Degradation mechanism of 2,4,6-trinitrotoluene in supercritical water oxidation

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Abstract

The 2,4,6-trinitrotoluene (TNT) is a potential carcinogens and TNT contaminated wastewater, which could not be effectively disposed with conventional treatments. The supercritical water oxidation (SCWO) to treat TNT contaminated wastewater was studied in this article. The TNT concentration in wastewater was measured by high-performance liquid chromatograph (HPLC) and the degraded intermediates were analyzed using GC-MS. The results showed that SCWO could degrade TNT efficiently in the presence of oxygen. The reaction temperature, pressure, residence time and oxygen excess were the main contributing factors in the process. The decomposition of TNT was accelerated as the temperature or residence time increased. At 550°C, 24 MPa, 120 s and oxygen excess 300%, TNT removal rate could exceed 99.9%. Partial oxidation occured in SCWO without oxygen. It was concluded that supercritical water was a good solvent and had excellent oxidation capability in the existence of oxygen. The main intermediates of TNT during SCWO included toluene, 1,3,5-trinitrobenzene, nitrophenol, naphthalene, fluorenone, dibutyl phthalate, alkanes and several dimers based on the intermediate analysis. Some side reactions, such as coupled reaction, hydrolysis reaction and isomerization reaction may take place simultaneously when TNT was oxidized by SCWO.

Key words: supercritical water oxidation; TNT; degradation mechanism; wastewater treatment

Introduction

2,4,6-Trinitrotoluene (TNT) has been widely used as an explosive in military all over the world since 1900s. As a result, a large amount of contaminated wastewater is generated during the manufacture of TNT. In addition, residuals of TNT in soil can pollute both the environment and groundwater system (Nijs and Frank, 2002). TNT is classified as potential carcinogens (Zoh and Stenstrom, 2002) and listed as a significant pollutant to public health and aquatic life by the USEPA (USEPA, 1988). It has remained to be difficult to decontaminate, TNT wastewater. Currently, TNT contaminated water is treated by incineration, activated carbon adsorption (Rajagopal and Kapoor, 2001), biodegradation (Tang, 1995), oxidation with hydrogen peroxide/ozone (Wu *et al.*, 2003), photocatalytic oxidation (Son *et al.*, 2004). These measures are inefficient and can not meet the more rigorous effluent standards. In particular, the residual products with these methods are still pollutants or hazard materials.

Supercritical water oxidation (SCWO) is a high temperature and pressure technology that utilizes the properties of supercritical water to destroy organic compounds and toxic wastes. The SCWO has been used to treat streams, sledges and contaminated soils (Magdalena *et al.*, 2004; Killilea *et al.*, 1992). It can also be used to treat a wide range of contaminants including acrylonitrile, cyanide, pesticide, PCBs, halogenated aliphatic and aromatics, aromatic hydrocarbons, and organic nitrogen compounds (Zhang and Wang, 2003).

In this study, SCWO technology to degrade TNT wastewater and the mechanism of degradation were studied. The results show that SCWO is an effective method in treating TNT wastewater and TNT removal rate can exceed 99.9%.

1 Experiments and methods

1.1 SCWO system

The SCWO system contains reactor, heating apparatus, gas feed, plunger type flow control pump, cooler, gas-liquid separator and waste water tank. A schematic diagram of the SCWO system is shown in Fig.1. The reactor is made of stainless steel ([1]Cr$_{18}$Ni$_9$Ti) with an inside diameter of 55 mm and a free volume of 2.5 L. The reactor is equipped with all auxiliaries such as temperature and pressure indicators and controllers, time-delay device, appropriate valves and relief devices. The exterior surface of reactor is wrapped with high frequency magnetism to heat it. Temperature was controlled within ±2°C of the set
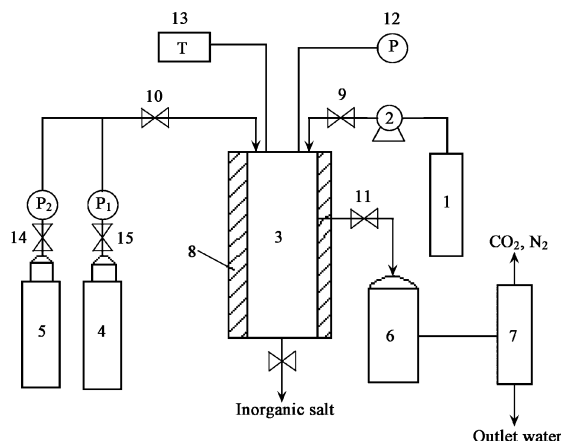
Fig. 1 Process chart of SCWO. (1) wastwater container; (2) high pressure pump; (3) reactor; (4) nitrogen cylinder; (5) oxygen cylinder; (6) cooler; (7) gas and liquid separator; (8) heater; (9) water inlet valve; (10) gas inlet valve; (11) discharge water valve; (12) pressure gauge; (13) thermormeter; (14, 15) relief valve.

