Electrochemical destruction of dinitrotoluene isomers and 2,4,6-trinitrotoluene in spent acid from toluene nitration process

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ABSTRACT

Mineralization of dinitrotoluene (DNT) isomers and 2,4,6-trinitrotoluene (TNT) in spent acid was conducted by in situ electrogenerated hydrogen peroxide. The electrolytic experiments were carried out to elucidate the influence of various operating parameters on the performance of mineralization of total organic compounds (TOC) in spent acid, including electrode potential, reaction temperature, oxygen dosage and concentration of sulfuric acid. It is worth noting that organic compounds could be completely mineralized by hydrogen peroxide obtained from cathodic reduction of oxygen, which was mainly supplied by anodic oxidation of water. Based on the spectra identified by gas chromatograph/mass spectrometer (GC/MS), it is proposed that oxidative degradation of 2,4-DNT and/or 2,6-DNT, 2,4,6-TNT results in o-mononitrotoluene (MNT) and 1,3,5-trinitrobenzene, respectively. Due to the removal of TOC and some amount of water, the electrolytic method established is promising for industrial application to regeneration of spent acid from toluene nitration process.

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1. Introduction

Toluene nitration processes using sulfuric and nitric acids have been well established because of great importance of dinitrotoluene and trinitrotoluene, which are precursors of tolylene diisocyanate (TDI) and explosives, respectively. The spent acid composed of an excess of water, DNT isomers and 2,4,6-TNT was traditionally treated by sequential steps, including purification and concentration procedures [1]. For the former, the oxidative degradation of nitrotoluenes in spent acid was mainly conducted by hydrogen peroxide, ozone [2–4] and potassium permanganate [5,6]. On the other hand, Parks and Martin [7] heated organic compounds into higher molecular weight nitroaromatics, which would be removed by distillation columns sequentially. For the latter, the contaminant-free sulfuric acid was concentrated to a concentration necessary for nitration, typically ranging from 80 to 95 wt%, by multiple vacuum evaporators operated at sub-atmospheric pressure [2,5,6]. Besides, the spent acid might be disposed by incineration method, which converted sulfuric acid and organic compounds into sulfur dioxide, carbon dioxide and steam [8,9]. The low concentration of sulfuric acid was concentrated by absorption of sulfur trioxide derived from oxidation of sulfur dioxide.

In our previous work with regard to treatment of spent acid in toluene nitration process [10–13], it has been found that high purity crystal of 2,4-DNT ($\geq$99 wt%) could be recovered from spent acid by a simple diluting method. Additionally, the DNT isomers and 2,4,6-TNT may also be partially removed from spent acid by means of hexane extraction. Moreover, it has been verified that the total organic compounds residual in spent acid could be almost completely destructed by either Fenton's reagent with optimal concentrations of $H_2O_2 = 7.6$ M and $Fe^{2+} = 0.06$ M or combination of ozonation with UV irradiation. Nonetheless, the above methods have the disadvantage of diluting the spent acid in consideration of its regeneration.

It has been reported that hydrogen peroxide can be electrochemical generated by reduction of dissolved oxygen in acidic solution at the cathode [14–21]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

The other side reaction, which simultaneously occurs at the cathode, is the hydrogen gas evolution, as shown as follows [19–23]:

$$2H^+ + 2e^- \rightarrow H_2 \tag{2}$$

At the anode, the oxidation of water releases oxygen gas and protons:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{3}$$

Owing to the oxidizing agent being in situ electrogenerated at the cathode, that prevents the sulfuric acid concentration of spent

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acid from decreasing. In another respect, the oxidation reaction happened at the anode, which leads to elimination of water in spent acid. That is, the sulfuric acid concentration of spent acid would gradually increase during the course of electrochemical treatment.

Until now, literature was lacking in deal with oxidative degradation of nitrotoluenes in spent acid which was regenerated simultaneously. Therefore, this research investigated the feasibility of mineralization of nitrotoluenes and concentration of sulfuric acid in spent acid by an electrochemical technique. The effects of electrode potential, reaction temperature, flow rate of oxygen and sulfuric acid concentration on the removal efficiency of nitrotoluenes were elucidated. Besides, the oxidation pathways of DNT isomers and 2,4,6-TNT would be explored.

