Factors affecting wet air oxidation of TNT red water: Rate studies

Oliver J. Hao[a,*], Kotu K. Phull[a,b], Jin M. Chen[a], Allen P. Davis[a] and Stephen W. Maloney[c]

[a] *Department of Civil Engineering, University of Maryland, College Park, MD 20742 (USA)*
[b] *U.S. Army Toxic and Hazardous Materials Agency,*
Aberdeen Proving Ground, MD 21010 (USA)
[c] *Construction Engineering Research Laboratory, U.S. Army Corps of Engineers,*
Champaign, IL 61826 (USA)

Abstract

Preliminary experiments have demonstrated wet air oxidation (WAO) to be feasible for TNT red water treatment. This paper presents the results of rate studies for the evaluation of temperature, partial oxygen pressure P_{O_2}, initial red water concentration, salt concentration, and catalyst/initiator addition on WAO performance. Results show the WAO efficiency to be a function primarily of temperature, and to a lesser extent, the initial P_{O_2}. A significant initial (usually <5 minutes) rapid reduction in total organic carbon (TOC) or chemical oxygen demand (COD) is observed in all experiments. The extent of reduction varies with the experimental conditions: the harsher the condition, the higher the initial reduction. At lower temperatures, the subsequent WAO of red water proceeds as a first-order reaction with respect to TOC or COD. Under harsher temperature conditions, the reaction follows two distinct first-order phases. High salt concentrations (Na_2SO_4 and $NaNO_3$) slightly enhanced the overall oxidation. Addition of Cu(II) as a catalyst results in rate enhancement. Several issues regarding application of WAO are discussed.

Introduction

The 2,4,6-trinitrotoluene (α-TNT) is the most widely used military explosive. Crude TNT produced from a three-stage nitration of toluene contains 4 to 5% unsymmetrical TNT isomers, which must be removed in order to meet military specifications. Sodium sulfite is added to crude TNT to produce dinitrotoluene (DNT) sulfonates by selectively reacting with the undesirable TNT isomers (e.g., 2,4,5-TNT). The dinitrotoluenesulfonates (DNTS') so formed (e.g., 2,4-DNT-5-SO₃Na) are water-soluble and are easily separated from the sparingly

---

*To whom correspondence should be addressed.

soluble α-TNT. After phase separation, the wastewater has an intense red color and is commonly referred to as "red water." In addition to the DNTS', red water also contains products of incomplete nitration (e.g., priority pollutants 2,4-DNT and 2,6-DNT) and complex byproducts formed during the nitration and purification stages. A typical red water composition is shown in Table 1. Currently, red water is classified by the U.S. Environmental Protection Agency (EPA) as a RCRA-regulated hazardous waste based on its reactivity.

Based on a recent report by PEI [1] indicating that WAO (wet air oxidation) was one of the promising technologies for hazardous waste treatment, a study was initiated to evaluate WAO for red water treatment. WAO is the oxidation of soluble or suspended oxidizable materials using air or pure oxygen in an

TABLE 1

Red water composition [2][a]

Parameter	Value
pH, units	7.6
Sp. Gravity	1.0
Solids	
Total	2840
Volatile	1020
Fixed	1820
% Organics	36
Inorganic salts	
$[NaNO_2]$	209
$[NaNO_3]$	0
$[Na_2SO_3]$	55
$[Na_2SO_4]$	514
$[Na_2SO_3 + Na_2SO_4]$	569
Alkalinity	
(as $[CaCO_3]$)	43
Organic content	
COD	685
TOC	544
Nitrobodies	
α-TNT	2.27
2,4-DNT	0.21
2,6-DNT	0.03
1,3,5-TNB	3.10
DNTS'[b]	
2,4-DNT-3-SO_3Na	272
2,4-DNT-5-SO_3Na	228

[a] All concentration results in mg/L based on diluted red water (1:100), unless otherwise noted.
[b] Estimated values.

aqueous phase under high temperatures (150–350 °C) and pressures (5.5–17.5 MPa). Preliminary experiments have demonstrated that WAO is effective for diluted red water treatment [2]. For example, at 320 °C and 0.62 MPa P_{O_2}, only small amounts of COD (8 mg/L; 99% removal), TOC (30 mg/L; 94% removal), acetic acid (HAc, 38 mg/L) and total volatile solids (TVS, 127 mg/L; 91% removal) remained after 1-h WAO of 1:100 diluted red water [3]. The DNTS' were not detectable and only a trace amount of 1,3-dinitrobenzene (DNB) remained in the WAO effluent. As a result of the desulfonation of the S-bearing organic compounds in red water (e.g., DNTS'), a significant amount of inorganic sulfate accumulated in the oxidized wastewater. The HAc accumulated up to a temperature of about 300 °C; thereafter the HAc concentration decreased due to its further oxidation.

Results of the preliminary experiments, however, only describe the system performance after 1-h WAO. The transient fate of contaminants during WAO is unknown. Contaminant removal efficiencies under different operating conditions (e.g., longer contact time at lower temperatures), therefore, must be quantified in order to initiate practical and cost-effective engineering applications. Consequently, rate studies were performed to examine WAO efficiencies under different conditions of temperature, oxygen pressure, red water concentration, salt concentration, and catalyst/initiator addition. The results provide additional insight as to the fate of organic compounds, measured either as a gross parameter (i.e., COD) or as a specific compound, under WAO conditions. The results of this study should be useful in the future pilot-scale WAO evaluation for red water treatment.

Materials and methods

Experiments

TNT red water was obtained from ICI-explosives, Canada. A schematic of the apparatus used for the rate studies is shown in Fig. 1. Initially, distilled water was added to the 2-L stainless steel reactor (Parr Instrument) and the 50-mL rinse water cylinder. The raw red water was added to the 50-mL sample cylinder. The amounts of distilled water and sample depended on the red water concentration to be studied. For example, for a 1:25 dilution of red water, the volumes of distilled water, raw red water, and rinse distilled water were 910, 40 and 50 mL, respectively, in the reactor, sample cylinder, and rinse water cylinder.