point by a temperature controller (XMT6000, NinboYang-ming Electromechanically Co. Ltd., China). The reacting temperature was measured and continuously recorded using thermocouple (WRN, 0–1300°C). The pressure was controlled with a back pressure regulator and measured by a digital gauge (YCD-02A, Anhui Jinda Instrument Co., Ltd., China). When the reactor reached the preset temperature, oxygen was added to the reactor vessel by opening the gas inlet valve. Then TNT wastewater is pumped by a high pressure pump (J-X, 15 L/h, 40 MPa, Hangzhou HuaLi Pumping Industrial Co. Ltd., China) into the reactor vessel. After SCWO, the liquid was collected for sample analysis.

1.2 Materials

Two types of wastewater were used in the study. One was simulated TNT wastewater prepared in laboratory. The other was from the effluent of TNT manufacturing plant. The concentration of simulated TNT wastewater is 100 mg/L which was prepared using industrial grade TNT (375 productions). In preparing the TNT solution, dry TNT was dissolved in acetone, and then acetone was vaporized through adding boiled de-ionized water. The chromaticity of TNT wastewater from the manufacturing plant is higher and its color is crimson and opaque. The TNT concentration of manufacturing plant wastewater was 210 mg/L and its COD_{Cr} value was 60615 mg/L measured using bichromate method (GB 11914-89). The oxygen was used as oxidizer in SCWO process.

1.3 Analytical methods

High-performance liquid chromatograph (HPLC, CXTH-3000, China) and a gas chromatograph coupled with a mass spectrophotometer (GC6890/MS5973, Agilent, USA) were used to analyze TNT and its intermediates. For HPLC analysis, the chromatographic column C_{18} was used with a size of 25 cm × 4.6 mm, 5 μm. The mobile phase was methanol:water (50:50) at a flow rate of 1 ml/min. TNT wastewater sample of 20 μl

was applied to the column at room temperature. A UV detector was used and the wavelength set at 254 nm. For the GC-MS the runs the oven temperature program was as follows: isothermal at 70°C for 5 min, 70–210°C at 5°C/min and 210–250°C at 10°C/min ramping, and 250°C for 10 min.

Five experiments under the same condition were conducted to identify the intermediates. The 1000 ml sample from five experiments was collected, extracted with dichloromethane and concentrated to 2 ml. The sample treatment method is as follows:

To reduce the solubility of organic compounds in water, solid NaCl was added into 1000 ml sample until saturation was reached. After stillness, the residual solid NaCl was removed. Then 300 ml dichloromethane was used to extract the reacted solution thrice. The extracting solution was dried 24 h in anhydrous Na_2SO_4. After filtration of Na_2SO_4, dichloromethane solution was distilled to 2 ml under decompression and kept to be used for GC-MS analysis.

2 Results and discussion

The TNT concentration of wastewater for different experiment conditions was tested by HPLC. TNT removal rate (R) was calculated by Eq.(1) to estimate SCWO efficiency.

$$R = \frac{C_o - C_i}{C_o} \times 100\% \tag{1}$$

where, C_o and C_i are TNT concentration in original wastewater and treatment liquid, respectively.