2. Experimental methods

2.1. Electrolysis testing

Fig. 1 shows the schematic diagram of the reaction system. The experiments were conducted in a batch-wise mode under atmospheric pressure at 323, 333 and 343 K. Both cathode and anode were made of corrosion-resistant platinum of 99.9% purity with dimensions of 2.0 cm × 2.0 cm × 0.1 cm. Prior to tests, a proportionate amount (200 ml) of spent acid (pH −2.3, rendered by military ammunition plant) was situated in the reactor (PIIN JIA Technology Co., JC-A18 Model), which was agitated by a magnetic stirrer. During the course of electrolysis, oxygen gas was introduced into the spent acid through a porous pipe-diffuser placed right under the cathode wherein the solution temperature was controlled by a thermostat (VWR Scientific Co., 1167 Model) and a water bath. The pH of spent acid was simultaneously measured by a pH meter (SUNTEX SP-701 PH/mV/TEMP.Meter). In this study, constant electrode potential mode was applied by a dc power supply (INS Power) throughout the reaction time in which the spent acid was periodically sampled from the reactor and undergone TOC and Karl–Fischer analyses to evaluate the residual organic compounds content and water amount, respectively.

To investigate the effect of electrode potential on the destruction of organic compounds, four tests with various electrode potentials (2 up to 8 V) were carried out. In addition, for the sake of

elucidating the influence of dosage of oxygen on the removal of organic compounds, a series of tests with various flow rates of oxygen (100 up to 140 ml min^{-1}) were undertaken. Besides, electrochemical oxidation tests were also performed under atmospheric pressure at 343 K in the sulfuric acid concentration of 50, 60 and 74 wt%, respectively to find out the optimal conditions upon mineralization of organic compounds. By the way, the oxygen-free electrolysis was conducted to make clear the oxidizing agent responsible for the oxidative degradation of organic compounds.

2.2. Total organic compounds (TOC) analysis

The spent acid undergone electrolysis test was analyzed using a Tekmar Dohrmann Phoenix 8000 instrument fitted with an UV reactor and a NDIR detector. The organic compounds contained in samples were oxidized into carbon dioxide by sodium persulfate and UV irradiation, which was quantified by the NDIR detector. Nonetheless, the inorganic compounds in samples acidified by phosphoric acid were stripped in the form of carbonic acid. Prior to analysis, the concentration of organic compounds in samples was diluted to one-fortieth to meet the measuring ranges (20.0–1000.0 mg l^{-1}), which had been calibrated by the potassium hydrogen phthalate standard solution.

2.3. Gas chromatograph/mass spectrometer (GC/MS) analysis

As electrolysis experiments were in progress, the spent acid sampled (ca. 5 ml) was blended with dichloromethane (≥99.5%, Fluka) in an extractor, as described in our previous report [11], to extract and concentrate tenfold the reaction intermediates involved in the acid phase. Subsequently, the dichloromethane obtained was analyzed by a gas chromatograph/mass spectrometer (Hewlett Packard 59864B/HP 5973 MASS) fitted with a capillary column (Metal ULTRA ALLOY UA-5, 30 m × 0.25 mm, film thickness 0.25 μm), which was programming from 313 to 573 K at an elevation rate of 20 K min^{-1}. To identify reaction intermediates involved in the extract, the mass spectra shown was compared with those of the authentic standard compounds in database (Wiley 275 L).
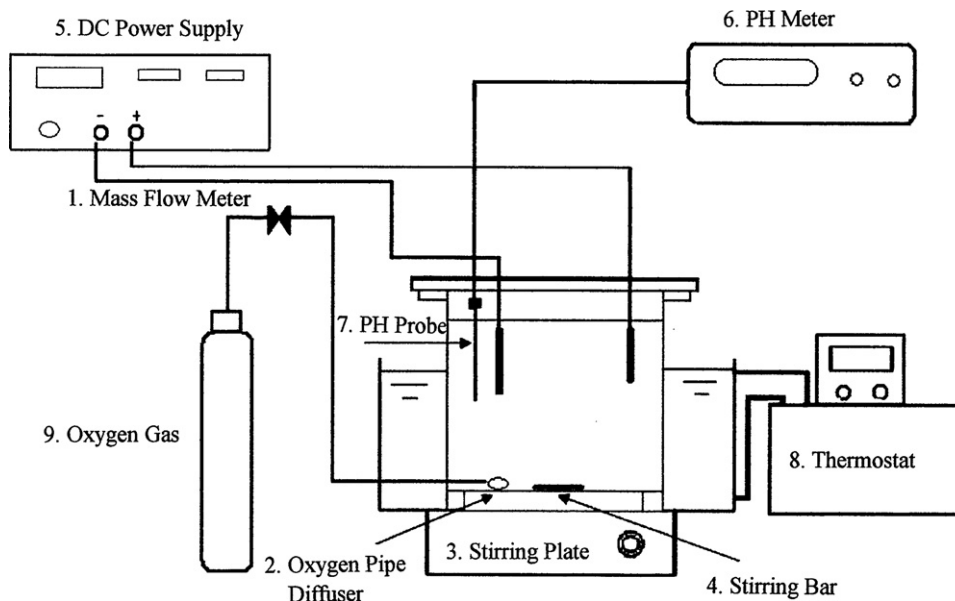