After sealing the reactor, a prescribed amount of O_2 was discharged into the reactor and the contents were heated to the desired temperature. The stirrer speed was maintained at 200 rpm to minimize mass transfer limitation [3]. Once the desired temperature was reached, the raw red water sample was discharged into the reactor via helium backpressure. Subsequently, the distilled water was charged into the sample cylinder for rinsing and finally to the reactor for a total liquid volume of 1 L. After the introduction of the sample and distilled
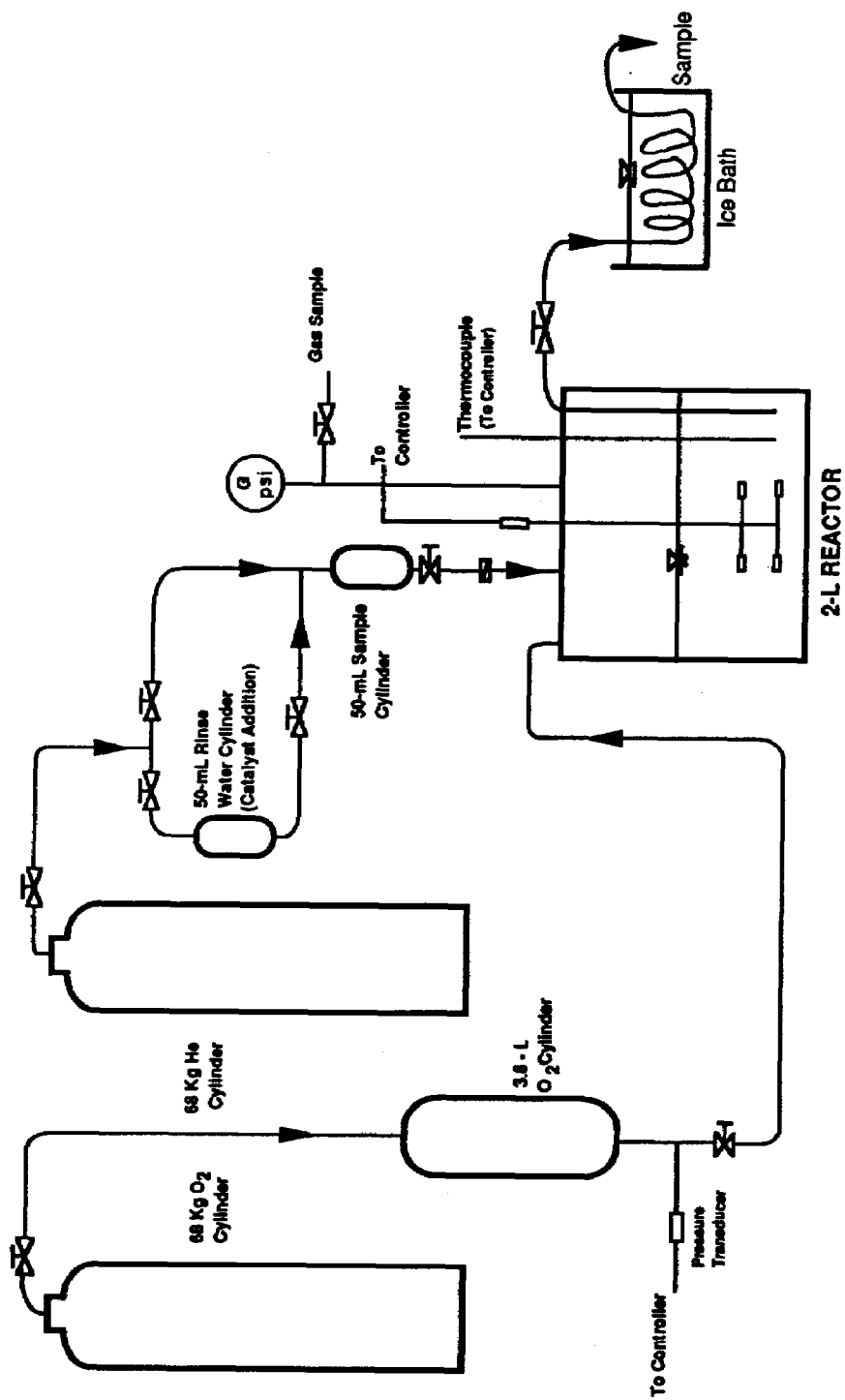
Fig. 1. Schematic of WAO apparatus used for rate studies.

water into the reactor, the temperature dropped slightly and the pressure increased somewhat; both stabilized within 2–3 minutes. The total run time for each experiment was approximately 2 h. An experimental mass balance check has demonstrated that the sample injection technique is reliable [3]. The final pressure after the experiment was slightly less than the initial oxygen pressure.

A radical initiator (H_2O_2) and two different homogeneous catalysts [Mn(II) and Cu(II)], were used to assess their effectiveness for enhancing contaminant removals. The initiator or the catalyst was added to the 50-mL distilled water cylinder and discharged into the reactor as described above.

Samples were withdrawn from the reactor periodically through a stainless-steel coil that was submerged in an ice–water bath. The first sample (10–15 mL) was obtained within 5 min of sample injection. 10–15 mL liquid from the reactor was discarded prior to each sampling event. All samples were analyzed for pH, COD and TOC; some for inorganic salts (sulfite, sulfate, nitrite, and nitrate), solids (total and volatile), HAc, DNTS', six nitroaromatics (nitrobenzene (NB), 1,3-DNB, 2,4- and 2,6-DNT, 1,3,5-TNB, and α-TNT), and UV/VIS absorbance.

The experimental conditions for evaluating the effects of temperature, P_{O_2}, initial red water concentration, salt concentration, and catalyst/initiator addition are summarized in Table 2.

TABLE 2

Experimental conditions for rate studies of WAO of TNT red water

Run No.	Dilution	Temperature (°C)	Initial P_{O_2} (MPa)
1	1:100	260	1.21
2	1:100	300	1.21
3	1:50	260	1.55
4	1:25	260	0.31
5	1:25	260	0.62
6	1:25	260	1.21
7	1:25	260	1.93
8	1:25	260	1.55
9	1:25	260	2.19
10	1:25	230	0.62
11	1:25	280	0.62
12	1:25	300	0.62
13[a]	1:25	260	1.55
14[a]	1:25	260	1.55
15[b]	1:100	260	0.55

[a] With addition of $NaNO_3$ and Na_2SO_4.
[b] With addition of catalyst/initiator.

Analytical methods

A detailed description of analytical methods is presented elsewhere [3]. Briefly, TOC was measured using acid digestion and IR detection of the CO_2 produced. Gas chromatography was used for the analysis of the six nitroaromatics and acetic acid. The DNTS concentrations were estimated using reverse phase ion-pairing chromatography. Ion exchange chromatography was used for sulfite, sulfate, nitrite, nitrate, and acetic acid. Standard Methods [4] were used for COD and solids.

Results and discussion

Typical profiles for TVS, TOC, and COD as a function of WAO reaction time (Fig. 2; $T = 260\,°C$ and $P_{O_2} = 0.31\,MPa$, dilution ratio $= 1:25$) showed similar trends. There was a significant initial reduction of TOC, COD, and TVS immediately after sample injection (within the first sampling event, usually $< 5\,min$). After the initial "flash" destruction, the reaction proceeds as a first-order reaction:
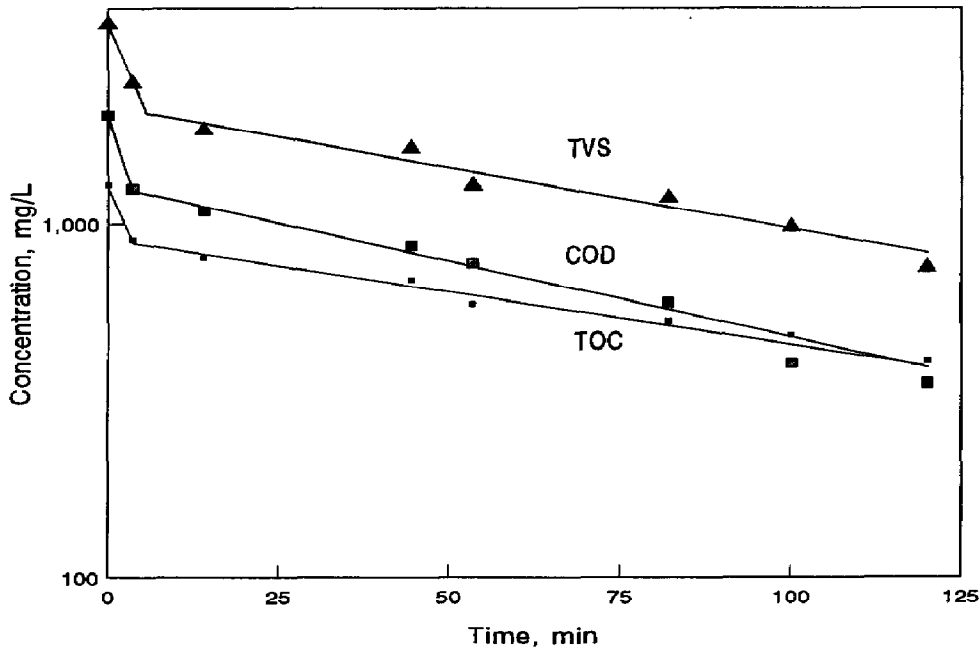
$$r = -\mathrm{d}C/\mathrm{d}t = kC \tag{1}$$

