



## Short communication

# Characterization of wastewater from the Brazilian TNT industry

Marcio Barreto-Rodrigues<sup>a,\*</sup>, Flávio T. Silva<sup>b</sup>, Teresa C.B. Paiva<sup>b</sup>

<sup>a</sup> FEDERAL TECHNOLOGICAL UNIVERSITY OF PARANÁ – UTFPR, Via do Conhecimento s/n, km 01 Bairro Fraron, CEP85501-970, Pato Branco-PR, Brazil

<sup>b</sup> LORENA ENGINEERING SCHOOL – EEL/USP, Estrada Municipal do Campinho s/n, CEP12602-810, Lorena-SP, Brazil

## ARTICLE INFO

## Article history:

Received 28 May 2008

Received in revised form 9 July 2008

Accepted 30 July 2008

Available online 13 August 2008

## Keywords:

Brazilian TNT industry

Acute toxicity test

Yellow water

## ABSTRACT

The objective of this work was to characterize the effluent originating from a Brazilian TNT production industry. Analyses were performed using physical, chemical, spectroscopic and ecotoxicological assays, which demonstrated that the effluent had a significant pollution potential, mainly due to the low pH and high concentration of TNT ( $156 \pm 10 \text{ mg L}^{-1}$ ). The results also demonstrated that the effluent presented significant acute toxicity, and could cause countless damages if released into the receiving body without being adequately treated first. The observed pollution potential justifies studies to evaluate treatment technologies or recover the residue generated in the TNT industry.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

The production of nitroaromatic explosives has resulted in their dissemination into the environment, where their presence in waterways and soil represents an ecological and health hazard [1,2]. The hazardous characteristics of these compounds need to be studied in-depth, so that the impact of their discharge into the environment can be better evaluated [3].

The main source of contamination for nitrocompounds is associated with industrial processes, storage operations and use in military installations. In Germany and the United States, there are a great number of sites highly contaminated by explosives and ammunition [4,5]. In Brazil, the largest amount of explosives is produced by the army [6]. The discharge of residues generated during explosive manufacturing and processing as well as the associated level of contamination varies widely, depending on the intensity of the manufacturing operations and the effectiveness of the technologies used to treat the residues [7]. Conventional biological wastewater treatment processes (e.g., activated sludge) are not effective in treating the residues because the electron-withdrawing nitro constituents in these explosives inhibit the electrophilic attack through enzymes [8,9]. Chemical oxidation methods (e.g., advanced oxidation processes) are also not considered effective because the nitrofunctional groups inhibit oxidation [9]. Currently, one of the more commonly used methods is incineration. Although

efficient, its applicability is questioned due to the emission of gaseous pollutants [10].

The toluene nitration process that uses a mixture of sulfuric and nitric acid has been well developed due to the industrial importance of 2,4-dinitrotoluene (DNT), 2,6-DNT, and 2,4,6-trinitrotoluene (TNT) [8]. Before DNT is hydrogenated into toluenediamine, the organic product generated in the toluene dinitration process is first washed by a weakly basic aqueous solution to remove entrained nitric and sulfuric acid. Subsequently, the washed organic product is submerged in clean water to eliminate basic impurities [6–8]. The two wash water streams described above produce the bulk of the wastewater and result from the toluene dinitration process. Likewise, wastewater was also generated at the company with the production of 2,4,6-TNT [6]. Due to the severe toxicity and doubtful carcinogenicity of 2,4-DNT, 2,6-DNT and 2,4,6-TNT, they should be removed from the wastewater before it is re-released into the environment [3,7].

This work presents the characterization of wastewater from the Brazilian TNT industry using the analytical techniques of mass spectroscopy, chromatography, toxicity assays and other physical–chemical analyses.