Fig. 1. Schematic diagram of the experimental apparatus employed in electrolysis tests.

Table 1
Compositions of TOC in spent acid identified by GC/MS and GC/FID

Component	wt%	m/z (relative abundance)
2,4-DNT	78.0	39 (12.8%), 51 (13.2%), 63 (36.0%), 64 (13.3%), 78 (16.6%), 89 (60.9%), 90 (26.2%), 119 (25.8%), 165 (100%)
2,6-DNT	17.9	51 (16.3%), 63 (36.0%), 77 (19.9%), 78 (16.6%), 89 (40.4%), 90 (27.3%), 121 (17.8%), 148 (21.1%), 165 (100%)
2,3-DNT	0.7	30 (13.4%), 51 (12.4%), 63 (32.8%), 64 (14.5%), 78 (16.6%), 89 (51.4%), 90 (17.9%), 119 (25.6%), 166 (100%)
3,4-DNT	1.4	30 (64.5%), 39 (32.8%), 52 (32.8%), 63 (47.3%), 66 (33.1%), 78 (46.5%), 89 (51.3%), 94 (32.5%), 182 (100%)
2,4,6-TNT	2.0	30 (14.9%), 51 (11.2%), 62 (16.5%), 63 (32.1%), 76 (15.0%), 89 (43.2%), 180 (13.7%), 193 (13.4%), 210 (100%)

2.4. Gas chromatograph/flame ionization detector (GC/FID) analysis

The organic compounds in spent acid were continuously extracted by dichloromethane in multiple stages, as mentioned in previous work [11], to disclose the compositions involved. The extract decanted from the extractor was preliminary analyzed by a gas chromatograph/mass spectrometer in the procedures as above paragraph to identify the ingredients. Subsequently, the compositions were measured using a gas chromatograph (Hewlett Packard 6890 SERIES) equipped with a flame ionization detector, wherein a capillary column (DB-1, 100 m × 0.25 mm, film thickness 0.5 μm, J & W Co.) operated from 373 to 493 K at a programming rate of 20 K min^{-1}.

2.5. Karl–Fischer analysis

The water contents of spent acid undergone electrolysis were measured by a Karl–Fischer Coulometric Moisture Titrator (MKC-510N Model), in which iodine serves as a titrant. Prior to an analysis, the weight of sample was maintained below 0.5 mg to avoid the interference of sulfuric acid.

2.6. Hydrogen peroxide concentration analysis

The concentration of hydrogen peroxide was determined by the titanic sulfate method wherein the light absorbance of titanic–hydrogen peroxide colored complex was measured by a visible spectrophotometer (Metertek SP-830 Model) at a wavelength of 410 nm [24]. The data obtained were corrected by the standard solutions with the range of hydrogen peroxide concentration of 0–200 mg l^{-1}.

3. Results and discussion

3.1. Effect of electrode potential on electrolysis

The typical spent acid from toluene nitration process was composed of 74.47% H_2SO_4, 2.70% HNO_3, 21.97% H_2O and 0.86% TOC on the weight basis. Based on the analyses of GC/MS and GC/FID, the compositions of TOC in spent acid have been determined, wherein they are 78.0% 2,4-DNT, 17.9% 2,6-DNT, 0.7% 2,3-DNT, 1.4% 3,4-DNT and 2.0% 2,4,6-TNT on the weight basis (as listed in Table 1).