Fig. 2. Typical COD, TOC and TVS removal profiles at 260 °C, 0.31 MPa P_{O_2}, 1:25 dilution.

where r is the rate of reaction, and C and k are the concentration (TOC, COD or TVS) and the apparent (observed) first-order rate constant, respectively. From the semi-log plots, the rate constants were determined to be 6.5×10^{-3} ($R^2 = 0.98$), 1.1×10^{-2} ($R^2 = 0.97$), and $8.5 \times 10^{-3}\,min^{-1}$ ($R^2 = 0.91$) , respectively, for TOC, COD, and TVS. The first-order rate dependence with respect to a gross parameter, such as COD or TOC, has also been reported by Baillod et al. [5] for WAO of phenol and nitrophenol; Freeze and Rolinski [6] for coal gasification wastewater; Foussard et al. [7] for paper-mill black liquor; Joglekar et al. [8] for phenol; and Phull [3] for 5-nitro-o-toluenesulfonic acid.

Effect of red water concentration

At a constant temperature of 260 °C, three different red water dilutions (1 : 25, 1 : 50 and 1 : 100) were used to observe the effects on the reaction rates. The COD, TOC, and UV absorbance (@200 nm) results (e.g., Fig. 3 for COD) indicate essentially the same phenomena — the initial rapid contaminant destruction and a subsequent first-order contaminant removal rate. The semi-log plots had identical slopes, thus confirming a first-order reaction with respect to the monitored parameter.
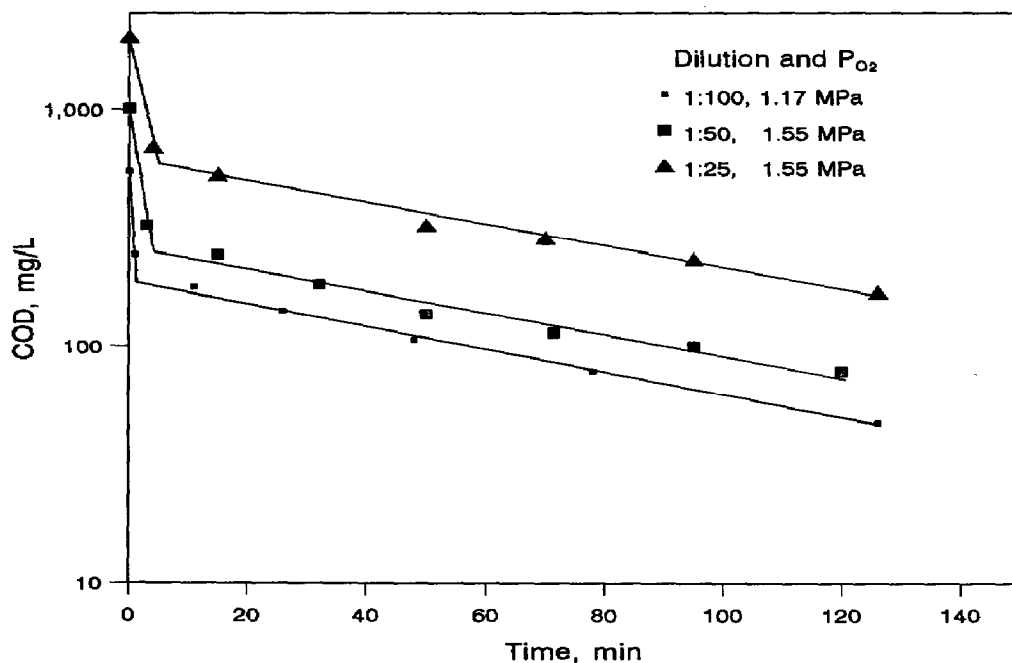

Fig. 3. Effect of red water concentration on WAO rate at 260 °C: COD.

Effect of partial oxygen pressure

For a 1:25 sample dilution ratio at a constant temperature of 260 °C, several different oxygen pressures were used to evaluate the effect on the reaction rates. As shown in Fig. 4a, the initial COD was significantly reduced within the first 5 minutes (e.g., from 2020 mg/L to 580 mg/L in 4 min at 260 °C and 2.19 MPa P_{O_2}). The initial rapid COD reduction is apparently due to the presence of easily oxidizable compounds in red water. The degree of the initial "flash" destruction depends on oxygen pressure, as can be easily seen from the two extreme pressure cases (Fig. 4a). After the initial COD reduction, the removal of slowly oxidizable compounds follows the first-order reaction rate (slopes are all parallel, except for the 2.19 MPa case) and P_{O_2} has no further effect on the COD destruction rate constant. The first-order rate constant is approximately 1.1×10^{-2} min^{-1}. Eckert et al. [9], in their WAO studies of p-chlorophenol, also reported that O_2 (varied by a factor of 11) did not exert any effect on the first-order reaction rate with respect to p-chlorophenol. Although the P_{O_2} did not affect COD destruction rate, the oxygen pressure influenced the extent of overall COD removal due to its effect on the initial COD reduction.

At the highest oxygen pressure (2.19 MPa) used, however, there appear to be two distinct first-order removal phases (Fig. 4a), with a rate constant of 2.2×10^{-2} min^{-1} with respect to COD for the second phase, and 5.7×10^{-3} min^{-1} for the slower phase. The presence of two or more phases of WAO reaction has been reported by others. For example, Foussard et al. [7] divided the organic loading in WAO of biological sludge into two parts: easily oxidized and not easily oxidized. They proposed first-order rate expressions with respect to organic concentration for both parts. A two-phase reaction, first-order in each phase, was also presented by Joglekar et al. [8] for WAO of substituted phenols. Other reactions with two distinct first-order phases include BOD and nitrification in streams [10], chlorine disinfection [11], and endogenous nitrate respiration of activated sludge [12].

The observed TOC destruction with time (Fig. 4b) is similar to that of COD: initial rapid TOC removal dependent on oxygen pressure [e.g., from 1260 to 600 mg/L within 4 min (260 °C and 2.19 MPa)]; a first-order rate with respect to TOC for the subsequent reaction with no effect exerted by the initial P_{O_2} on rate constants for this phase; and two distinct phases under the harshest condition.