## 2. Material and methods

### 2.1. Chemicals and supplies

All chemicals were of an analytical grade or higher and were purchased from Merck, Reagen or Sigma. The wastewater samples were collected in the IMBEL, Belics Materials Industry, localized in

\* Corresponding author. Tel.: +51 46 3220 2596; fax: +51 46 3220 2556.  
E-mail address: [marciorodrigues@utfpr.edu.br](mailto:marciorodrigues@utfpr.edu.br) (M. Barreto-Rodrigues).

**Table 1**  
Physical and chemical characteristics of TNT process wastewater and EPA maximum values

	pH	COD (mg L <sup>-1</sup> )	Total nitrogen (mg L <sup>-1</sup> )	Total solids (mg L <sup>-1</sup> )	Total suspending solids (mg L <sup>-1</sup> )	TNT (mg L <sup>-1</sup> )
Wastewater	1.0 ± 0.03	638 ± 12	729 ± 60	13,260 ± 60	1110 ± 60	156 ± 10
EPA maximum values	100	120	0.68	–	100	0.06 <sup>a</sup>

<sup>a</sup> EPA recommended ambient water quality criteria. Human health criteria for consumption of water.

São Paulo State, Brazil. The wastewater originated from the preliminarily washes performed during the TNT purification process. This effluent is called yellow water, while the effluent produced by the second washing designed to extract the organic impurities is called red water [6–8]. Because the TNT purification process is performed using hot water laundering (around 90 °C), when the temperature of the generated effluent reaches 30 °C, the crystal precipitation of the TNT takes place. It is later redirected for the purification process. The effluent sample was collected at the washer exit at a temperature of approximately 60 °C. After collected, the effluent was collected at ambient temperature and stored under refrigeration for later analysis. Although the majority of the effluent is incinerated, there are still frequent contaminations that reach the ground or streams and can get as far as Paraíba of the South River, the main river of Southeastern Brazil.

## 2.2. Methods

In order to determine the pollution potential of the effluent under study, its characterization was determined based on the following parameters:

### 2.2.1. Chemical oxygen demand (COD)

A sample was refluxed in a strongly acid solution with a known excess of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Oxygen consumed was measured against a standard at 600 nm with a spectrophotometer [11].

### 2.2.2. Total solids

A well-mixed sample was evaporated in a weighed dish and dried to constant weight in an oven set at between 103 and 105 °C [12].

### 2.2.3. Total suspending solids

A well-mixed sample was created through a weighed standard glass-fiber filter and the residue retained on the filter was dried to a constant weight at between 103 and 105 °C [13].

### 2.2.4. Molecular mass distribution

The molecular weight distribution of the effluent compounds was determined by HPSEC using a Shimadzu chromatograph with an Ohpak SB-803 HQ column eluted with degassed water at a flow rate of 1.0 mL min<sup>-1</sup> at 25 °C. The peaks of the compounds were monitored by a LC-10 refractive index detector. The chromatographic column was calibrated with polyethylene glycol (PEG) from 35,000 to 300 g mol<sup>-1</sup> and ethylene glycol (62.07 g/mol) [14].

### 2.2.5. Liquid chromatograph analysis

TNT decay was followed by reversed phase liquid chromatography. The HPLC consisted of a LC Shimadzu pump 10AT equipped with a UV detector selected at λ = 254 nm and fitted with a LiChrosphere RP-18 column 250 mm × 4.6 mm i.d., 5 μm particle size (Merck). The system was operated in isocratic mode (methanol/water; 60/40, v/v) at a flow rate of 1 mL/min. The retention time of TNT under these conditions was 9.4 min (±30 s).