2.1 TNT degradation

Simulated TNT wastewater was treated under two different conditions. In the first, nitrogen was injected into the reactor until pressure getting to 1 MPa. The purpose of using nitrogen is to investigate the reaction of TNT without oxygen in supercritical water at low concentration. The molecular formula of TNT is $C_7H_5O_6N_3$ and its decomposition temperature is about 280–300°C. Since the TNT molecular contains a large quantity of oxygen, the reaction maybe run by the oxygen. Second, extra oxygen was added in SCWO. To investigate the reaction mechanism of TNT in SCWO, twelve experiments were performed at various temperatures and constant residence time of 120 s. The temperature range was 350–550°C(±2°C). The levels of TNT degradation under different conditions were analyzed using HPLC. Fig.2 shows that oxidation reaction of TNT occurs in supercritical water without oxygen. When the temperature was raised, the TNT concentration reduced. When the reaction temperature was at 500°C, TNT did not exist in simulation wastewater any more. It should be noted that the oxidation reaction without extra oxygen might be due to the oxidative effect of supercritical water and the oxygen in TNT itself.
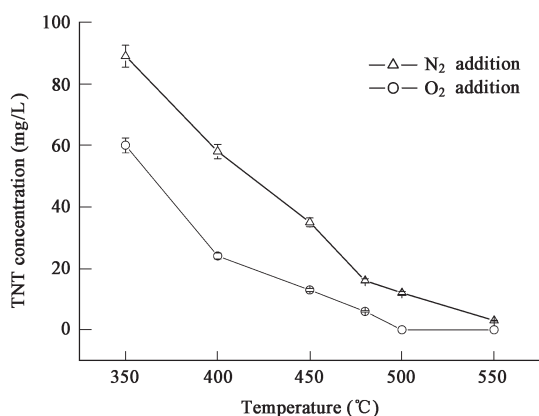
Fig. 2 SCWO of TNT at different temperaturs.

2.2 Influence of operation parameters on SCWO TNT reaction

To study the effect of TNT wastewater treatment in SC-WO, industrial TNT wastewater was tested under different conditions.

2.2.1 Residence time, temperature and pressure

The residence time is also an important factor affecting TNT removal rate. With the reaction time of 90 s and temperature of 500°C, TNT removal rate may reach 93.55% and it continuously increased with reaction time, which are shown in Fig.3a. The effect of residence time on TNT removal rate is very small when it exceeds a definite value. The suitable residence time of SCWO TNT wastewater is about 120 s.
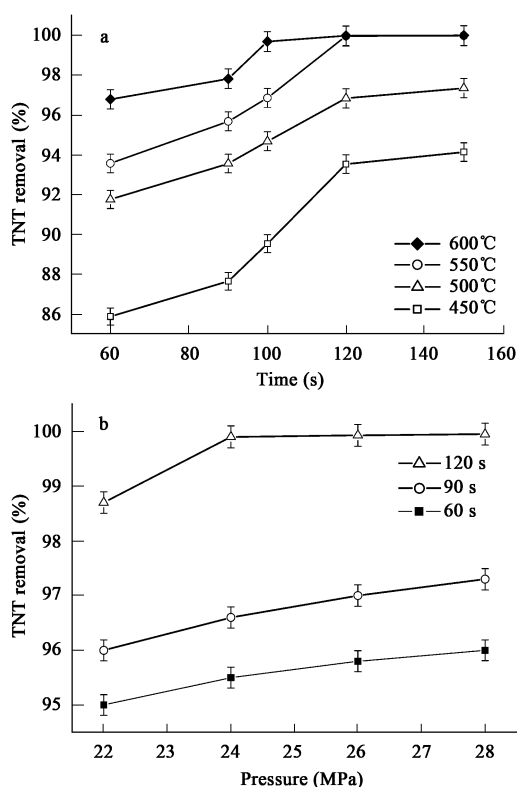

Fig. 3 Influence of temperature (a) and pressure (b) variations.