Effect of temperature

At a constant pressure of $P_{O_2} = 0.62$ MPa and a dilution factor of 1:25, the effect of WAO temperature on COD destruction is substantial (Fig. 5a). Again, it appears that after the initial COD destruction, slowly oxidizable compounds follow first-order removal and the apparent rate constants are 5.4×10^{-3} and 1.1×10^{-2} min^{-1}, respectively, at 230 and 260 °C. However, at higher temperatures, two distinct phases are present as previously observed in Fig. 4a with the highest P_{O_2}. The rate constants for the first phase were calculated to be 2.3×10^{-2} and 4.2×10^{-2} min^{-1}, respectively, at 280 and 300 °C. For the slower
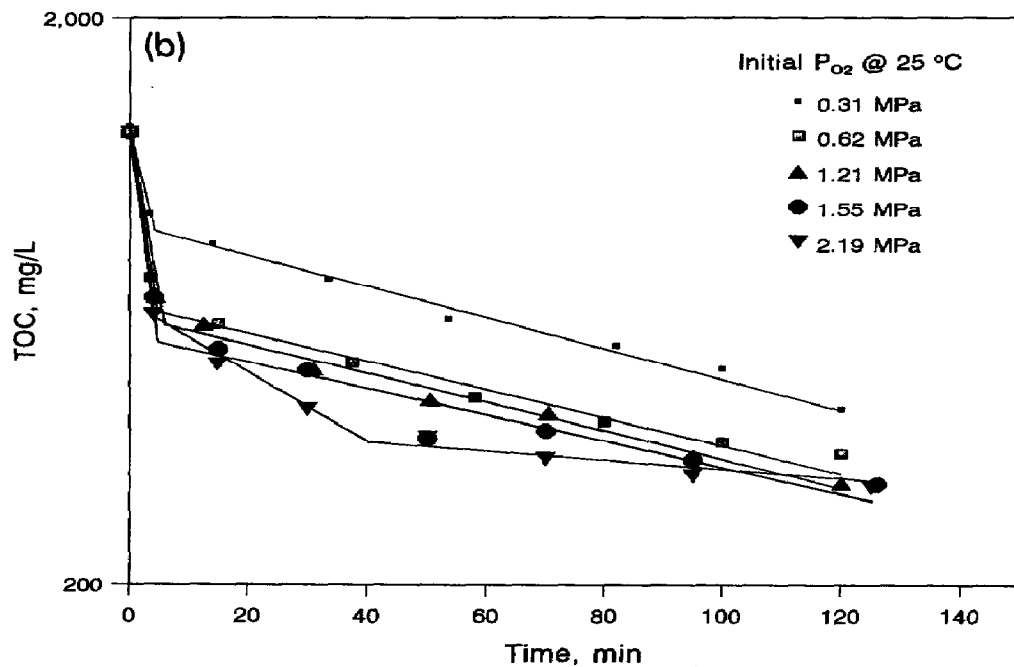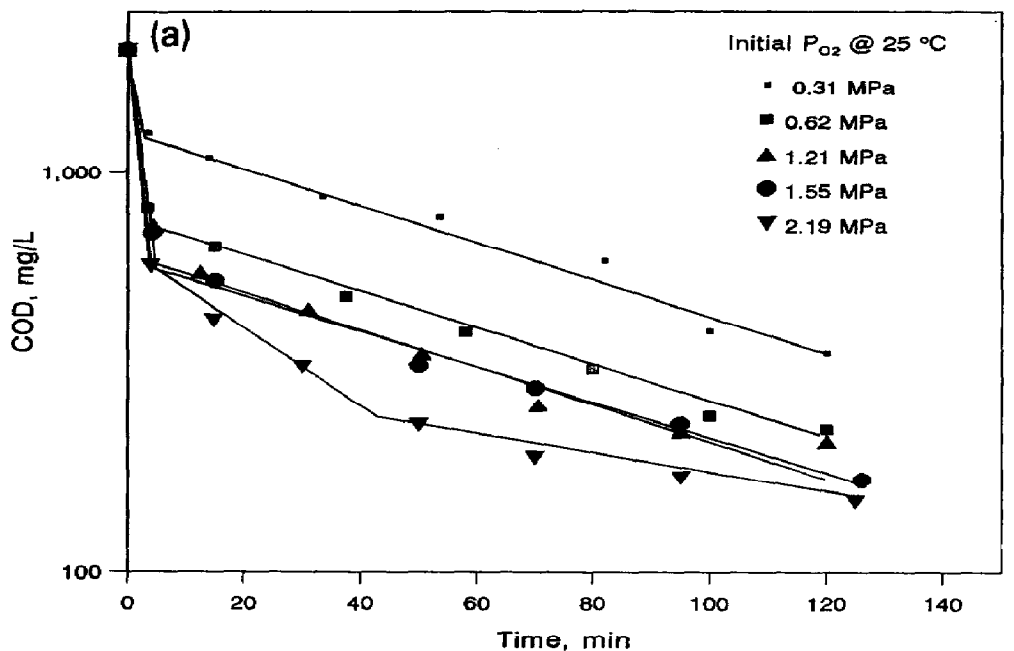
Fig. 4. Effect of initial P_{O_2} on WAO rate at 260 °C, 1:25 dilution. (a) COD, and (b) TOC.

step, the rate constants at 280 and 300 °C were determined to be 9.8×10^{-3} and 1.0×10^{-2} min^{-1}, respectively.

The pattern for TOC reduction (Fig. 5b) as a function of temperature is similar to that for COD. Similar observations were made for UV absorbance reduction at 200 nm. Arrhenius plots for COD and TOC, using the rate constants for the faster reaction phases indicate activation energies to be 17 and 18 kcal/mol, for COD and TOC, respectively. These values are similar to the values reported by other investigators for WAO of different compounds, e.g., 14 kcal/mol for phenol [13] and 16 kcal/mol for acetone [14].

Effect of salt concentration

Inorganic salts (e.g., Na_2SO_4) are not destroyed as a result of WAO; in fact, their amounts increase due to oxidation of inorganic sulfite and organic sulfo groups. In order to evaluate the effects of high salt concentrations on WAO of red water under continuous treatment conditions, two experiments were performed by adding $NaNO_3$ and Na_2SO_4. In the first experiment 1.56% salt solution (15 g/L Na_2SO_4 plus 0.6 g/L $NaNO_3$) was added to the reactor; 5.2% salt concentration (50 g/L Na_2SO_4 plus 2.0 g/L $NaNO_3$ was employed in the other experiment. The COD results (Fig. 6) indicate that the increased salt concentrations enhanced the extent of COD removal. The exact reasons for this are unclear. The trace metals present as impurities in the large quantities of $NaNO_3$ and Na_2SO_4 added might have catalyzed the WAO reactions, resulting in a slightly better overall COD removal. The effects of salt concentration on TOC removal rates (not shown) are similar to those for COD. The higher salt concentration at 5.2% enhanced the TOC removal rate more noticeably.

Effect of catalyst/initiator

A mild WAO condition was selected to observe any enhancement in rates upon the addition of the catalyst or an initiator (Fig. 7). H_2O_2 dosages at 20 and 150 mg/L appear to have an adverse effect as compared to the control system; Mn(II) at 10 mg/L exhibited little effect. Cu(II) catalyst, however, enhanced the overall TOC removal. The enhanced effect of Cu(II) on WAO of other organics has also been cited, e.g., WAO of nitrotoluenesulfonic acid [3].

