH}^*}} = 1 : 39. \)
According to the reaction rate equation \( v = k [A]^m [B]^n \), we have:

\[
5.03 \times 10^{-7} = k [C_{\text{TNT}}]^m [C_{\text{OH}^*}]^n \\
1.24 \times 10^{-6} = k [C_{\text{TNT}}]^m [C_{\text{OH}^*}]^n
\]

\[
\Rightarrow \frac{1.24 \times 10^{-6}}{5.03 \times 10^{-7}} = \frac{k [C_{\text{TNT}}]^m [C_{\text{OH}^*}]^n}{k [C_{\text{TNT}}]^m [C_{\text{OH}^*}]^n}
\]

\[
\Rightarrow 1.33^n = 2.49
\]

\[
\Rightarrow n \times \log(1.33) = \log(2.49)
\]

\[
\Rightarrow n = 3.2
\]

Thus, the m-reaction tier determined by the OH* radical is \( n = 3.2 \).

With the reaction order \( m = 1.1 \) and \( n = 3.2 \), we have the equation representing the reaction rate (mathematical modelling) of the TNT and OH* radical is \( v = 4.3 \times 10^8 \times [C_{\text{TNT}}]^{1.1} \times [C_{\text{OH}^*}]^{3.2} \) with \([C_{\text{TNT}}], [C_{\text{OH}^*}]\) are respectively the concentrations of TNT and the OH* radical in the reaction.

### 3.2. Mathematical modelling for the reaction between the 2,4,6-trinitrotoluene compound and the OH* radical

#### 3.2.1. Mathematical modelling according to the equation representing the reaction rate between the TNT and OH* radical: \( v = 4.3 \times 10^8 \times [C_{\text{TNT}}]^{1.1} \times [C_{\text{OH}^*}]^{3.2} \).

From the experimental results, we have the molar concentration of TNT compound participating in the reaction shown in Table 3:

| Times (minute) | Experiment 1 \([C_{\text{TNT}}]_o = 3.9 \text{ mg/L}\) | Experiment 2 \([C_{\text{TNT}}]_o = 8.7 \text{ mg/L}\) | Experiment 5 \([C_{\text{TNT}}]_o = 18.3 \text{ mg/L}\) | Experiment 6 \([C_{\text{TNT}}]_o = 27.3 \text{ mg/L}\) |
|--------------|-----------------|-----------------|-----------------|-----------------|
| 0            | 0               | 0               | 0               | 0               |
| 15           | 1.16 \times 10^5 | 2.87 \times 10^5 | 4.89 \times 10^5 | 5.70 \times 10^5 |
| 30           | 1.57 \times 10^5 | 3.55 \times 10^5 | 6.07 \times 10^5 | 8.41 \times 10^5 |
| 45           | 1.59 \times 10^5 | 3.72 \times 10^5 | 7.25 \times 10^5 | 1.02 \times 10^5 |
| 60           | 1.56 \times 10^5 | 3.75 \times 10^5 | 7.69 \times 10^5 | 1.06 \times 10^5 |
| 75           | 1.68 \times 10^5 | 3.75 \times 10^5 | 7.78 \times 10^5 | 1.08 \times 10^5 |
| 90           | 1.69 \times 10^5 | 3.77 \times 10^5 | 7.85 \times 10^5 | 1.10 \times 10^5 |
| 105          | 1.71 \times 10^5 | 3.78 \times 10^5 | 7.88 \times 10^5 | 1.15 \times 10^5 |
| 120          | 1.71 \times 10^5 | 3.80 \times 10^5 | 7.99 \times 10^5 | 1.16 \times 10^5 |
| 135          | 1.71 \times 10^5 | 3.83 \times 10^5 | 8.00 \times 10^5 | 1.18 \times 10^5 |
| 150          | 1.72 \times 10^5 | 3.83 \times 10^5 | 8.04 \times 10^5 | 1.19 \times 10^5 |
| 180          | -               | -               | -               | 1.19 \times 10^4 |
| 210          | -               | -               | -               | 1.19 \times 10^4 |

According to the calculation results in Table 3, substitute in the equation \( v = 4.3 \times 10^8 \times [C_{\text{TNT}}]^{1.1} \times [C_{\text{OH}^*}]^{3.2} \), we can calculate the reaction rate between TNT compound and OH* radical and show it in Figure 2:
Figure 2. Correlation between concentration attenuation and reaction rate

According to Figure 2 shows, the decrease in $[C_{\text{TNT}}]$ concentration and the reaction rate of the TNT compound and $\text{OH}^*$ radical is proportional to each other and over the first 0-30 minutes the reaction rate is very fast and the concentration $[C_{\text{TNT}}]$ decreases sharply.