The influence of temperature on TNT decomposition is shown in Fig.3a under the conditions of pressure 24 MPa and oxygen excess (O$_2$) 300%. It is evident that temperature has a obvious influence on the TNT decomposition rate. TNT removal rate increases very quickly as the temperature rising. After 120 s, TNT removal rate reaches 93.50%, 95.83%, 99.96% and 99.97% at 450, 500, 550 and 600°C, respectively. There may be higher activation energy in SCWO TNT reaction. When temperature is above 550°C, the activation energy barrier is reached and exceeded. The action of rising temperature is increasing kinetic energy of activated molecule or not increasing quantities. The influence of temperature on TNT removal rate is not obvious as SCWO reached definite temperature.

Pressure varied from 22 to 28 MPa at a fixed temperature of 550°C and oxygen excess (O$_2$) of 300%. The effect of pressure on TNT removal rate is shown in Fig.3b.

It is shown that the variation of TNT removal rate is smaller with pressure changes under the same residence time (Fig.3b). The reason may be that pressure influence on water density and other characteristic above 500°C is less than that of the critical state. Since pressure rising accompanied with the increasing density of supercritical water system so as to the density of oxygen, water and organic, TNT removal rate also have definite increasing. The results show that the effect of pressure on TNT removal rate is not obvious.

2.2.2 Excess oxygen

For a low concentration TNT wastewater (<100 mg/L), the TNT can be oxidized with the oxygen in TNT molecule. However, for high concentration TNT wastewater, the oxygen in TNT molecule is not enough to oxidize TNT completely and extra oxygen must be added. Three conditions (100%, 150% and 300% oxygen excess) were selected for comparison under pressure of 24 MPa and residence time of 120 s. The results are shown in Fig.4.

TNT removal rate increased with increasing oxygen excess. The reaction of SCWO is a free-radical reaction and the increasing quantity of oxidant may produce more free-radicals at the first reaction stage leading to fast reaction rate. Then the reaction rate turn to be stationary. The degradation rate of organic is not monotone increasing with the oxygen excess rising and there is an optimum val-
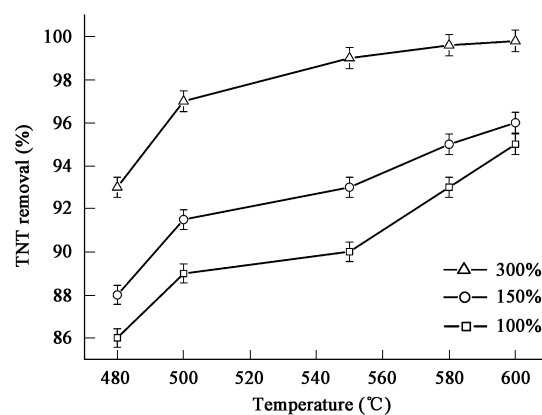

Fig. 4 Effect of oxygen excess on TNT removal rate.

ue in SCWO process. When oxygen exceeds the optimum value, the effect of oxygen excess on TNT removal rate is no obvious. The oxygen excess of 300% in SCWO is suitable for TNT degradation.

2.3 Degradation mechanism

2.3.1 Intermediate analysis

The intermediates in reaction liquid were analyzed with GC-MS to deduce the potential conversion pathway. Five experiments were carried out at 400, 450 and 500°C, respectively. The results are listed in Table1.

As shown in Table 1, the main compositions of the liquid effluent are toluene, trinitrobenzene, alkanes and undegraded TNT at 400°C. At 450°C, the intermediate is mainly composed of toluene, naphthalene, dibutyl phthalate, alkanes and several dimers, such as fluorene, phenanthrene, fluoranthene and bencyclopentanone. When the temperature reaches 500°C, the dimers are decomposed and alkanes, single-ring aromatics are dominant. The variation of intermediate products indicated that many side reactions, such as coupled reaction, hydrolysis reaction and isomerization reaction, happened simultaneously when TNT was oxidized by SCWO. Since the dimers generation is not the results of TNT direct oxidation; these are coupled reaction of phenyl radical. The above results are coincidence with the reports (Gopalan and Savage, 1994; DiNaro et al., 2000).

