

Degradation of 2, 4, 6-trinitrotoluene in aqueous solution by ozonation and multi-stage ozonation biological treatment

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Received 20 November 2008; revised 8 July 2009; accepted 22 August 2009

ABSTRACT: The objective of this study was to explore the extent of 2,4,6-trinitrotoluene synthetic solution and red water mineralization by comparing conventional direct ozonation and multi-stage ozonation-biological treatment process. The alkaline hydrolysis was used for remediation 2, 4, 6-trinitrotoluene and red water at pH = 10.9. Nevertheless, the hydroxyl radicals would be generated by ozone decomposition with ozone dose of 0.177 g/L. The samples were subjected to chemical oxygen demand and total organic carbon analysis to monitor pollutants removal. The rate of 2, 4, 6-trinitrotoluene and red water pollutants degradation were quantified using high performance liquid chromatography. 2, 4, 6-trinitrotoluene synthetic solution resulted 55.5 % chemical oxygen demand removal by 3 h direct ozonation. Following direct ozonation the biological treatment twenty four hours chemical oxygen demand reached 98.9 % and 98.7 % removal using humic acid and river water 1 % (v/v) inoculation singly and respectively. Conventional direct ozonation showed non significant change in total organic carbon degradation. While on using multi-stage ozone-biological treatment process where humic acid and/or river water were used as inoculums singly and respectively, total organic carbon fulfilled 73 % and 98.3 % removal. The process was one hour direct ozonation and followed by three days multi-stage ozone-biological treatment. In multi-stage ozone-biological treatment process, ozonation was effective to decompose total organic carbon and to produce biodegradable dissolved organic carbon easily removed by ozone oxidation up to 98.3 % in 2,4,6-trinitrotoluene synthetic solution. Pollutants removal achieved 99 % in authentic red water effluent using river inoculation 1 % (v/v) in 5 days. Nuclear Magnetic Resonance and Fourier Transformation Infra Red methods were performed to confirm types of pollutants content in red water.

Keywords: Chemical oxidation; Pollutants mineralization; Red water; Removal, Total organic carbon

INTRODUCTION

Nitro aromatic compounds are used in many industrial processes, including the preparation of pesticides, explosives, textile and paper. Therefore, these compounds are often detected as water pollutants as a result of their release in industrial effluents (Song *et al.*, 2007). 2, 4, 6-trinitrotoluene (TNT) is a common pollutant which has been the most widely used nitroaromatic explosive and is known to be mutagenic, carcinogenic and toxic to aquatic and terrestrial organisms (Won and Disalvo, 1976). Therefore, the United States Environmental Protection Agency has classified TNT as a possible human carcinogenic (class C) and has issued the health advisories for TNT to less than 0.002 mg/L (USEPA, 2002). Soil and ground water contaminated by TNT and its derivatives is a worldwide environmental problem related to production sites, ammunition plants and demilitarization activities. Alkaline hydrolysis

(Bandstra *et al.*, 2005) and zero valent iron (Thorn *et al.*, 2004) treatments have been successfully applied for TNT degradation in the water and soil treatments. However, these two technologies proceed through reductive pathways leading to the formation of an uncharacterized polymeric material of unknown toxicity, mainly in soil, upon prolonged TNT treatment (Thorn *et al.*, 2004). Incineration is the most effective remediation method but is expensive and generates concern about air emissions. 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, sludges and contaminated soils (Svanstrom *et al.*, 2004; Chang and Liu, 2007). Bioremediation is often effective, but cannot be applied in highly contaminated sites, requires long treatment times and often produces toxic and/or mutagenic by-products (Jarvis *et al.*, 1998; Adams and Guzmán-

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Osorio, 2008). Conventional biological wastewater treatment processes (eg. activated sludge) are not effective in treating the residues because the electron – withdrawing nitro constituents in these explosives inhibit the electrophilic attack through enzymes (Chen *et al.*, 2007; Behara *et al.*, 2007). Advanced oxidation processes (AOPs) have been shown great potentials for the treatment of a large range of refractory organic pollutants in waters and soils. AOPs rely on the generation of strong oxidants, such as hydroxyl radicals. This type of radicals can be easily generated using hydrogen peroxide and dissolved iron (Fenton chemistry), but low pH conditions (pH=3) are required to prevent the precipitation of iron. Fenton's reaction has also been used to treat TNT contaminated aqueous solution often resulting incomplete degradation and partial mineralization with accumulation of short chain carboxylic acid at the end of the reaction time (Chen *et al.*, 2005; Yardin and Chiron, 2006). Unlike the Fenton's reagent, the reaction of iron minerals with hydrogen peroxide can effectively catalyze. When TNT undergoes chemical reduction under anaerobic conditions, the nitro groups in the original structure can be transformed sequentially to amino groups (Barrows *et al.*, 1996), ultimately yielding 2,4,6-trinitrotoluene (Hofstetter *et al.*, 1999). Because intermediates are of environmental concern, field applications relying on the reduction of TNT using iron species must also consider subsequent reactions such as biodegradation or covalent binding of the intermediate products to natural organic matter, which can effectively be irreversible (Agrawal and Tratnyek, 1996). Vohara and Tanka (2002) studied photo-catalytic degradation of TNT while (Li *et al.*, 1998) studied UV-catalytic Fenton oxidation for complete mineralization. The main problem of (AOPs) lies in the high cost of reagents such as ozone, hydrogen peroxide or energy source such as ultra violet light. For the photocatalytic ozonation methods the energy demand of the $O_3 / TiO_2 / UV$ could be considerably decreased by the use of solar irradiation and in situ electrochemical O_3 generation (Agustina *et al.*, 2005). The organic compounds (e.g. DNT isomers and TNT) were gradually mineralized by ozonation of which oxidation efficiency was about 78.0 % after 7 h treatment (Sotelo and Beltrain, 1989). Sheng *et al.* (2007) studied mineralization of dinitrotoluene (DNT) and TNT in spent acid toluene nitration process by ozone and UV / O_3 . Peyton and Glaze (1988) studied the generation of hydroxyl radicals by photo-ozonation and stated that it should result in higher oxidation efficiency of organic