It has been well recognized that the electrode potential is a very important operating variable for electrochemical engineering [25]. Fig. 2 illustrates the time pattern of TOC removal percentage as a function of electrode potential. It clearly indicates that the mineralization rate of TOC exhibited increasing trend with increasing electrode potentials, of which current densities are 81, 263, 688 and 1000 mA cm^{-2}, respectively. Additionally, hydrogen peroxide has been proved to be an effective oxidant for mineralization of DNT and TNT in previous studies [12]. Consequently, this phenomenon may be interpreted with production of a greater amount of hydrogen peroxide, resulted from higher current density, as proposed by Brillas et al. [16]. Moreover, several investigators has approved
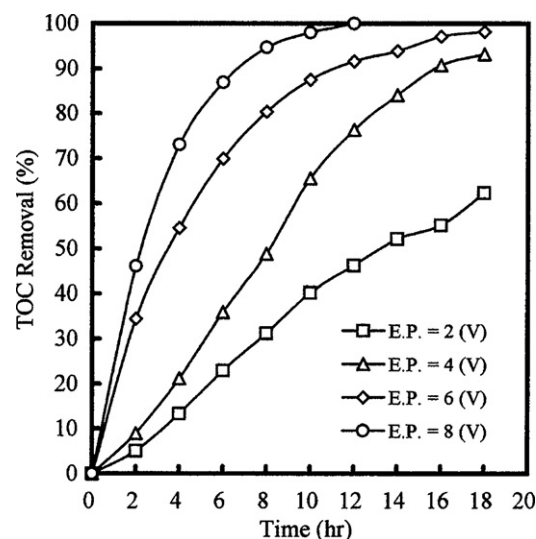
Fig. 2. Effect of electrode potential (E.P.) on the mineralization of organic compounds in spent acid under the condition of $O_2 = 120$ ml min^{-1} and $T = 323$ K.

that higher electrode potentials give rise to higher current density [26–29]. It is remarkable that the TOC in spent acid could be almost completely abated under the conditions of electrode potential = 8 V, $T = 323$ K, and $O_2 = 120$ ml min^{-1}. Nonetheless, it is avoided electrolyzing the contaminants at the electrode potential higher than 8 V due to lower current efficiency with evolution of hydrogen gas (referred to Eq. (2)) [30].

In order to assess the probability of reuse of spent acid from toluene nitration process, the water content involved was measured by means of Karl–Fischer method. As shown in Table 2, it appears that the water content in spent acid was gradually diminished at the electrode potential of four. That may be ascribed to the oxidation of water into oxygen gas at the anode (see Eq. (3)).

Table 2
The water content and pH value of spent acid electrolyzed under different electrode potentials at 323 K, $O_2 = 120$ ml min^{-1}

Electrolysis duration (h)	E.P. = 4 V	E.P. = 6 V	E. P. = 8 V
Water content (wt%)			
0	21.97	21.97	21.97
2	21.93	21.82	21.74
4	21.56	21.20	21.15
6	21.05	20.34	19.90
8	20.52	19.31	18.68
10	19.94	18.10	17.22
12	19.21	16.76	16.02
pH value			
0	−2.30	−2.30	−2.30
2	−2.31	−2.33	−2.34
4	−2.34	−2.38	−2.40
6	−2.38	−2.48	−2.56
8	−2.44	−2.60	−2.71
10	−2.52	−2.73	−2.82
12	−2.61	−2.83	−2.90

Likewise, similar decreasing trends of water content during the electrolysis were observed at the electrode potentials of six and eight. Consequently, the result supports previous hypothesis that water undertakes electrolytic oxidation into oxygen gas at the platinum anode, corresponding to the report of Oturan et al. [31]. It deserves to note that the effect on elimination of water content at the electrode potential of eight was more obvious than those of others, which was consistent with the arrangement of electrode potentials on the mineralization rate of TOC. Thus, it reveals that the TOC in spent acid were mainly destructed by electrolytic generation of hydrogen peroxide, derived from reduction of oxygen (see Eq. (1)), which depends strongly upon electrolytic oxidation of water.