2.3.2 Degradation mechanism

The supercritical water is a nonpolar solvent. The free radical is easily initiated at high temperature and oxygen-riched conditions. The TNT degradation reaction in SCWO is a freeradical reaction. The free-radical generation relied on O_2 attacking C–H bond of organic molecular. The mechanism reactions can be described as follows:
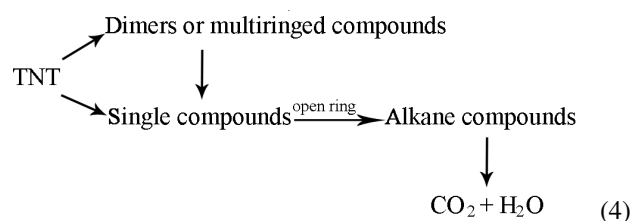
$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot \tag{1}$$

$$HO_2\cdot + RH \longrightarrow R\cdot + H_2O_2 \tag{2}$$

Table 1 Main intermediate products of TNT oxidation

Compound	Peak area ratio (%)		
	400°C	450°C	500°C
Toluene	8.65	3.73	5.58
Naphthalene	2.67	8.67	13.78
Heptane	3.72	4.85	5.35
1,4-Dinitrobenzene	2.56	4.63	7.50
2,6-Dinitrotoluene	7.32	2.52	1.37
Dodecane	2.56	3.85	4.23
Tetradecane	1.83	3.67	4.15
4-Nitrophenol	2.72	2.28	1.36
Phenol	2.35	3.26	5.23
Bencyclopentanone	–	5.83	6.78
9-Fluorenone	–	2.89	11.08
1,3,5-Trinitrobenzene	32.68	10.85	5.32
Phenanthrene	–	2.28	1.76
Anthracene	–	2.69	1.53
Fluoranthene	–	2.85	1.28
Pentacosane	–	1.64	2.18
Dibutyl phthalate	3.54	10.76	11.68
n-Hexadecanoic acid	–	1.27	2.78

Conditions: 24 Mpa, 0 s, and oxygen excess 300%.

Hydrogen peroxide is cleaved into hydroxyl radical:

$$H_2O_2 + M \longrightarrow 2HO\cdot \tag{3}$$

The hydrogen peroxide may also produce hydroxyl radical by pyrolysis on the definite reaction condition and the hydroxyl radical can react with almost any compounds containing hydrogen because of its strong oxidizing property. First, the hydroxyl radical oxidizes side chains of the benzene ring and generated toluene or nitrobenzene. Meanwhile, the phenyl radical of oxidation process in SC-WO may generate coupled reaction under high temperature and pressure leading to dimers or polycyclic compounds, such as naphthalene, fluorine, phenanthrene and so on. Then single- and multi-ringed aromatic products are further oxidized until the benzene ring is opened. After this, the three double-bonds of benzene ring react with free-radical to generate single-bond. The open loop products of linear paraffin are generated with three unsaturation double-bonds vanishing and are further oxidized small molecule compounds.

To study TNT reaction path, Fig.5 shows the variation of the main intermediates content with residence time at 500°C. The relative content of fluorenone reaches the maximum at 50–70 s and naphthalene reaches the maximum less than 50 s. The dinitrobenzene and dibutyl phthalate contents are no obvious change with longer residence time. According to the tendency of intermediates variation, it can be seen that at 400–500°C, 24 MPa, 120 s and oxygen excess 300%, TNT oxidation process in SCWO is similar to that of phenol (Gopalan and Savage, 1995) and benzene (DiNaro et al., 2000). It is expressed as follows:

$$TNT \nearrow \text{Dimers or multiringed compounds} \searrow \\ \text{Single compounds} \xrightarrow{\text{open ring}} \text{Alkane compounds} \\ \downarrow \\ CO_2 + H_2O \tag{4}$$