compounds in comparison with that of ozone. Chemical oxidation methods (eg. AOPs) are also not considered effective because the nitrofunctional groups inhibit oxidation (Barreto-Rodrigues *et al.*, 2008). Lin and Kiang (2003) combined physical and biological treatments consisted of air stripping, modified Fenton oxidation and sequencing batch reactor method. They achieved lowering of the wastewater COD concentration from as high as 80,000 mg/L to below 100 mg/L and the effluent was reused. Esplugas *et al.* (2002) added that although low costs were obtained with ozonation for phenol as TNT by-products during remediation in aqueous solution, but in the ozone combinations, the best results were achieved as UV/ H_2O_2 showed the highest degradation rate. Ozone followed by biological treatment is one of the promising processes to mineralize nitro aromatic compounds and to remove TOC completely from raw water (Fahmi *et al.*, 2003). Ozone transforms refractory natural organic matter (NOM) to biodegradable form. i.e.; biodegradable dissolved organic carbon (BDOC). BDOC produced by ozonation is removed by biodegradation in the subsequent biological treatment. Therefore, dissolved organic carbon (DOC) removal in this process is dependent on the production of BDOC in the ozonation. The transformation of refractory DOC to BDOC by ozonation may be inhibited by BDOC itself produced by ozonation, because BDOC may also consume ozone. Yasui *et al.* (1992) reported that re-ozonation of organic matter after biological treatment produced new assimilable organic matters (Yasui and Miyaji, 1992; Imo *et al.*, 2007). They added that ten times of 1min ozonation and subsequent biodegradation removed 95 % of DOC, whereas continuous ozonation for 64 min followed by biological treatment removed only 70 %. Besides, TNT is resistant to reaction with acids, but like all nitro compounds, it reacts easily with bases. The reactions of TNT with bases are often accompanied by intense color (violet, red or brown colors depending on the alkali system). Due to low solubility of TNT in water ($6 \times 10^{-4}M$) at 25 °C, hydrolysis of TNT has often been performed in an alcohol as co-solvent system. The use of excess strong base is probably the most efficient means of ensuring that hydrolysis is driven to completion. However elevated temperature (60 °C – 155 °C) and often elevated pressure (up to 14 Atm) may be needed in a strong base solution (pH > 12) representing vigorous process. These reaction conditions must be carefully monitored to prevent spontaneous and violent exothermic reaction where NaOH, KOH, $NH_4(OH)$ and Na_2CO_3 have been used. Hydrolysis rate of TNT

increase from 5.3 g/h to 40 b/L at the same NaOH concentration (3.4 M or 12 % by wt) and same temperature (95 °C), but changing stirring from gentle to vigorous agitation (Proposal submitted in response to U.S. Army Solicitation, 1997).

In this study, different experiments were carried out in which conditions, including O₃ dose, ozonation time, pH and initial TNT concentration were varied to examine the influence of these factors on the extent of TNT degradation. Pollutants mineralization was detected by measuring COD and TOC values in tested samples before and after treatment. After applying the optimum conditions, multi-stage ozone-biological treatment process was performed using prepared (humic acid and river surface water) with varying contact time to achieve complete mineralization of TNT and red-water tested sample. HPLC analysis was used for determination of pollutants complete removal in tested samples. This work has been performed in the National Research Center, Chemical Engineering and Pilot Plant Department, Cairo, Egypt, November 2007.

MATERIALS AND METHODS

TNT crystalline form of > 95 % purity obtained from local industry producing explosive materials and was used without further purification.

Red water was obtained from the effluent produced by the second washing designed to extract the organic impurities and stored under refrigeration for later use.

Humic acid was prepared by evaporating 1 L of supernatant of sewage wastewater on water bath at 40 °C. The solution was stirred 80 min and then filtered to remove insoluble residues before evaporation. The solution was evaporated till 1/5 of its original volume and stored in refrigerator for later use. River water

(surface water) was collected and filtered to be used for inoculation and stored under refrigeration for later use.