Other kinetic data

Typical pH profiles for WAO of red water (1:25) are shown in Fig. 8. As expected, the solution pH after the WAO is altered by the experimental conditions. It was significantly reduced from 7.6 to approximately 3.5 within the first sampling period (< 5 min). The red water has little buffer capacity and the reduction in pH indirectly infers that SO_3 groups are rapidly detached from the DNTS', resulting in the formation of H_2SO_4. Additionally, organic acids formed from WAO of the various organic compounds in red water may also depress the pH. Rapid desulfonation within the first sampling period is also confirmed by the increased sulfate concentrations (e.g., from 1510 to 2970 mg/L at 300 °C and 0.62 MPa; Fig. 9). The changes in pH and sulfate concentrations
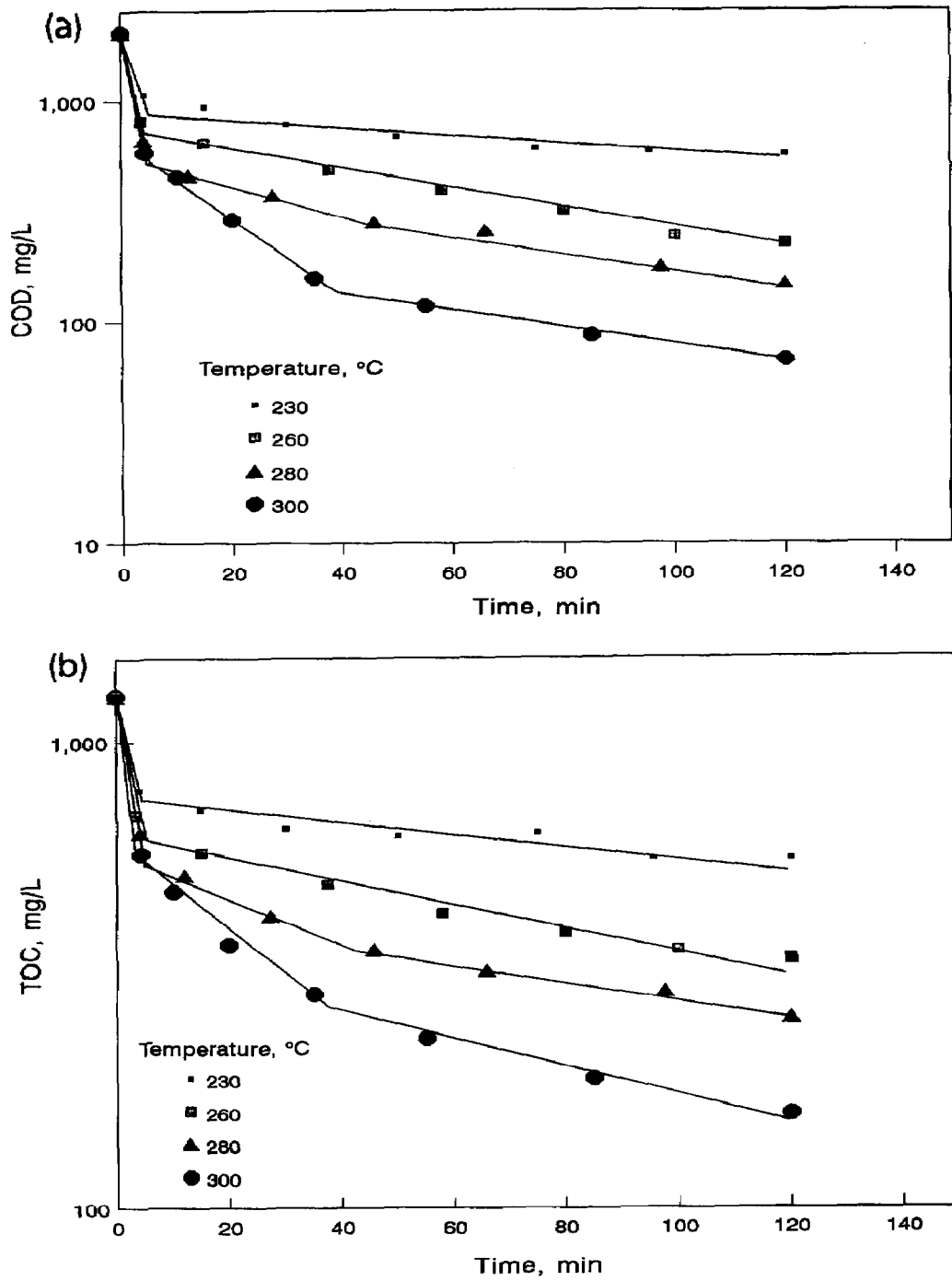
Fig. 5. Effect of temperature on WAO rate at 0.62 MPa P_{O_2}, 1:25 dilution. (a) COD, and (b) TOC.
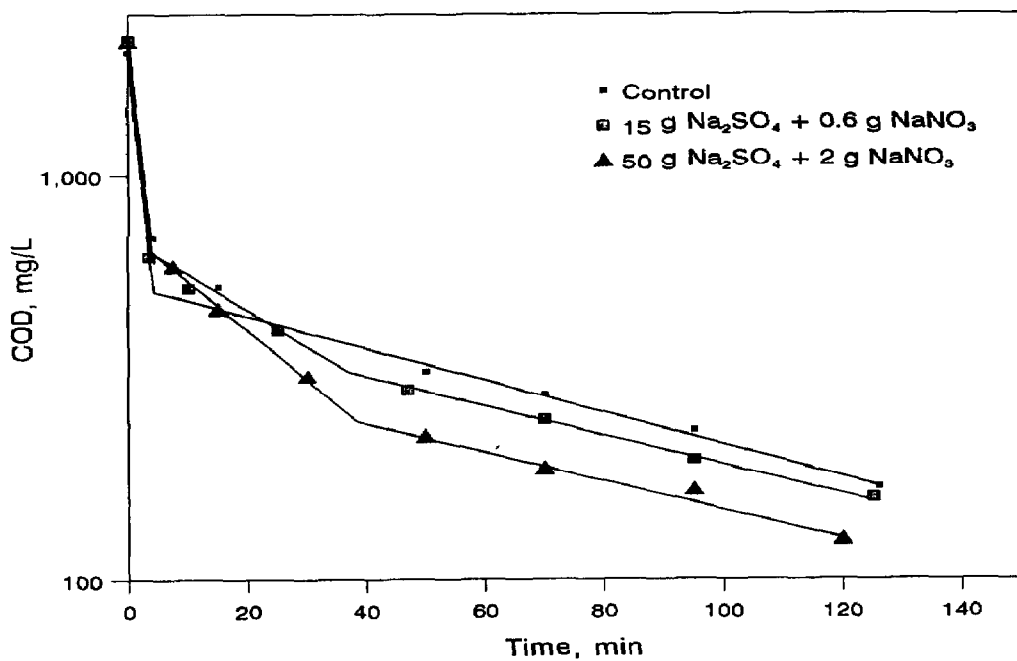
Fig. 6. Effect of salt concentration on WAO rate at 260 °C, 1.55 MPa P_{O_2}, 1:25 dilution: COD.
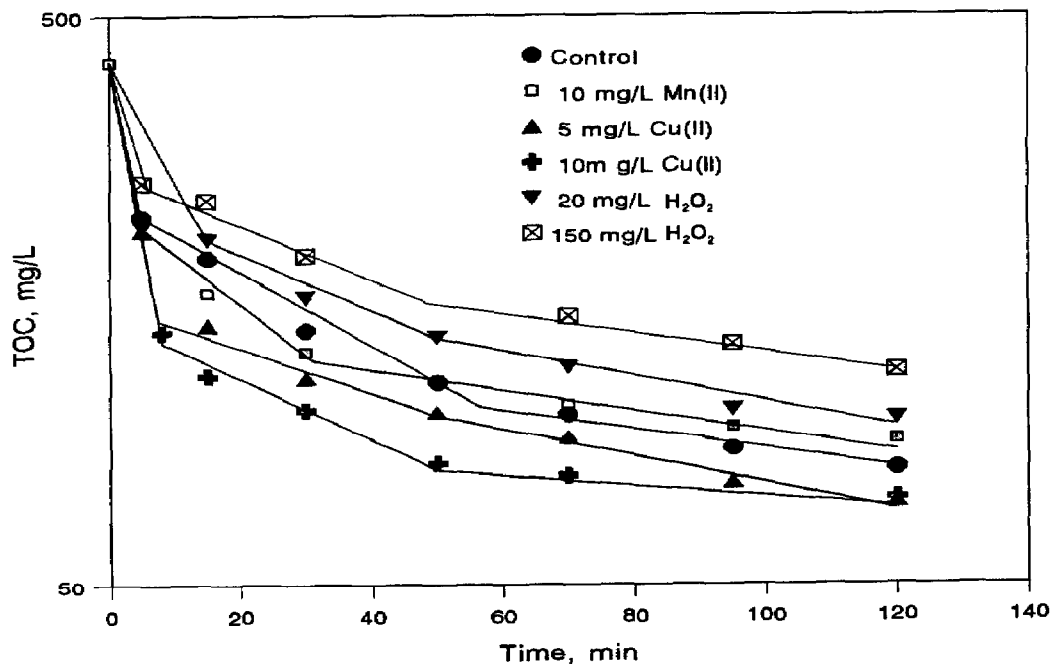