Another evidence is given on the pH values of spent acid treated (referred to Table 2). Apparently, they show decreasing trends with a progressive electrochemical disposal at the electrode potentials of four, six and eight. It may be attributed to the water molecules in spent acid consumed by electrolytic oxidation. As expected, the effect on the acidification of spent acid at the electrode potential of eight was more obvious than those of others. The result is consistent with previous inference that electrolytic production of hydrogen peroxide lies in electrolytic oxidation of water. As taking the sulfuric acid concentration into consideration after an electrolytic treatment, it has been elevated to about 82 wt%, which meets the concentration of nitrating acid industrially [32]. It means that the regenerated spent acid would be suitably recycled into toluene nitration process.

3.2. Effect of electrolytic temperature

According to the toluene nitration process, the temperature of spent acid rendered was in the range of 323–343 K. Therefore, it is important to determine the appropriate electrolytic temperature at which higher removal efficiency of TOC was obtained. Three curves of Fig. 3 demonstrate the TOC removal percentage in spent acid at different electrolytic temperatures. Obviously, the TOC removal efficiency at 333 K was higher than that of 323 K (90% vs. 80% after 12 h treatment). In fact, an identical trend was also observed as compared the data of 343 K with that of 333 K. This phenomenon may be explained by enhancing oxidation reactivity of hydrogen peroxide induced from electro-reduction of dissolved oxygen with
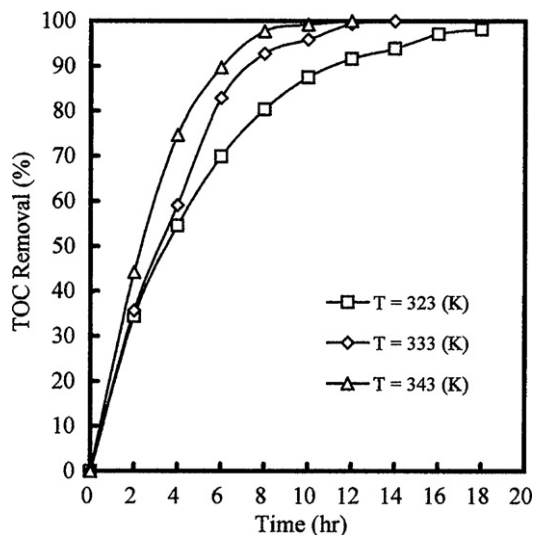
increasing temperature. Similar outcomes have been reported by Hsiao and Nobe [33], who showed the enhancement on mineralization rate of phenol and chlorobenzene with increasing electrolytic temperature. It seems that electrochemical oxidation rate of TOC destructed by hydrogen peroxide was controlled by the mass transfer rate of oxygen which was significantly accelerated by increasing electrolytic temperature. On the contrary, the higher electrolytic temperature is unfavorable to the solubility of oxygen in spent acid [34].

3.3. Effect of dosage of oxygen gas

For the sake of enhancing mineralization efficiency of TOC in spent acid, the dosage of oxygen was adjusted. Effect of flow rate of oxygen on the TOC removal efficiency is illustrated in Fig. 4. It appears that the TOC removal efficiency in the oxygen flow rate of 120 ml min^{-1} was higher than that of 100 ml min^{-1}. Nonetheless, an identical TOC removal efficiency was found between those of 120 and 140 ml min^{-1}. The result implies that the electrochemical oxidation of DNT isomers and TNT depends mainly upon the mass transfer rate of oxygen but the solubility of oxygen in spent acid. The observation in our experiments was in agreement with that reported by Sudoh et al. [24], who states that the production of electrogenerated hydrogen peroxide is proportional to the mass transfer rate of dissolved oxygen to the cathode surface.