Phosphate buffer was prepared in distilled water by reaction of calculated amounts of sodium hydroxide solution and phosphoric acid solution. A 1000 mL TNT aqueous stock solution was prepared by dissolving 1 g of TNT in 1 L buffer solution (after dissolving TNT in 3 -5 mL of acetonitrile) and stored at 4 °C (Song *et al.*, 2007). Various strengths were made from the stock by the appropriate dilution with buffer.

Ozone is produced by Fisher ozonator by passing 20 L/h of oxygen at 5 Atm., through the generator Fig. 1. Oxygen is supplied by compressed bottled gas. Electrical input is changed from 120 – 240 MA in order to vary ozone concentration output. Leakage of ozone from reactor is detected by potassium iodide trap (1). Ozone concentration in the gas stream is measured by iodine / thiosulphate, using standard iodometric method. Chemical oxygen demand and total organic carbon were performed and measured according to APHA (1999) and were completed using HACH- DR 2000 spectrophotometer. MSDS MO 174 vials were incubated during 120 min at 150 °C and at 100 °C, respectively. Air compressor (air flow rate 680 mL/ min and 220 Volt) for aerating the samples during inoculation. Fourier transform infra red (FTIR) spectrum of the red-water sample was recorded using Jasco 460 FTIR spectrometer from 600 to 4000/cm. Nuclear Magnetic Resonance (NMR) was recorded on Varian 200 MHz, Gemini, 200 instruments. High performance liquid chromatography (HPLC) was performed with HPLC system (Waters) equipped with model 600 delivery system, model (Waters 486). UV detector set at 254 nm and the data recorded by millennium chromatography. Manager software 2010 (Waters, Milford MA 01757).

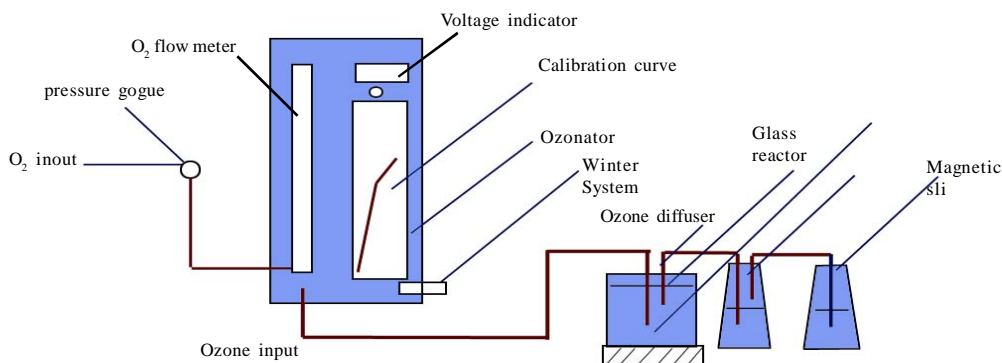


Fig. 1: Experimental set-up of the ozonation system

Reverse phase C₁₈ Nucleosil column 250 XY mm, 10 µm (Macherey – Nagyel. CO, Germany) was used. Mobile phase methanol : water (1 : 1) isocratic program, flow rate 1 mL/min.

The ozone is dispersed directly into the prepared synthetic-TNT samples or authentic red-water samples and mixed perfectly with magnetic stirrer. Residual ozone contaminated in the exit gas is absorbed by potassium iodide solution and determined by titrimetric technique. The 200 mL of the TNT-synthetic solution (of 20 mg/L prepared from 100 mL TNT stock solution by appropriate dilution with buffer) or (200 mL authentic red-water with appropriate dilution with buffer) are agitated by a magnetic Teflon bar at room temperature (20°C). Gas of different ozone concentrations is dispersed into the solution through the orifice glass tube for (1, 1.5, 2 and 3 h) to give the predetermined ozone application rates. Ozone flow is stopped, stirring is continued in the closed batch system for both TNT degradation in synthetic solution and/or nitro-amines degradation in red water. Ozone concentrations are determined at time intervals, for reaction time 15, 20, 30 and 60 min. The 1 h and 3 h ozone reaction time were selected as effective time for pollutants degradation. The extent of degradation was evaluated by COD and TOC spectrophotometer measurements.

A well - mixed red - water sample was evaporated in evaporating dish and dried to constant weight in an oven set at 70 - 80 °C. The sample was grounded dry by a mortar and pestle to fine powder. The powder was packed into a black-filled mount with a circular cavity that was 15 mm in diameter. The samples were scanned using FTIR spectrum of the red-water samples after evaporation and drying. Pollutants present in red - water recorded using FTIR spectrum from 600 – 4000 cm⁻¹, Material Data (2003).