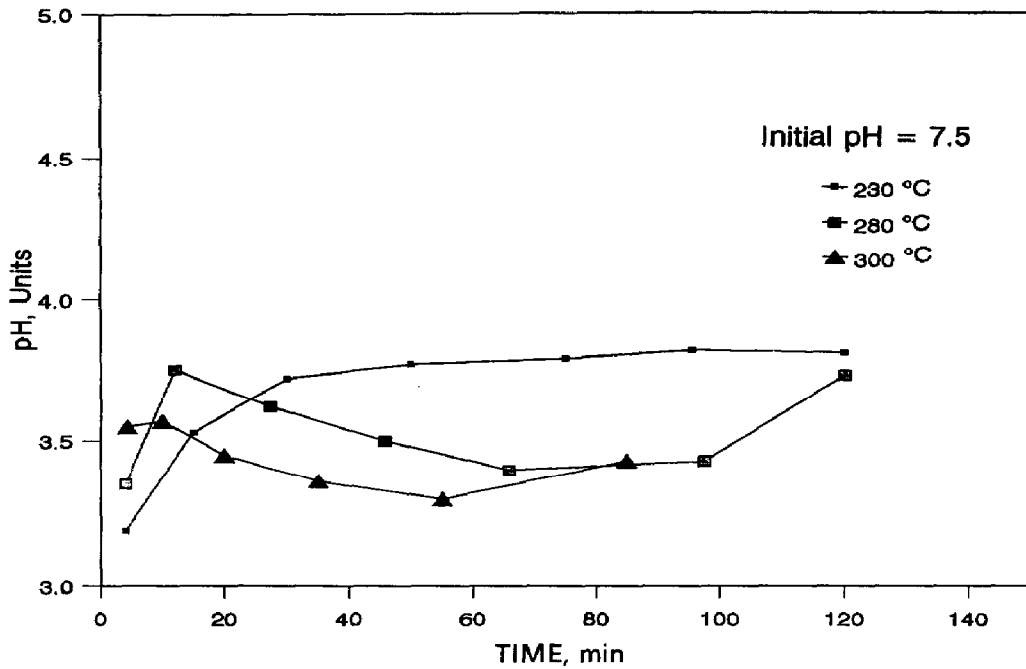Fig. 7. Effect of catalyst/initiator on WAO rate, 260 °C, 0.55 MPa P_{O_2}.

Fig. 8. Typical pH profiles as a function of temperature, 0.62 MPa P_{O_2}, 1:25 dilution.
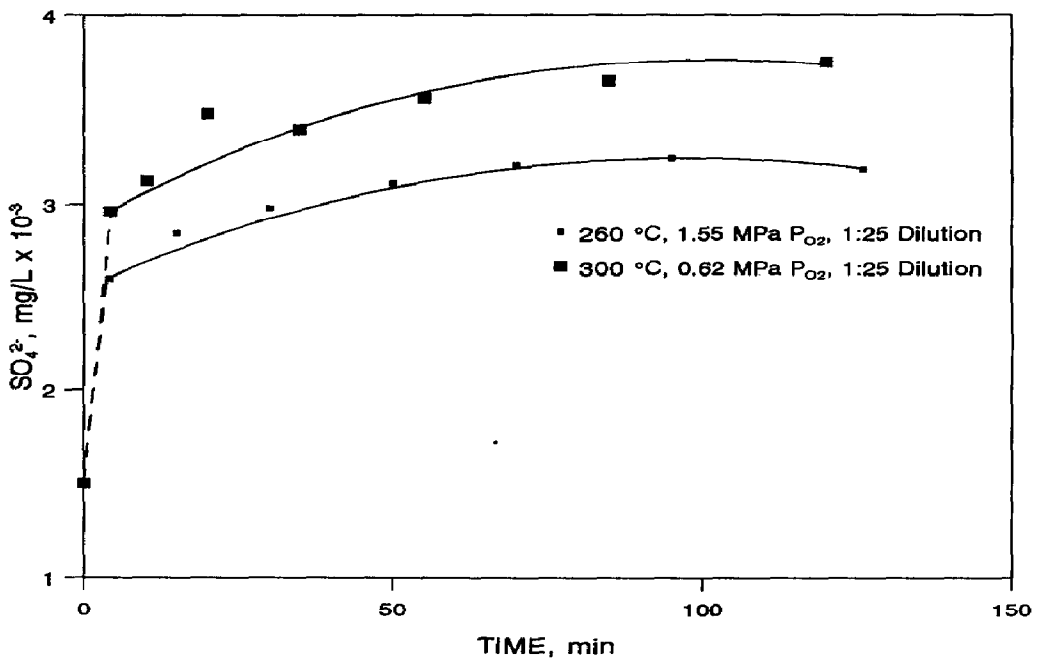

Fig. 9. Accumulation of sulfate during WAO of TNT red water.

correspond well to the initial rapid reduction in COD, TOC, and TVS as discussed earlier. The measured nitrate concentrations were, however, lower than the combined nitrite and nitrate concentrations initially present, without even considering the organic nitro groups present in red water. The unaccounted nitrogen is attributed to the formation of ammonium and N_2 gas [3]. Generation of N_2 from wet oxidation of the nitro group was also reported for other explosives [15, 16].

