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Remediation of dinitrotoluene contaminated soils from former ammunition plants: soil washing efficiency and effective process monitoring in bioslurry reactors

Chunlong Zhang [a], Rebecca C. Daprato [b], Shirley F. Nishino [c], Jim C. Spain [c], Joseph B. Hughes [b,*]

[a] *School of Natural and Applied Sciences, University of Houston-Clear Lake, Houston, TX 77058, USA*
[b] *Department of Environmental Science and Engineering, Rice University, Houston, TX 77005, USA*
[c] *Air Force Research Laboratory — MLQL, Tyndall Air Force Base, Tyndall AFB, FL 32403, USA*

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Abstract

A pilot-scale bioslurry system was used to test the treatment of soils highly contaminated with 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT). The treatment scheme involved a soil-washing process followed by two sequential aerobic slurry reactors augmented with 2,4-DNT- and 2,6-DNT-mineralizing bacteria. Test soils were obtained from two former army ammunition plants, the Volunteer Army Ammunition Plant (VAAP, Chattanooga, TN) and the Badger Army Ammunition Plant (BAAP, Baraboo, WI). Soil washing was used to minimize operational problems in slurry reactors associated with large particulates. The Eimco slurry reactors were operated in a draw-and-fill mode for 3 months and were monitored for the biodegradation of 2,4-DNT and 2,6-DNT, nitrite production, NaOH consumption, and oxygen uptake rate. Results show that soil washing was very effective for the removal of sands and the recovery of soil fines containing 2,4-DNT and 2,6-DNT. Bioslurry reactors offered rapid and nearly complete degradation of both DNT isomers, but require real time monitoring to avoid long lag periods upon refeeding. Results found a significant discrepancy between the measured DNT concentrations and calculated DNT concentrations in the slurry reactors because of solids profiles in the slurry reactors and the presence of floating crystal of DNTs. Based on the actual amount of dinitrotoluene degradation, nitrite release, NaOH consumption, and oxygen uptake were close to the theoretical stoichiometric coefficients of complete DNT mineralization. Such stoichiometric relationships were not achieved if the calculation was based on the measured DNT concentrations due to the heterogeneity of DNT in the reactor.

*Corresponding author. Tel.: +1-713-348-5903; fax: +1-713-348-5203.
E-mail address: hughes@rice.edu (J.B. Hughes).

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Results indicate that nitrite release, NaOH consumption, and oxygen uptake rates provide a fast assessment of 2,4-DNT degradation and microbial activity in a slurry reactor, but could not be extended to a second reactor in series where the degradation of a much lower concentration of 2,6-DNT degradation was achieved.

Keywords: Soil washing; Process monitoring; Bioslurry reactor; Explosives; Nitroaromatic compounds; 2,4-Dinitrotoluene; 2,6-Dinitrotoluene

1. Introduction

Dinitrotoluene (DNT) isomers are common soil contaminants at Department of Defense (DoD) and commercial polyurethane foam facilities. The two primary isomers of dinitrotoluene found at these facilities are 2,4-DNT and 2,6-DNT, and the US EPA lists both as priority pollutants. Soils contaminated with DNTs can be treated by traditional means such as incineration, but the cost is high. Over the past decades, aerobic bioremediation of DNT contaminated media has been an area of extensive research [1–5] in an attempt to develop a low-cost alternative.

In a previous report [6], we demonstrated the use of pilot-scale aerobic slurry-phase bioreactors to treat highly contaminated soils containing both 2,4-DNT and 2,6-DNT following augmentation of DNT-mineralizing bacteria. Two factors that complicated the operation of these systems were identified. First, sands or other large particulates clogged the reactors and eliminated mixing. Second, the sustainability of rapid degradation rates required that systems be adequately monitored throughout feeding cycles (carried out by HPLC analysis). If DNT was allowed to be completely depleted from a reactor for as short as several hours without refeeding, a long lag period followed and reduced levels of activity were observed. In extreme cases, activity was lost and reinnoculation was required. This need for nearly continuous monitoring — relying on HPLC analysis — for biodegradation activity translated into a significant component of the overall cost estimates for treating contaminated soils with this approach [7].