Nuclear Magnetic Resonance spectrum was measured at ambient temperature, 107 scans, using minimum mg of sample dissolved with internal standard. Spectrometer operating in the FT model at 199.9752 MHz under total proton decoupled conditions. The red-water sample was dissolved in 1mL DMSO. A 39.4 degree pulse flipping angle, a 5000 ms pulse width and a 1.994 sec acquisition time was used.

EPA standard method 8330 for trace analysis of explosive residues by HPLC using UV detector was monitored at 254 nm. Reverse phase C₁₈ nucleosil column 250 XY mm, 10 µm (Macherey – Nagyel. CO, Germany) was used. Mobile phase methanol water (1:1) isocratic program, flow rate 1 mL/min. Calibration of the HPLC was performed using external standards with

concentrations ranging from 0 – 10,000 µg/L. Calibration of the standard solutions was prepared in both acetonitril and deionized water (1 : 1) using serial dilutions of the stock solution. Five standard concentrations were prepared in all cases for HPLC calibration. All samples were prepared as standard and placed in ultrasonic bath more than 2 h. After sonication, the samples were allowed to settle for 30 min. 5 mL of supernatant was removed and combined with 5 mL of calcium chloride solution (5 g/L). The mixture was shaken and then left to stand for 15 min. The supernatant was introduced into HPLC using automatic injector. Transformation products were identified by retention time in the system. Sorbed concentrations were estimated as the difference between the original concentration and final aqueous concentration.

RESULTS AND DISCUSSION

Table 1 represents the characteristics of authentic red water. Fig. 2 shows the pollutants contents in red water which corresponds to dissolved by-products obtained in wastewater effluent from explosives production plant. The solid part from the effluent wastewater represents the TNT from the production plant. The solid part was studied as synthetic solution treatment, which is prepared through the study by hydrolysis in buffer solution. The following parameters affecting pollutants degradation were studied. Changing ozone doses (0.015, 0.070, 0.112, 0.177 g/L) each at contact time 5, 15, 30 and 60 min, respectively were applied to samples at pH 10.9, showed optimum ozone dose 0.177 g/L at 300 mA. The results indicated that ozone dose had a positive effect on TNT degradation. All ozone doses tested less than 0.177 g/L indicated negative effect on TNT degradation determined by no remarked COD or TOC reduction.

This was attributed to increasing ozone dose, increases the area of the gas - liquid interface, which resulted in an increase of ozone concentration in the solution and an increase of the formation of the free radicals with a consequent increase in the rate of TNT degradation. This COD removal up to 55.5 % was achieved at ozone dose 0.177 g/L indicated by COD measurements. The actual optimum dose of ozone can be determined by the ozone / TNT ratio required for complete degradation (Vohara and Tanaka, 2002). Therefore, optimization of ozone dose is necessary to minimize energy consumption and amount of exhaust ozone gas. The effect of pH on pollutants degradation experiment was repeated over the range of 5 – 10. Only

pH value 10.9, the TNT degradation rate increased. While at pH (5, 8 and 9) no significant degradation in TNT was indicated by measurements of COD and TOC values for tested samples. These results were attributed to the decomposition of ozone, as the solution became more basic. While to secondary oxidants such as hydroxyl radicals, results are more agreed with (Sivakumar, 2002). Hwang *et al.* (2005) achieved the highest 74 % TNT reduction at pH of 11.9 and 2 days hydraulic retention time under steady-state conditions.

The effect of different initial TNT concentrations (4, 10, 20 mg/L) on degradation extents with ozone dose 0.177 g/L was studied. The results showed that higher initial concentration led to a slower TNT degradation rate as indicated by COD values of (30, 150 and 430 mg/L) at optimum pH = 10.9 and ozonation time 3 h. The overall degradation rate of TNT depends on number

of hydroxyl radicals generated and the rate of release of hydroxyl radicals into the surrounding medium (Rauch and Drewes, 2005). FTIR spectroscopy was performed to red water dried sample to identify types of pollutants present. Various bands (1-12) (Fig. 2) in the spectrum were identified from which corresponding to alkenes-stretching bands of CH and C=C at wave number (3040 – 3010)/cm and (1680 – 1620)/cm. The wave number at (3040 -3010) and (1623 – 1622)/cm for Ph-CH=CH-R identified alkenes stretching bands and aromatic C-H and C=C. The bands at wave number (1650-1340)/cm could be due to ph-NH₂ and bands at wave number (1350-1260)/cm represent the C-N group. The amides groups also represented at wave number (3375 – 3325)/cm indicating primary amides. The carbonyl group C=O stretch and the amide group NH₂ represented a band at wave number (1638 – 1618)/cm identified group. The