### 2.2.6. Gas chromatograph/mass spectrometer analysis

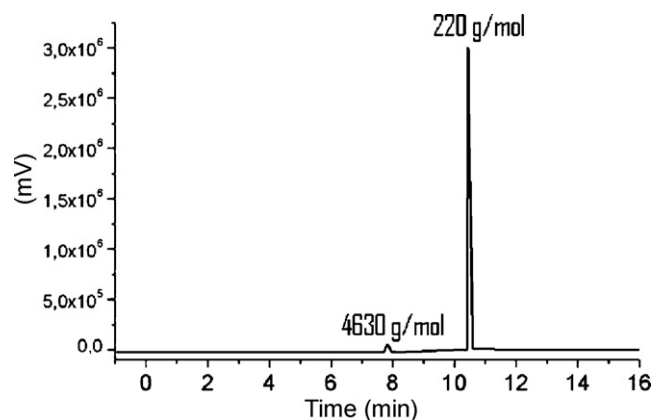
The proportionate amount (0.4 μL) of wastewater was injected into a gas chromatograph/mass spectrometer (Varian CP-3800) equipped with a capillary column (Metal ultra alloy ua<sup>-5</sup>, 30 m × 0.25 mm, film thickness 0.25 μm), operated from 313 to 573 K at a programming rate of 20 K min<sup>-1</sup>. The mass spectra obtained were used to identify the components involved in both the wastewater and extract as compared to the authentic standard compounds.

### 2.2.7. Acute toxicity test

The effluent acute toxicity test was conducted by determining the microbial respiration inhibition of *Escherichia coli* [15]. Basically, the assay consists of the incubation of *E. coli* cultures (ATCC 25922) at 37 °C with known amounts of the stressing agent. When the CO<sub>2</sub> concentration produced by microbial respiration reached 0.5 mmol L<sup>-1</sup>, or approximately 9 × 10<sup>8</sup> cells/mL, 45 mL of the *E. coli* culture was transferred to several flasks and each one received 5 mL of the sample 10% (v/v). As a control, 5 mL of distilled water was introduced in one of the flasks and the CO<sub>2</sub> production was monitored every 20 min using Flow Injection Analysis (FIA). The toxicity test was conducted for a maximum period of 120 min. For incubation periods of more than 120 min, there is loss of CO<sub>2</sub> into the atmosphere due to CO<sub>2</sub> over-saturation (>5 mmol L<sup>-1</sup>) in the aqueous culture medium.

## 3. Results and discussion

Through the physical and chemical analyses, it was observed that the effluent is formed by a significant amount of total solids (13260 mg L<sup>-1</sup>) and that the following components most contributed to its composition: 1110 mg of solid suspension constituted by TNT crystal, 729 mg of total nitrogen, in which the forms of nitrite and nitrate beyond form the symmetrical and anti-symmetrical components of TNT. Table 1 illustrates the analysis of the physical and chemical characteristics found in the effluent. Within this context, it can be observed that all the parameters exceed the maximum values permitted by law [16].



**Fig. 1.** Molar chromatogram distribution of the effluent originating from TNT processing.

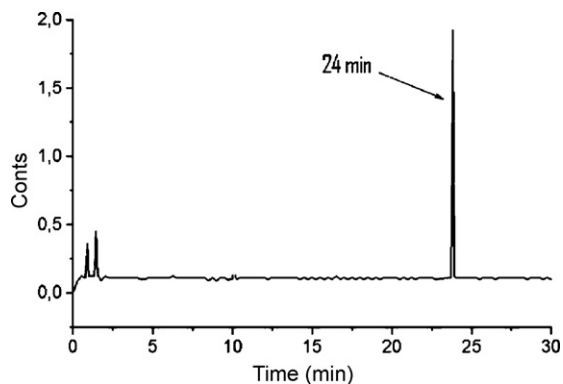


Fig. 2. Chromatogram obtained for the gaseous chromatography of the effluent.

The pH of strong acid found in the effluent was attributed to the mineral residues acid of  $H_2SO_4$  and  $HNO_3$  adsorbed into the product. This characteristic is a factor for concern, since it could cause countless damages to any type of receiving body, in addition to requiring great amounts of alkali in order to achieve the necessary neutrality for many types of remediation processes, which would significantly raise the costs of these processes. It was also observed that the effluent presented a considerable high degradable organic load ( $638 \pm 12 \text{ mg OL}^{-1}$ ). The molar distribution mass of the effluent components was determined through exclusion chromatography, with UV detection at 254 nm. The obtained chromatogram is illustrated in Fig. 1.