To further clarify the oxidizing agent generated during the electrochemical oxidation of TOC in spent acid, the experiment with oxygen-free conditions was performed (see Fig. 4). It clearly indicates that the TOC removal efficiency without dosage of oxygen is slightly lower than those with dosage of oxygen. The plausible explanation is that at the anode water was oxidized to release oxygen, which was reduced to generate hydrogen peroxide at the cathode sequentially no matter with the dosage of oxygen, in agreement with the results by Hsiao and Nobe [35]. Moreover, the hydrogen peroxide produced solely from electrolytic oxidation of water combined with oxygen reduction plays a major role for mineralization of TOC in spent acid. Therefore, this result gives another evidence on the previous hypothesis that electrochemical oxidation of TOC depends strongly upon electrolytic oxidation of water into oxygen. Experiments of electrosynthesis of hydrogen peroxide without dosage of oxygen were conducted using fresh
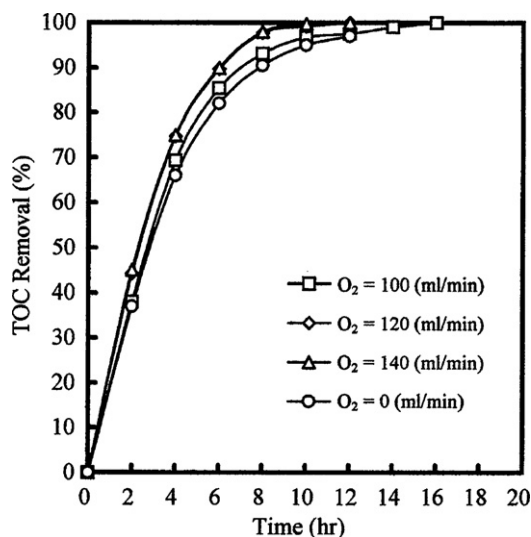

Fig. 3. Effect of electrolytic temperature on the mineralization of organic compounds in spent acid under the condition of O$_2$ = 120 ml min^{-1} and electrode potential = 6 V.

Fig. 4. Effect of dosage of oxygen on the mineralization of organic compounds in spent acid under the condition of electrode potential = 6 V and T = 343 K.
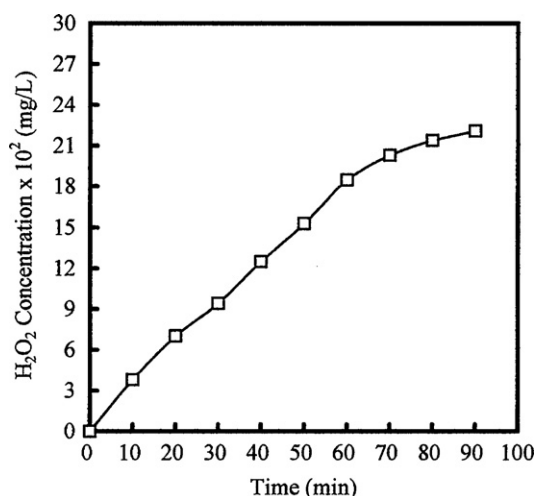
Fig. 5. Time pattern of hydrogen peroxide concentration accumulated in fresh sulfuric acid during the course of electrolysis under the condition of $O_2 = 0\,ml\,min^{-1}$, electrode potential = 6 V and $T = 343$ K.

Fig. 6. Effect of sulfuric acid concentration on the mineralization of organic compounds in spent acid under the condition of $O_2 = 120\,ml\,min^{-1}$, electrode potential = 6 V and $T = 343$ K.

sulfuric acid of which concentration is identical to that of spent acid except for the DNT isomers and TNT. As shown in Fig. 5, the hydrogen peroxide concentration accumulated in fresh sulfuric acid increases linearly with electrolytic time proceeded. It is evident that in acidic medium (pH −2.3) hydrogen peroxide could be synthesized by cathodic reduction of oxygen derived from anodic oxidation of water, corresponding to the studies reported by Gallegos and Pletcher [36]. That is, the oxidizing agent responsible for the electrochemical oxidation of TOC in spent acid is hydrogen peroxide electrogenerated by cathodic reduction of oxygen, which was supplied with both anodic oxidation of water and oxygen cartridge.