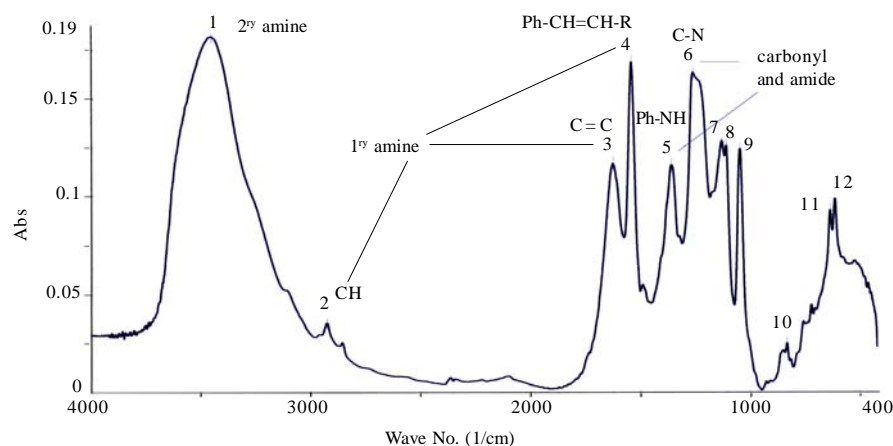


Fig. 2: FTIR- Chromatogram main pollutant present in red wastewater

Table 1: Characteristic of red water, municipal wastewater and river water

| Prameter | Red- water | Limits in Law 89 to the Year 82 |
|------------------------------------|-------------------------|---------------------------------|
| pH | 7.98 | 7 – 8.5 |
| color | Dark redish brown water | no color |
| COD mg/L | 5250 | 40 |
| Volatile solids mg/L | 92.4 | - |
| TDS mg/L | 27.44 | 800 |
| TS mg/L | 27.852 | 1000 |
| TSS mg/L | 0.412 | 30 |
| Turbidity FTU | 207×10 ³ | 50 |
| Conductivity ms/cm | 1 | |
| Hardness as CaCO ₃ mg/L | 2.86 | |
| Mg mg/L | | |
| Ca mg/L | 1.75 | |
| P mg/L | 5.80 | |
| N mg/L | 10.15 | 1 |
| | 71.4 | not exceed 1 |

C=O stretching bands at wave number (1640 – 1540)/cm identifies presence of ketones.

The broad band at wave number (850 – 750)/cm representing N-H group and bands at wave number (638 – 1022)/cm representing C-N group. The bands at wave number (3500 – 3300) cm⁻¹ stretching represented secondary amine.

NMR –Spectra for the dried red-water tested sample showed the H¹NMR chart in Fig (3) and Table (2) the signal at (2.5-2.2 ppm) (P-2h, CH₂), (4.336 ppm) (Gamma protons) and (alpha protons). The broad band at (3.457ppm) indicated the DMSO while (7.738 ppm) indicated ethylenic and aromatic protons.

The biological treatment was performed by supplying appropriate amount of ozone dose 0.177 mg/L to TNT synthetic solution of 20 mg/L concentration for each tested sample. Time of continuous ozonation was studied at (1, 2, 2.5 and 3 h). COD and TOC analysis were subjected to evaluate the residual organic compounds contents (Fig. 4). The direct ozonated samples 1 h were then aerated for 10 min to remove residual ozone and were incubated with 1 % (v/v) of humic acid or 1 % (v/v) of river water as an inoculum, each singly and at ambient temperature for 24 h. 20 min ozonation were followed to each inoculated sample to remove biodegradable dissolved organic carbon (BDOC) (Guest and Smith, 2002; Rauch and Drewes, 2005). COD achieved 72.5 % and 94.6 % removal when using one hour direct ozonation followed by one day humic acid or river water inoculation respectively. To perform multi-stage ozone-biological treatment, TNT and red-water tested samples were subjected to 3 h direct ozonation and followed by 72 h river water biological inoculation. Samples were subjected to 20 min ozonation after each 24 h, to mineralize the BDOC produced through treatment performed.

After the ozonation, the samples were subjected to COD and TOC measurements to evaluate the effect of multi-stage ozonation biological treatment (MSOB). The treatment achieved 98.49 % and 97.56 % TOC removal for TNT and red-water samples, respectively (Fig. 5).

The optimum ozone dose and subsequent biodegradation was performed using samples of the authentic red water containing nitro-compounds was diluted and subjected to ozone treatment. The treatment followed the (1 h and 3 h) ozonation singly with ozone dose 0.177 g/L, at pH = 10.9. The treated wastewater samples were then subjected to 10 min flashing with air to get rid of residual ozone before adding 1 % (V/V) of river water as an inoculums at ambient temperature for

24 h. After which, ozonation for 20 min was undertaken at same previous ozone dose. The tested samples were undertaken to COD and TOC measurements. These previous treatment steps (MSOB) were repeated up to five days for 3 h direct ozonation process (Fig. 5) and repeated up to eight days for 1 h direct ozonation treatment process (Fig. 6). HPLC analysis was performed to detect extent of remediation as shown in Figs. 7-10a and b. High performance liquid chromatography (HPLC) analysis was subjected to evaluate the destructive effect of direct ozonation for 3 h and direct ozonation for 1 h both followed by multistage ozonation-biological treatment for complete mineralization of nitrogenous species have been studied. The HPLC chromatogram illustrates extent of pollutants removal from red water contaminated by nitro-amines till complete mineralization. The HPLC chromatogram of the original red water in Fig. 7 illustrates main peaks at retention time 1.044 and 1.141 besides trace of uracil at retention time 1.47 and phenols at 1.670.