The chromatogram (Fig. 1) shows a peak retention time of 10.3 min, which after interpolation with the curve standard, resulted in a molar mass of  $220 \text{ g mol}^{-1}$ , whose molar fraction corresponds to 98% of the total area of the chromatogram. It is important to point out that this molar mass corroborates with the mass of the nitrate compound, probably the symmetrical TNT, during which time the anti-symmetrical forms have minor solubility in water [8]. There was a relatively lesser contribution (2%) for an effluent made up of high molar mass ( $4630 \text{ g/mol}$ ) for a retention time of 7.9 min. In order to characterize the monodispersed molar fraction observed in the chromatogram of distribution for the components found in the effluent and confirm the presence of anti-symmetrical TNT and/or isomers, gaseous chromatography assays were conducted together with mass spectrometry. The chromatogram and relative mass spectrometry results for this analysis are illustrated in Figs. 2 and 3, respectively.

The chromatogram (Fig. 2) demonstrates the presence of a grouping of three characteristic peaks for a retention time of 24 min. Among these, the central peak was attributed to the TNT for the peak of the molecular ion ( $w/z$  ratio=210), common ionic fragments and certain eliminated fragments. The adjacent peaks were

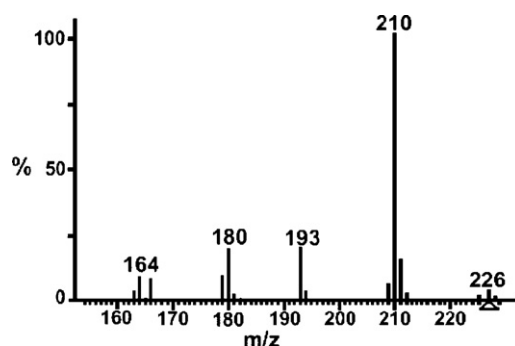


Fig. 3. Mass spectrometry results obtained from wastewater analysis.

associated with the aliphatic hydrocarbons (ftalates), with its presences attributed to the fact that the effluent samples were stored in polyethylene bottles.

Considering the TNT solubility at the ambient temperature ( $25^\circ\text{C}$ ) of  $130 \text{ mg L}^{-1}$  and the constant precipitation of the composition with the reduction of the temperature [8], we can conclude that the effluent is a saturated solution of the composition, with the time quantified and chromatographic analysis,  $156 \pm 10 \text{ mg L}^{-1}$ . We attribute to this dissolved TNT the yellowish coloration presented by the effluent. It is important to emphasize that Brazilian and European law does not establish restrictions for TNT or composites specifically. On the other hand, the U.S. Environmental Protection Agency (EPA) allows a maximum level of  $0.06 \text{ mg L}^{-1}$  for TNT in waters designed for human consumption [16].

It was observed that the effluent presented significant acute toxicity, comparable to other industrial effluents with high potential polluting agents. The measurement of the acute toxicity with *E. coli*, for example, resulted in a 86.5% inhibition of cellular growth, indicating that, specifically for this bioindicator, the TNT industry effluent is relatively more toxic. It is important to point out, however, that with the addition of more assays, there are other levels that must be analyzed.

#### 4. Conclusion

In general, the effluent characterization showed that certain parameters such as total solids, total organic nitrogen, COD and pH were present at levels above those allowed by the criteria for release into a receiving body. However, the parameter that is cause for greater concern is the 2,4,6-trinitrotoluene composition, whose presence and raised concentration explains the recalcitrance of the effluent during the conventional remediation processes of a chemical and biological nature. The ecotoxicological profile is another cause for concern and was attributed to the TNT and increased ionic force of the effluent, the resultant of one of the mineral residues of the sulfuric and nitric acids used in the process. The recognized pollution potential of the effluent, as well as the difficulties presented for its remediation makes it crucially important to develop feasibility studies to explore clean technologies that involve the modification and optimization of processes, product recovery and reuse of residuary waters resulting from the nitroaromatic industry.