3.2.2. Mathematical modelling according to the laws of kinematics.
Experimental results the decrease in TNT concentration over time are presented at Table 4.

| Times (minute) | TNT concentration (mg/L) |
|---------------|--------------------------|
| 0             | 3.900                    |
| 15            | 1.270                    |
| 30            | 0.338                    |
| 45            | 0.292                    |
| 60            | 0.153                    |
| 75            | 0.078                    |
| 90            | 0.070                    |
| 105           | 0.025                    |
| 120           | 0.011                    |
| 135           | 0.007                    |
| 150           | 0.000                    |
| 180           | -                        |
| 210           | -                        |

According to Figure 2 shows, the decrease in $[C_{\text{TNT}}]$ concentration and the reaction rate of the TNT compound and OH* radical is proportional to each other and over the first 0-30 minutes the reaction rate is very fast and the concentration $[C_{\text{TNT}}]$ decreases sharply.

3.2.2. Mathematical modelling according to the laws of kinematics.
Experimental results the decrease in TNT concentration over time are presented at Table 4.
From the equation representing the reaction rate (mathematical modelling) between the TNT compound and OH* radical is \( v = 4.3 \times 10^8 [\text{C}_{\text{TNT}}]^{1.1} [\text{C}_{\text{OH}*}]^{3.2} \). So the order of reaction is 4.3.

According to the law of the reaction tier n, we have:

\[
k = \frac{1}{(n-1)t} \left[ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right] = \frac{1}{3.3t} \left[ \frac{1}{(a-x)^{3.3}} - \frac{1}{a^{3.3}} \right]
\]

With \( a \) is the initial concentration of TNT compound, \( (a-x) \) is the concentration of TNT compound at time \( t \) and the decrease in concentration \( [\text{C}_{\text{TNT}}] \) over time in Table 4, we get a diagram of the relationship between decrease in \( [\text{C}_{\text{TNT}}] \) concentration and reaction rate of TNT and OH* radical (see Figure 3).

**Comment:** According to mathematical simulation of the reaction process between TNT and OH* radical by kinetic law shows the rate and reaction time correlated with each other (see Figure 3), in the first 0-30 minutes of the reaction rate reaction occurs very quickly and then decreases over time.

3.3. Evaluation of the treatment efficiency of 2,4,6-trinitrotoluene compounds in wastewater by nonthermal plasma technology

In order to assess the performance of TNT compound treatment in wastewater using nonthermal plasma technology, the team conducted experiments and fixed them under optimal conditions: \( Q_{\text{dd}} = 1.5 \text{ liters/min}, Q_{\text{ik}} = 5 \text{ liters/min}, P = 120\text{W}, \text{pH} = 9 \). The results of the experiments are shown as shown in Figure 4.

The results of Figure 4 show that the TNT decomposition efficiency tends to increase strongly in the first 30 minutes of the reaction and then decrease gradually. The longer the processing time with nonthermal plasma technology, the greater the contact time and impact of strong oxidizing radical on the TNT molecule, resulting in a sharp decrease in TNT concentration. If the time is longer, the concentration of TNT and the frequency of interaction of TNT and oxidizing agents also decrease. With the input TNT concentrations of 3.9 mg/l and 8.7 mg/l, after 30 minutes the reaction efficiency increased very high (91.3% and 92.7%) and then slowly increase; with an input TNT concentration of 18.3 mg/l that requires 60 minutes of reaction to achieve 95.3% efficiency; as for the input TNT concentration of 27.3 mg/l requires 90 minutes of reaction to achieve 91.8% efficiency. Thus, the higher the concentration of TNT, the longer the processing time required; the appropriate time to achieve high efficiency is 30 minutes with input TNT concentration of 3.9 mg/l, 8.7 mg/l and 90 minutes with input TNT concentration of 18.3 mg/l and 105 minutes, respectively. Corresponding input TNT concentration is 27.3 mg/l. When decomposing pollutants at high concentrations, many intermediate products will be produced, which further reduces the effective interaction energy.
between the plasma source and the active substance because it is evenly divided among the particles in the solution passing through the plasma layer leads to a decrease in the reaction rate between the TNT compound and the OH* radical.