Fig. 8 shows the effect of direct ozonation on degradation of wastewater, including disappearance of main peaks and leaving uracil and phenols. Pollutants such as nitrobenzene was detected too. The 1 h direct ozonation increased the decomposition rate of the major pollutants at retention time 1.044 and 1.191 up to 93 % and 89.75 %, respectively. The transformation products increased the content of uracil and phenols up to 98.2 % and 62.15 % detected by the peaks area of retention time 1.47 and 1.67. The combination of (MSOB) produces large quantities of oxygen due to continuous air bubbling and (BDOC) are easily formed. The ozone oxidation of the formed (BDOC) increases very quickly as the removal rates increased and are shown in Fig. 9. The direct ozonation 1 h followed by (MSOB) treatment three, four and eight days showed a decline up to 98.95 % for uracil peak area mAU. The undetected transformed products at retention time 0.487 and 0.685 achieved 100 % removal. The major pollutants which appeared at retention time 1.044 and 1.191 achieved 98 % and 94.8 % removal too.

On the other hand, the HPLC chromatogram in Fig. 10 a describe the mineralization of the above pollutants after 3 h direct ozonation followed by (MSOB) up to five days. The undetected transformation products appeared at retention time 0.487 and 0.685 were 100 % mineralized. The pollutants at retention time 1.044, 1.191 and 1.395 showed removal rates reached 68 %, 96 % and 96.6 %, respectively. Uracil showed removal rates reaches 46.8 % compared to original sample. During

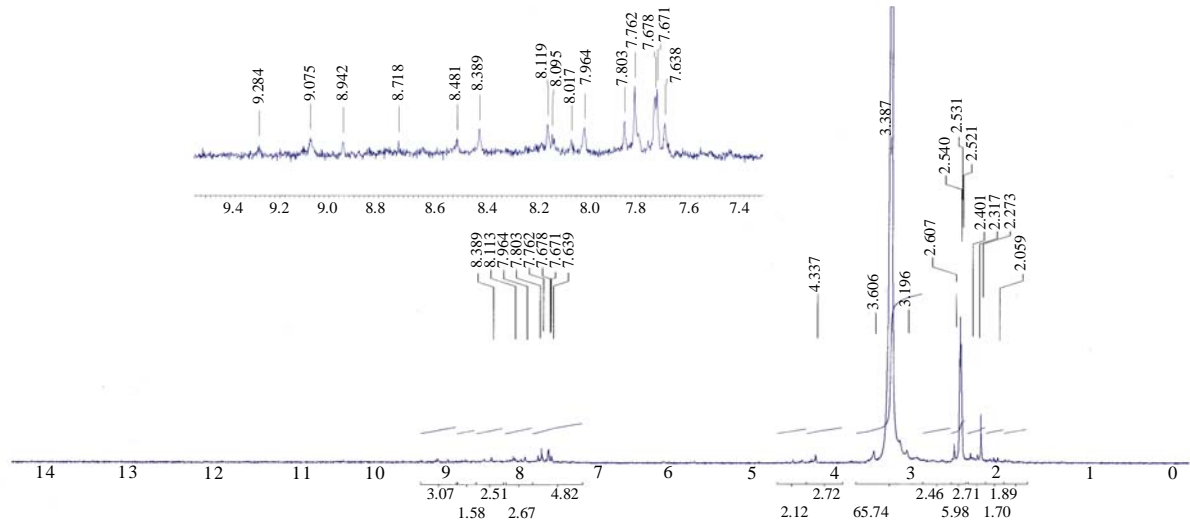


Fig 3: C-NMR chromatogram demonstrating the aromatic carbon area and ethylenic and aromatic protons of authentic red-wastewater

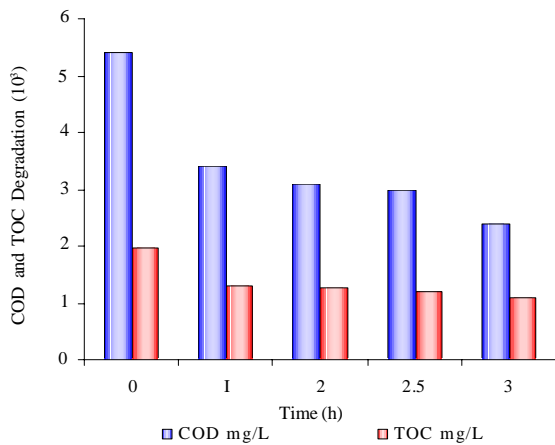


Fig. 4: Effect of direct ozonation on cod and TOC degradation in TNT synthetic solution