#### Acknowledgments

The authors are grateful to CAPES/PICDT, FAPESP and SCTDE/SP for their financial support. We would also like to extend our thanks to Lúcia A.B.A. for providing technical support.

#### References

- [1] D. Kalderisa, S.B. Hawthorne, A.A. Clifford, E. Gidarakosa, Interaction of soil, water and TNT during degradation of TNT on contaminated soil using subcritical water, *Journal of Hazardous Materials* 159 (2008) 329–334.
- [2] S.L. Yost, J.C. Pennington, J.M. Brannon, C.A. Hayes, Environmental process descriptors for TNT, TNT-related compounds and picric acid in marine sediment slurries, *Marine Pollution Bulletin* 54 (2007) 1262–1266.
- [3] B.R. Flokstra, B.V. Aken, J.L. Schnoor, Microtox® toxicity test: detoxification of TNT and RDX contaminated solutions by poplar tissue cultures, *Chemosphere* 71 (2008) 1970–1976.
- [4] H.K. Boparai, S.D. Comfort, P.J. Shea, J.E. Szecsody, Remediating explosive contaminated groundwater by in situ redox manipulation (ISR) of aquifer sediments, *Chemosphere* 71 (2008) 933–941.
- [5] B. Clark, R. Boopathy, Evaluation of bioremediation methods for the treatment of soil contaminated with explosives in Louisiana Army Ammunition Plant, Minden, Louisiana, *Journal of Hazardous Materials* 143 (2007) 643–648.
- [6] M. Barreto-Rodrigues, F.T. Silva, T.C.B. Paiva, Caracterização física, química e ecotoxicológica de efluente da indústria de fabricação de explosivos, *Química Nova* 26 (2008) 1–5.

- [7] S.W. Maloney, N.R. Adrian, R.F. Hickey, R.L. Heine, Anaerobic treatment of pinkwater in a fluidized bed reactor containing GAC, *Journal of Hazardous Materials* 92 (2002) 77–88.
- [8] W. Chen, W. Chiang, C. Lai, Recovery of nitrotoluenes in wastewater by solvent extraction, *Journal of Hazardous Materials* 145 (2007) 23–29.
- [9] W. Chen, C. Juan, K. Wei, Decomposition of dinitrotoluene isomers and 2,4,6-trinitrotoluene in spent acid from toluene nitration process by ozonation and photo-ozonation, *Journal of Hazardous Materials* 147 (2007) 97–104.
- [10] J.C. Pennington, J.M. Brannon, Environmental fate of explosives, *Thermochemica Acta* 384 (2002) 163–172.
- [11] APHA, American Public Health Association, Standard Methods for the examination of water and wastewater, Method 2540A 20 (1999) 5–68.
- [12] APHA, American Public Health Association, Standard Methods for the examination of water and wastewater, Method 5520C 20 (1999) 12–32.
- [13] APHA, American Public Health Association, Standard Methods for the examination of water and wastewater, Method 2540D 20 (1989) 39–81.
- [14] J.V.B. Souza, E.S. Silva, F.T. Silva, T.C.B. Paiva, Fungal treatment of a delignification effluent from a nitrocellulose industry, *Bioresource Technology* 96 (2005) 1936–1942.
- [15] W.F. Jardim, C. Pasquini, J.R. Guimarães, L.C. Faria, Short-term toxicity test using *Escherichia coli*: monitoring CO<sub>2</sub> production by flow injection analysis, *Water Research* 24 (1990) 351–354.
- [16] U.S. EPA. Water Quality Standards Handbook, second ed., Washington, DC, 1993.