4. Conclusion
The study has built an equation representing the reaction rate (mathematical modelling) of TNT compound and OH* radical as \( v = 4.3 \times 10^8 x[C_{\text{TNT}}]^{1.1-x}[C_{\text{OH}*}]^{3.2} \) with \([C_{\text{TNT}}], [C_{\text{OH}*}]\) are respectively concentrations of TNT and OH* radical. Since then, the study has described mathematically for the reaction process between the TNT compound and the OH* radical. Simulation results show that the decrease in \([C_{\text{TNT}}]\) concentration and reaction rate are directly proportional, in the first 30 minutes of the reaction, the reaction speed is very fast.

Besides, the study also determined that the treatment efficiency of TNT compounds in wastewater by nonthermal plasma model is very high, reaching more than 99% when increasing the treatment time to 120 minutes. The research results will be the basis for evaluating the efficiency of TNT in wastewater treatment by nonthermal plasma technology.

The results of this research will help the application units become more aware of the technology, reduce the number of experiments and determine the optimal conditions when designing, operating, controlling and troubleshooting, thereby building a technological process for wastewater treatment containing TNT compounds in accordance with low investment costs and simple operation.

Acknowledgments
The experimental research was done at the Institute For Tropical Technology And Environmental Protection, Institute Of Science Technology And Military.

References
[1] Dai B Q 2016 Research on internal electrolysis method to treat wastewater contaminated with 2,4,6-trinitrotoluene (Viet Nam: Ha Noi University Of Science and Technology - Master thesis in Engineering).
[2] Byungjin L and Seung W J 2009 Effects of additives on 2,4,6-trinitrotoluene removal and its mineralization in aqueous solution by gamma irradiation J. Hazard. Mater. 165 435-440.
[3] Daniel C S, Kimberly A G and Prashant V K 1998 Radiation-induced reactions of 2,4,6-trinitrotoluene in aqueous solution (Indiana: University of Notre Dame/ Department of Civil Engineering and Geological Science) (32):971-974.
[4] Tiep D L 2017 Research and test nonthermal plasma technology in wastewater treatment with high pollution concentration - A case study with yeast production wastewater of AB Mauri Vietnam Co., Ltd. (Viet Nam: Vietnam National University HCMC/ Institute of Environment and Natural Resources - Master thesis Environmental Engineering).
[5] Khue D N 2004 Current status and some opinions on development orientation of toxic waste treatment technology for national defense, Symp. on Environment (Viet Nam: Scientific And Technical Centers And Military Technology) 35-39.
[6] Khue D N, Cuong P K, Minh D B and Thiep T V 2007 Research on the possibility of decontamination of TNT contaminated wastewater by L. Cyperus alternifolius, J. Sci. Technol. 45 81-87.
[7] Yufang G, Xiaobin L and Daiqi YE 2008 Detection of hydroxyl radical in plasma reaction on toluene removal, Journal of Environmental Sciences 20 1429-1432.
[8] James H 2005 Photocatalytic demethylation of 2,4,6-trinitrotoluene (TNT) by porphyrins, Chemosphere 63 1094-1097.
[9] Makinia J 2010 Mathematical modelling anh computer Simulation of Activated Sludge Systems IWA publishing (London: SW1H 0QS - United Kingdom).
[10] Duc L T, Khue D N, Dat N V, Ha B T and Huong T T T 2004 Research on treatment of TNT containing wastewater by anaerobic biological method, Journal of Engineering Science and Technology Research Military Technology 8.

[11] Mirostaw Dors 2014 Plasma for water treatment Centre for Plasma and Laser Engineering (Polish: Polish Academy of Sciences/ The Szewalski Institute of Fluid-Flow Machinery).

[12] Phuong N T T, Lam N H and Anh D D 2018. Research and application of nonthermal plasma technology to remove organic components and color in textile dyeing wastewater, Environmental Journal (topic 4).

[13] Chat N V 2011 Research on the influence of some oxidizing agents on the photolysis reaction to 2,4,6 trinitrotoluene and 2,4,6 trinitroresocxin (Viet Nam: Institute of Science and Technology Military Technology - PhD thesis in Chemistry).

[14] Roger M, Khalil H and Serge C 2007 Fenton-like oxidation of 2,4,6-trinitrotoluene using different iron minerals, Sci. Total Environ 385 242-251.

[15] Thanh T 2010 Modeling in environmental technology and management (Viet Nam: Hanoi University of Science and Technology/ Institute of Environmental Science and Technology).

[16] Y. Wu, C. Zhao, Q. Wang and K. Ding 2006 Integrated effects of selected ions on 2,4,6-trinitrotoluene-removal by O3/H2O2 J. Hazard. Mater. 132 232-236.