3.4. Effect of sulfuric acid concentration

To elucidate the role played by sulfuric acid, experiments of electrolytic mineralization of TOC at different sulfuric acid concentration were carried out (see Fig. 6). Apparently, the TOC in spent acid was gradually mineralized during the course of electrolysis testing. It is worth noting the TOC removal efficiency at sulfuric acid concentration of 74 wt% is higher than those of others. The observation may be interpreted with Eq. (1), wherein the dissolved oxygen reacts with electrons and protons sequentially to give unstable peroxyl radicals ($HO_2^\bullet$), which disproportionate to hydrogen peroxide. The yield of hydrogen peroxide is significantly enhanced by the presence of higher concentration of protons, in coincidence with the report by Oturan and Pinson [19]. Thus, it reveals that the electrochemical oxidation method established is suitable for direct regeneration of spent acid from toluene nitration process, which was avoided diluting before it was in disposal.
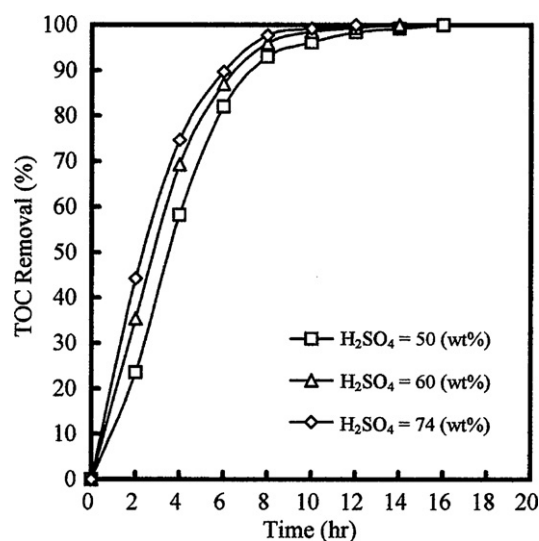
3.5. Reaction pathways of electrochemical oxidation of TOC

In order to identify the oxidative degradable intermediates involved in electrochemical oxidation, the samples obtained from dichloromethane extraction of spent acid treated were analyzed by GC/MS spectrometer. Table 3 summarizes the data achieved, wherein the compositions consist of o-mononitrotoluene (MNT), 2,6-DNT, 2,3-DNT, 2,4-DNT, 3,4-DNT, 1,3,5-trinitrobenzene (TNB) and 2,4,6-TNT. With regard to the ingredients of 2,6-DNT, 2,3-DNT, 2,4-DNT, 3,4-DNT and 2,4,6-TNT, they may be ascribed to the organic compounds feedstock in spent acid, as listed in Table 1. Nevertheless, owing to the higher oxidation rate of MNT than that of DNT [37], and none of MNT being found in organic compounds feedstock, the o-MNT may be proposed as reaction intermediates during electrolysis testing. It seems that o-MNT results from 2,4-DNT and/or 2,6-DNT, of which methyl group with electron-donating character would promote the electron density of nitro groups to be oxidized more readily [38]. Subsequently, the methyl group of o-MNT would be oxidized to aldehyde group and decarboxylation of o-nitrobenzoic acid occurred in next step. Consequently, the reaction pathways of 2,4-DNT and/or 2,6-DNT in spent acid by electrochemical oxidation may be demonstrated in Fig. 7.

As indicated, a little amount of 1,3,5-TNB being detected, the mineralization pathway of 2,4,6-TNT may be proposed as follows. Firstly, the methyl group of 2,4,6-TNT was oxidized to aldehyde group, consistent with the report by Li et al. [39]. Subsequently, trinitrobenzoic acid was generally considered as a possible intermediate. Finally, decarboxylation of nitroaromatic acid and mineralization of nitro group would result in the ultimate products of carbon dioxide, nitrate ion and water, as presented in Fig. 7.