The data for DNTS removal for two experiments at 260 °C, 1.55 MPa P_{O_2} and 300 °C, 0.62 MPa P_{O_2} (Fig. 10) indicate that 2,4-DNT-5-SO_3Na is more easily oxidized than 2,4-DNT-3-SO_3Na and temperature rather than oxygen pressure exhibits a more significant effect. The results for 1,3-DNB (Fig. 11) compare well with those from 2-h batch experiments [2]. The 1,3-DNB concentration increases with temperature and time, supposedly following DNTS′ → DNT → DNB, and then decreases as a result of further oxidation.

Application

Although WAO may be effective strictly from a technological standpoint, several issues need to be adequately addressed to ensure successful practical application of WAO for the treatment of TNT red water. These issues include cost, energy recovery, corrosion and materials of construction, and toxicity of WAO-treated waste streams.
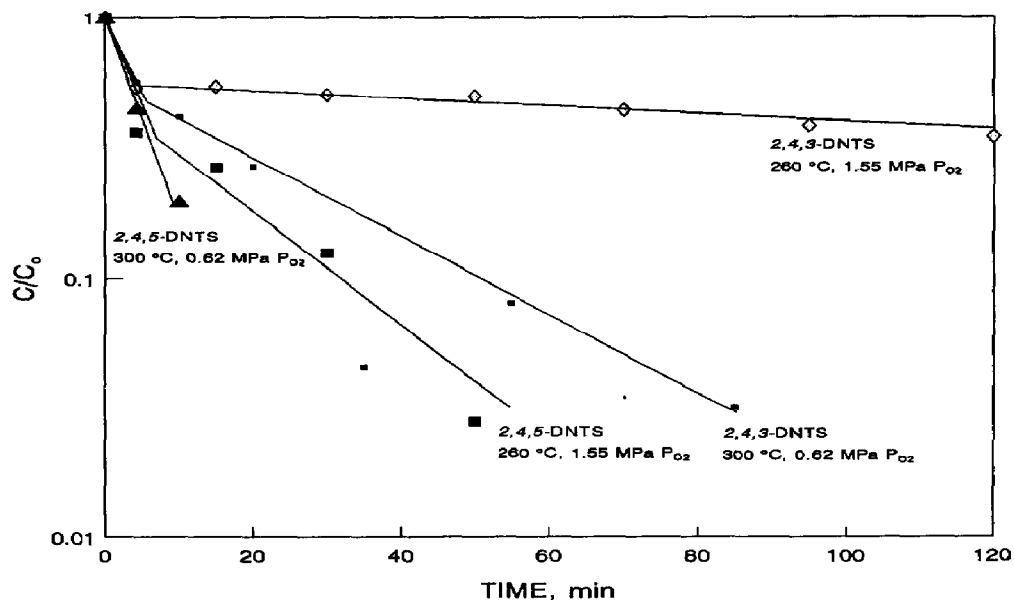

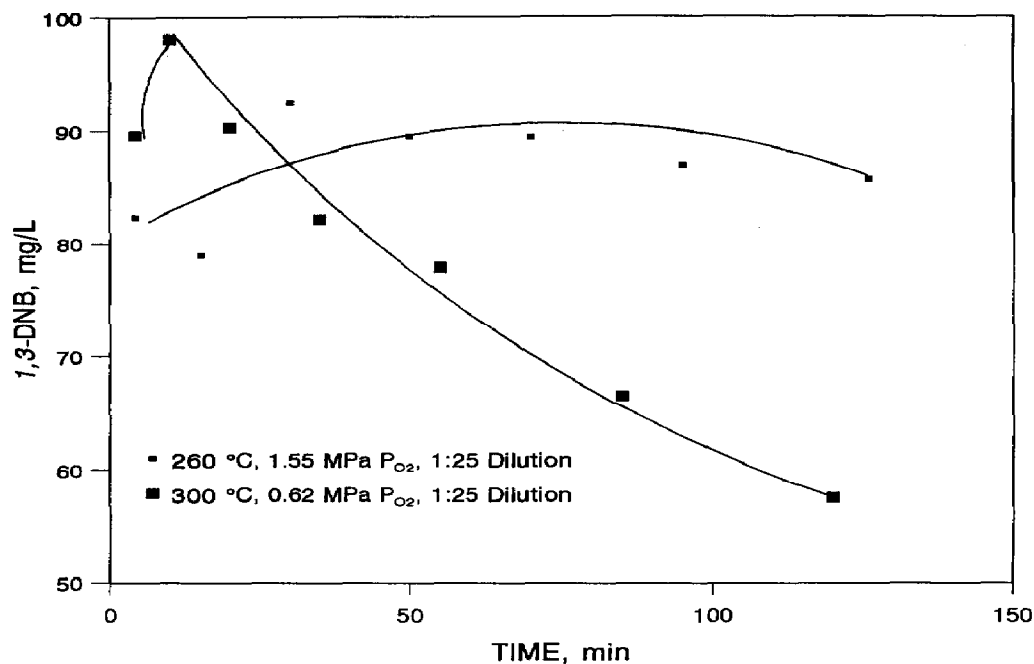Fig. 10. Effect of temperature and P_{O_2} on DNTS removal.

Fig. 11. Accumulation of 1,3-DNB during WAO of TNT red water.

Cost and energy

Economics and regulatory compliance are the most important factors influencing the choice of a waste treatment method. The selected method must provide the desired treatment, while keeping capital and operational/maintenance/repair costs to a minimum. The capital cost of a WAO unit is related to the capacity (reactor size) and the desired system pressure (miscellaneous high pressure pumps and air compressors). The major operational cost is the amount of air used, which depends on the degree of oxidation and system conditions.

Generally speaking, full-scale WAO plants require higher capital investment compared to the equivalent treatment alternatives. Other factors, such as minimal "cross-media" pollution, however, may still render the WAO process more desirable. As an alternative, WAO may be used as a pretreatment step to enhance the biotreatability of red water at milder WAO conditions than required for complete mineralization of the waste. Such an operation would result in significantly lower operational costs.

The WAO process offers an opportunity for energy recovery in the form of thermal (steam generation or heating the waste influent), mechanical (expansion of hot offgas), and electrical energy. Recovery of WAO reaction enthalpy for supplementing heat input or even for attaining a self-sustaining process has been reported by several investigators. The minimum concentration of organics required for the process to become self-sustaining depends on temperature and pressure (e.g., 8 g/L COD at 271 °C, 10.4 MPa [17]; 10–20 g/L ΔCOD at

275 °C [18]; and TOD > 15 g/L at T > 300 °C [7]) based on a heat of reaction of 12,500–13,000 kJ/kg. Some full-scale WAO plants currently in operation are, in fact, used to generate steam [19].