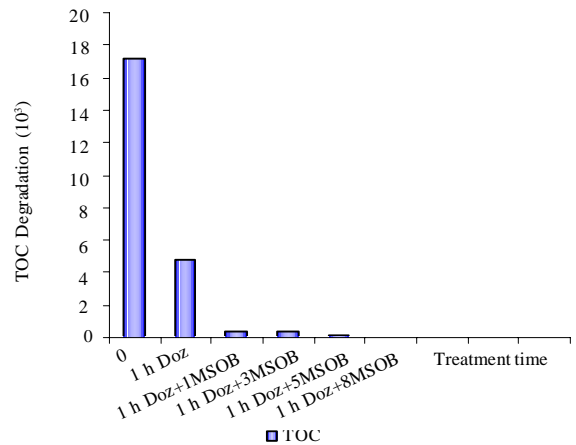


Fig. 5: Effect of 1 h direct ozonation followed by multistage ozonation biological treatment on TOC degradation in red water

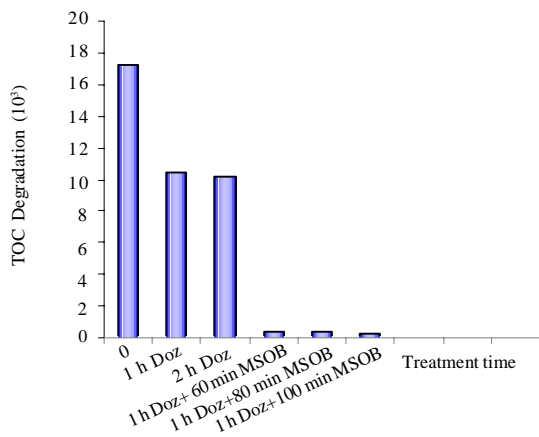


Fig. 6: Effect of 3 h direct ozonation followed by MSOB treatment on TOC degradation in red water

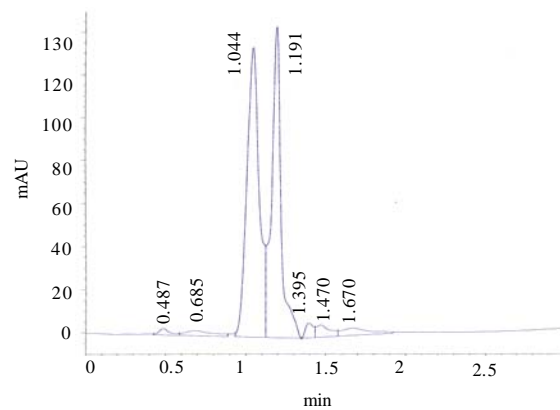


Fig 7: HPLC Chromatogram of major pollutants shown at retention -time at 1.044 and 1.191 investigated on the LC column

transformation a slight increase in phenols peak area (%) appeared. Nitrobenzene existed at retention time 3-4 indicated by broad peak area and continuous degradation for uracil and phenols up to 12.9 % and 51.88 %, respectively were detected. The (MSOB) for the fifth day showed 100 % removal for both undetected pollutant at retention time 0.487 and 0.685 also the major pollutants in the wastewater of retention time 1.044 and 0.191 showed 100 % removal besides the complete 100 % disappearance of uracil. HPLC chromatogram (Fig. 10b) illustrated the best removal of all pollutants both that were present in the original red wastewater and transformed products detected through the degradation of (MSOB) treatment.

CONCLUSION

Based on the above discussion, it appears that TNT and red water effluent were mineralized by ozonation and (MSOB) treatment. Noting that red-water is treated more easily than solid TNT. The solid TNT is to be previously hydrolysed in acetonitrile alkaline buffer solution. It is also remarkable that the complete removal of TOC can be achieved by ozonation combined with biological treatment. Besides direct ozonation is not powerful enough to mineralize materials such as TNT and red water. It may affect COD removal from wastewater till certain extent, but TOC was not easy removed and seemed to be forbidden till biological inoculation helped in dissolving organic carbon and

hence facilitated complete mineralization. Addition of humic-acid to tested samples as inoculum, showed slight decrease in COD % removal at the end of the treatment when compared to that COD % removal achieved by river water inoculation to the same tested samples. Although both river water and humic acid addition to tested samples succeeded for biological inoculation and achieved good results in multi-stage ozone biological treatment, river water was selected as better inoculum to be added to MSOB process. Results of HPLC chromatograms proved that both 3 h direct ozonation followed by 3 days MSOB and 1 h direct ozonation followed by MSOB 5 days are powerful tools for complete destruction of pollutants present in tested samples. Three hours direct ozonation followed by MSOB 3 days shows less treatment contact time (112 h) compared to treatment contact time (121.5 h) consumed for 1 h direct ozonation followed by 5 days MSOB treatment.

ACKNOWLEDGMENTS

The authors gratefully thank the energetic materials producing factory for supplying with products and effluents. The author would also like to introduce his thanks to all colleagues who helped through the birth of this work in the Chemical Engineering Department, National Research Center, Egypt.