At first, TNT is degraded in two parallel paths. Its methyl and nitryl are oxidized into single compounds.
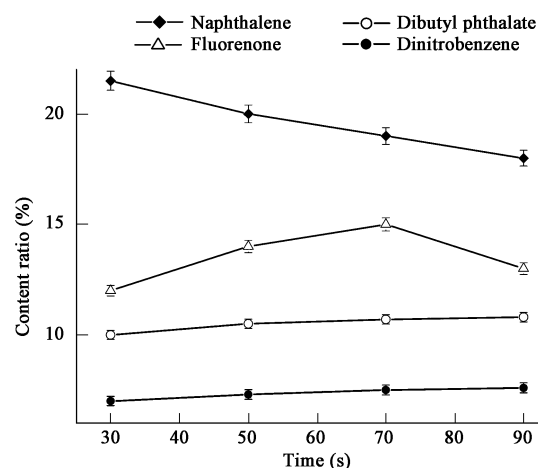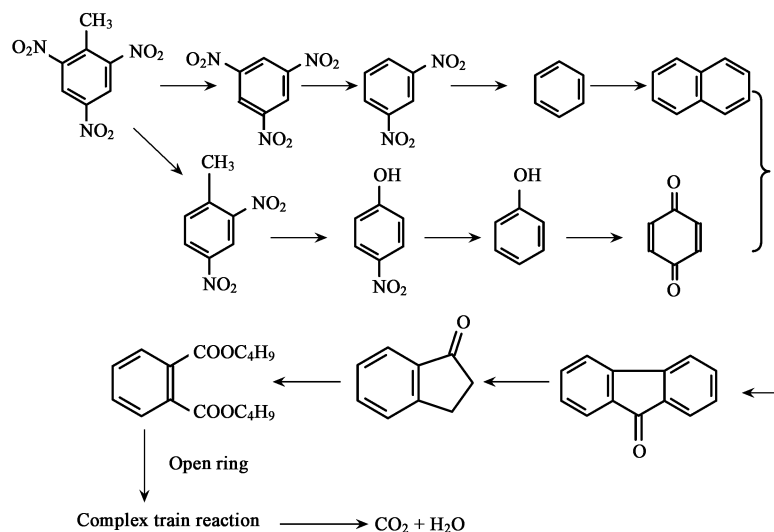

Fig. 5 Variations of organic content with time.

Fig. 6 TNT degradation pathway.

Meanwhile there is coupled reaction of radical leading to dimers or multi-ring compounds. Since the dimers are large in a great temperature range, further oxidation of dimer is the main reaction path. Finally, the ring of single compound is opened generating linear paraffins until final decompositions carbon dioxide and water are generated. The degradation mechanism of TNT may be considered as three steps, methyl group oxidation, decarboxylation and mineralization of nitro-groups (March, 1985). Li *et al*. (1997) have reported the intermediates of Fenton oxidation of TNT were 2,4,6-trinitrobenzonic acid and 1,3,5-trinitrobenzene by using LC-MS. But the degradation mechanism of SCWO TNT have large difference with other oxidation technology, such as photo-Fenton (Liou *et al*., 2004), photocatalytic (Son *et al*., 2004) and hydrogen peroxide/ozone (Wu *et al*., 2003). The main intermediate products of SCWO TNT are linear paraffin and dimers. Based on the above analysis, TNT degradation pathway under SCWO condition can be described in Fig.6.

As compared to other oxidation technology, SCWO has been claimed to possess higher potential of complete oxidation (Modell, 1987). But it must be noticed that the intermediate products in SCWO may have high toxicity. The result in the present study indicates that such potential might be realized only when careful selections of the appropriate reaction conditions are made.

3 Conclusions

This present study is focused on TNT degradation under SCWO condition. The results show that TNT can be degraded rapidly and almost completely in SCWO. Meanwhile, supercritical water has definite oxidation because of hydrolysis. The SCWO effect for low concentration TNT wastewater is satisfied without extra oxidant. Temperature, pressure, residence time and oxygen excess are the main factors that affect TNT removal rate in the SCWO process. Increasing the reaction temperature and residence time can effectively increase TNT removal rate. The TNT removal

rate may exceed 99.96% under the optimal conditions at 550°C, 24 MPa, 120 s and oxygen excess 300% The main intermediate products of TNT degradation are linear paraffin, several dimers and directly oxidation products of TNT, such as toluene, trinitrobenzene and dinitrotoluene. The degradation mechanism is proposed by identifying TNT products with GC-MS.

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