For simplicity, the entire amount of the heat of reaction is assumed to be available for heating the influent and the heat loss from the system is considered to be insignificant. The minimum concentration of organics (C_{min}) for a WAO system to become self-sustaining can be roughly estimated:

$$C_{min} = (\Delta T \times C_p)/H_R \tag{2}$$

where, C_{min} is the minimum organic concentration for self-sustainment, wt%; ΔT the temperature difference between waste influent and the reactor temperature, °C; C_p the heat capacity of water (4.1 kJ/kg °C); and H_R the heat of reaction, kJ/day.

For red water, the heat of reaction in terms of joules per kg of organics must be estimated in order to calculate C_{min}. Based on the reported heat value of 7430 kJ/kg for TNT red water [1], C_{min} is approximately 14% for a ΔT of 260 °C. Because the heat losses may be quite significant, C_{min} determined from reaction (2) may be underestimated. Thus, an initial concentration step may be required for a dilute waste stream for an effective energy recovery. On the other hand, if heat recovery is considered for a given ΔT between the influent and heat exchange effluent, C_{min} should be much lower than that from reaction (2).

Corrosion

WAO is generally more effective at both high and lower pHs [3], however, it is more desirable for COD removal at low pHs. Additionally, the process itself results in a low effluent pH due to the generation of mineral acids and low molecular weight organic acids, as well as the high concentration of aqueous CO_2 at elevated system pressures. For example, the pH of WAO-treated propellants and explosives ranged from 0.7 and 2.9 [15, 16]. The pH of TNT red water decreased from 7.5 to about 3 after WAO; oxidized 5-nitro-o-toluenesulfonic acid had a pH of less than 2 [3].

The design of full-scale WAO reactors must take into account the unique operational conditions of high temperatures and pressures in addition to the low pH of the oxidized solutions, since the corrosivity of the waste is enhanced under such conditions. Furthermore, red water is expected to be more corrosive when subjected to WAO due to the formation of inorganic sulfate. Stainless steel may not be the preferred material of construction for such wastes; special alloys or metals (e.g., Inconel 600, Hasteloy C-276, titanium) may be needed. The proper choice of the material of construction should include bench-scale corrosion tests as well as pilot studies.

Toxicity

A general review of previous WAO studies [3, 20, 21] indicates that the WAO-treated wastes may exhibit higher inhibitory effects on microbial species than the starting material(s). Some literature results further indicate that,

although the WAO process was more efficient in destroying the starting material(s) under harsher conditions, the treatment under these conditions also produced byproducts with higher toxic effects [3]. It is quite clear that the toxicity of the oxidized material should be determined to ensure that direct discharge of treated red water would not pose any environmental problems.

Conclusions

Rate studies of WAO of red water revealed several interesting points. First, a major portion of the COD, TOC, and TVS was destroyed immediately after the injection of the sample into the reactor, due to the oxidation of easily oxidizable compounds present in red water. The degree of this "flash" COD, TOC, or TVS reduction is related to the operating conditions. The higher the temperature and/or pressure, the more the contaminant reduction. After this initial fast activity, P_{O_2} had little effect, and reaction of the slowly oxidizable compounds proceeded at a typical first-order rate with respect to COD (TOC or TVS). Under harsher conditions, however, two distinct first-order rate phases appear. Temperature, as expected, significantly affects the first-order rate constants with an activation energy of approximately 17 kcal/mol for COD. Catalyst Cu(II) and high salt concentrations produced slight enhancements in the WAO rate of red water.

Acknowledgements

References

1   PEI Associates, Technological Evaluation for Treatment/Disposal of TNT Red Water, Report No. CETHA-TE-CR-90048, US Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD, 1990.
2   O.J. Hao, K.K. Phull, A.P. Davis, J.H. Chen and S.W. Maloney, Evaluation of wet air oxidation of TNT red water, Proc. 24th Mid-Atlantic Ind. Waste Conf., Morgantown, WV. Technomic, Lancaster, PA, 1992, pp. 110–119.
3   K.K. Phull, Wet Air Oxidation of TNT Red Water, Ph.D. Dissertation, Department of Civil Engineering, University of Maryland, College Park, MD, 1992.

4   Standard Methods for the Examination of Water and Wastewater, 16th edn., American Public Health Association, Washington, DC, 1985.
5   C.R. Baillod, B.M. Faith and O. Masi, Fate of specific pollutants during wet oxidation and ozonation, Environ. Prog., 1 (1982) 217–226.
6   R.A. Freeze and E.J. Rolinski, Wet air oxidation studies of coal gasification wastewaters, J. Hazardous Mater., 8 (1984) 367–375.
7   J.-N. Foussard, H. Debeilefontaine and J. Besombes-Vailhe, Efficient elimination of organic liquid wastes: wet air oxidation, J. Environ. Eng., ASCE, 115 (1989) 367–385.
8   H.S. Joglekar, S.D. Samant and J.B. Joshi, Kinetics of wet air oxidation of phenol and substituted phenols, Water Res., 25 (1991) 135–145.
9   C.A. Eckert, G.W. Leman and H.H. Yang, Homogenous catalysis for wet oxidation: design and economic feasibility of a mobile detoxification unit, Haz. Mat. Control, 3 (1990) 20–33.
10 A.K. Deb and S.D. Bowers, Diurnal water quality modelling — a case study, J. Water Pollut. Control Fed., 55 (1983) 1476–1488.
11 C.N. Haas and S.B. Kana, Kinetics of microbial inactivation by chlorine — II. Kinetics in the presence of chlorine demand, Water Res., 18 (1984) 1451–1454.
12 M.H. Kim and O.J. Hao, Comparison of activated sludge stabilization under aerobic and anoxic conditions, J. Water Pollut. Control Fed., 62 (1990) 160–168.
13 J.R. Katzer, H.H. Ficke and A. Sadana, An evaluation of aqueous phase catalytic oxidation, J. Water Pollut. Control. Fed., 48 (1976) 920–931.
14 J.E. Taylor and J.C. Weygandt, A kinetic study of high pressure aqueous oxidations of organic compounds using elemental oxygen, Can. J. Chem. Eng., 52 (1974) 1925–1933.
15 W.M. Fassel and D.W. Bridges, Wet oxidation destruction of propellants and explosives, Proc. Natl. Conf. on Management and Disposal of Residues from the Treatment of Ind. Wastewaters. Information Transfer, Rockville, MD, 1975, pp. 87–97.
16 W.M. Copa and T.L. Randall, Wet Air Oxidation of Propellants and Propellant Wastewater. Zimpro Passavant Report No. TA-97, Rothschild, WI, 1990.
17 C.L. Chou and F.H. Vernhoff, Process for power generation from wet air oxidation with application to coal gasification waste water, Ind. Eng. Chem. Process Res. Dev., 20 (1981) 12–19.
18 H.N. Akse, M.M.G. Senden, M. Tels and J.H.O. Hazewinkel, Detoxification and energy recovery by wet air oxidation of waste streams, Resources and Conservation, 14 (1987) 351–364.
19 W.M. Copa, Personal Communication, Zimpro Passavant, Rothschild, WI, 1992.
20 T.L. Randall and P.V. Knopp, Detoxification of specific organic substances by wet oxidation, J. Water Pollut. Control Fed., 52 (1980) 2117–2130.
21 R. Keen and C.R. Baillod, Toxicity to *Daphnia* of the end products of wet oxidation of phenol and substitute phenols, Water Res. 19 (1985) 767–772.