Table 3
Reaction intermediates detected and identified by GC/MS analysis

| Component	Retention time (min)	m/z (relative abundance)
Toluene	4.73	39 (8.1%), 51 (5.1%), 63 (7.1%), 65 (11.1%), 89 (4.3%), 91 (100%), 92 (59.8%), 93 (4.5%)
o-MNT	10.96	39 (28.3%), 63 (28.1%), 65 (83.2%), 77 (30.5%), 89 (30.8%), 91 (60.9%), 92 (62.3%), 120 (100%)
2,6-DNT	12.92	63 (36.0%), 77 (19.9%), 78 (16.6%), 89 (40.4%), 90 (27.3%), 121 (17.8%), 148 (21.1%), 165 (100%)
2,3-DNT	13.23	30 (13.4%), 63 (32.8%), 64 (14.5%), 78 (16.6%), 89 (51.4%), 90 (17.9%), 119 (25.6%), 166 (100%)
2,4-DNT	13.43	51 (13.2%), 63 (36.0%), 64 (13.3%), 78 (16.6%), 89 (60.9%), 90 (26.2%), 119 (25.8%), 165 (100%)
3,4-DNT	13.95	30 (64.5%), 39 (32.8%), 52 (32.8%), 63 (47.3%), 66 (33.1%), 78 (46.5%), 89 (51.3%), 182 (100%)
2,4,6-TNT	14.49	30 (14.9%), 62 (16.5%), 63 (32.1%), 76 (15.0%), 89 (43.2%), 180 (13.7%), 193 (13.4%), 210 (100%)
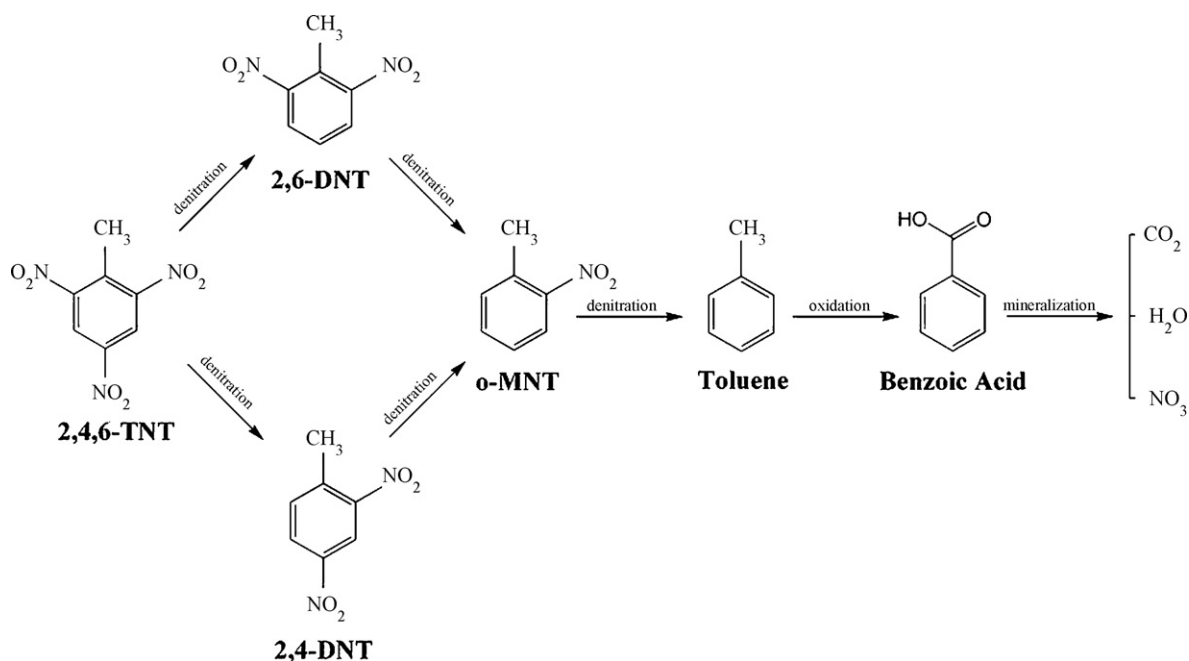
Fig. 7. Plausible reaction pathways of electrochemical oxidation of organic compounds in spent acid.

4. Conclusion

On the basis of the above discussion, it appears that hydrogen peroxide can be in situ electrogenerated by reduction of dissolved oxygen in spent acid at the cathode, which was mainly supplied by anodic oxidation of water. In this study, hydrogen peroxide provided was verified to be an effective oxidant for mineralization of DNT isomers and 2,4,6-TNT. Therefore, it is remarkable that the nearly complete mineralization of TOC can be achieved by electrochemical oxidation method, which abates some amount of water content in spent acid simultaneously. It reveals that the electrolytic technique established may be potentially utilized to regenerate spent acid industrially. According to the spectra identified by GC/MS spectrometer, the plausible mineralization pathways of organic compounds by electrolysis are suggested as follows. The oxidative degradation of 2,4-DNT and/or 2,6-DNT, 2,4,6-TNT leads to o-MNT and 1,3,5-TNB, respectively, which would be mineralized to final products of carbon dioxide, nitrate ion and water.

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