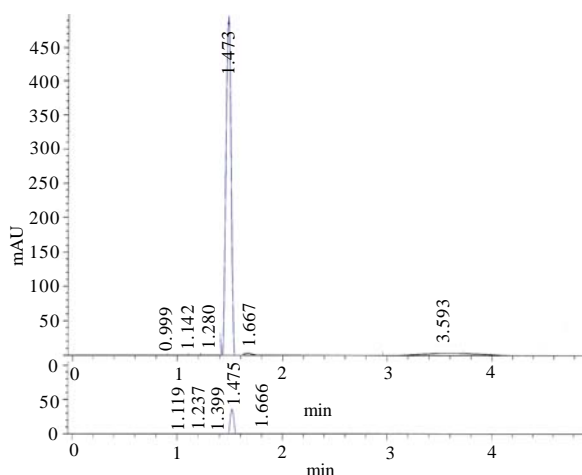


Fig 8: HPLC Chromatogram of pollutants shown at retention time investigated on the LC column after 1 h direct ozonation and (MSOB) treatment three days indicating main Peak of uracil and eight days indicating removal of main pollutant uracil

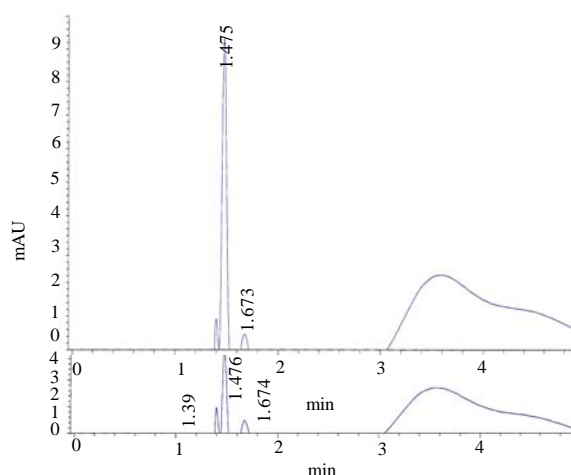


Fig 9: HPLC Chromatogram of pollutants shown at retention time investigated on the LC Column after three hours direct ozonation and (MSOB) treatment one day indicating existence of Uracil peak area. The second peak indicates (MSOB) treatment two days indicating Uracil peak area decline

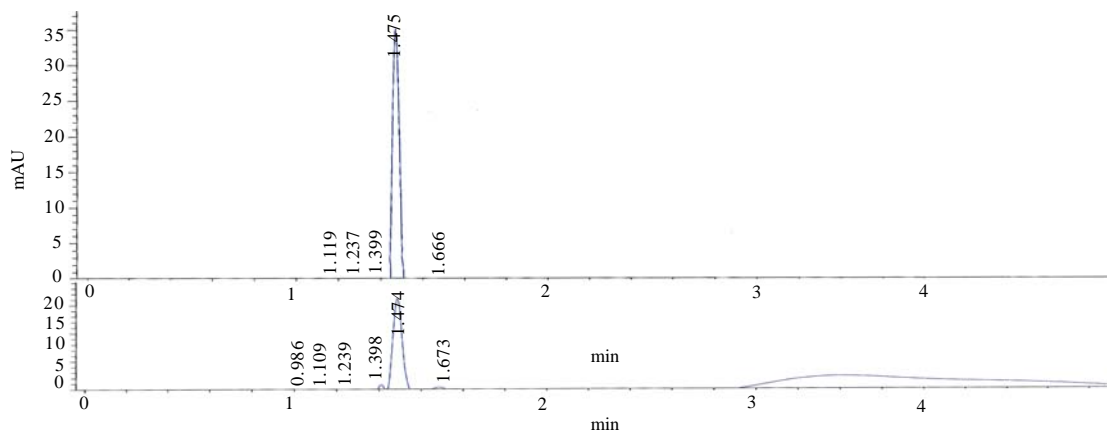


Fig. 10: HPLC chromatogram of pollutants shown at retention time investigated on the LC column after 3 h direct ozonation and (MSOB) treatment 3 days indicating uracil peak area of 53.22 % removal. The second peak indicates (MSOB) treatment. Five days indicating uracil peak area of 89.42 % removal and 34.11 % removal for phenols

Table 2: C-NMR spectrum assignment

| Signal | Chemical shift range | Assignment |
|--------|----------------------|---|
| 7. | 7.66 | Ethyleneic and aromatic protons. |
| 9. | 4.336 | Gamma protons in several structures and alpha protons in condensed structure. |
| | | DMSO |
| 10. | 3.457 | Aromatic |
| 11. | 2.585 | |
| 12. | 2.511 | |
| 13. | 2.274 | |
| 14. | 2.250 | Aliphatic |
| 15. | 2.109 | |
| 16. | 2.086 | |
| 17. | 1.932 | |

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This article should be referenced as follows:

El Diwani, G.; El Rafie, S.; Hawash, S., (2009). Degradation of 2, 4, 6-trinitrotoluene in aqueous solution by ozonation and multi-stage ozonation-biological treatment. Int. J. Environ. Sci. Tech., 6 (4), 619-628.