The clogging of the bioreactors was addressed by the use of a soil washing process to remove sands from the contaminated soils before addition to the reactors. Despite the fact that only fine grain material was then fed to the reactor, a heterogeneous solids concentration existed in tested pilot-scale systems. For example, fine DNT crystals were observed floating as a mat in the slurry reactor initially after feeding. Also, mixing was not ideal and accumulation of solids at the base of the system occurred. This heterogeneous solids concentration complicated the ability to directly assay contaminant levels, and to monitor the rates of degradation actually occurring. Furthermore, the inability to analyze the actual levels of contaminants in the system created uncertainty in the levels of amendments required.

The results of soil washing process efficiency and various low-cost monitoring strategies are presented herein as surrogates to direct measures of DNT degradation in these slurry reactor studies. The surrogate measures tested include release of nitrite, consumption of NaOH, and oxygen uptake rates. The comparison of results from HPLC analysis and these surrogate parameters suggest that effective routine monitoring of 2,4-DNT degradation (the

primary contaminant in soils tested) can be obtained without HPLC if the effectiveness of the soil wash process is known. The extension of these surrogate analytes as guides of 2,6-DNT degradation was problematic.

2. Experimental

2.1. Description of contaminated sites

Two soils obtained for study came from the Volunteer Army Ammunition Plant (VAAP, Chattanooga, TN) and the Badger Army Ammunition Plant (BAAP, Baraboo, WI). At the VAAP site, soil was collected from four points along the drainage ditch outflow from the Acid Recovery House of TNT production Line 4. Soil containing up to 200 g/kg of 2,4-DNT was found within 5 m of the Acid Recovery House, and soil with lower concentrations of 2,4-DNT (2–3 g/kg) but higher concentrations of 2,6-DNT (0.5–1 g/kg) were collected approximately 50–150 m down gradient. The soil was stored in 55 gal drums at ambient temperature for 6 months before processing. At the BAAP site, soil core samples were collected in 1997 from Propellant Burning Ground Waste Pits 1–3. Several drums of contaminated soils were shipped to Air Force Research Lab in February 1999.

2.2. Treatment scheme

A schematic of the unit process and unit operation developed in this study is shown in Fig. 1. The treatment scheme involved a soil pretreatment unit, a soil washing unit, two identical bioslurry reactors operated in series, and a coagulation/sedimentation tank. Soils from contaminated sites were air-dried followed by the removal of gravel and large debris. The dried soils were repeatedly passed through a sieving and tumbling machine until uniform soils were obtained. Because large amounts of sand interfered with reactor operation, soils were treated by soil washing before use. Soil washing was performed in a 14 l cylinder with an upward jet flow of warm (60°C) tap water to separate DNT-associated fines from the clean sand. The resulting soil slurry was used in bioreactors and the sand was discarded.

Slurries generated from soil washing were pumped into a 75 l Eimco Biolift slurry reactor (Model B75LA, Tekno Associates, Salt Lake City, UT). Two reactors were operated in series for the treatment of both isomers in a sequential mode as described previously [6]. Both reactors were equipped with agitation, aeration, and temperature control. The temperature was maintained at 30°C, and pH was maintained in the range of 6.75–7.25 using a pH controller and NaOH (12.5N).

Effluent from the second slurry reactor was further treated in a holding tank. This was accomplished by addition of a coagulant ($CaCl_2$), followed by the gravity separation of solids and supernatant liquid.

2.3. Slurry reactor operation

Two identical reactors were operated simultaneously and continuously for a period of 3 months. The term solids loading (i.e. mass of soil added per unit volume of reactor (w/v)) is

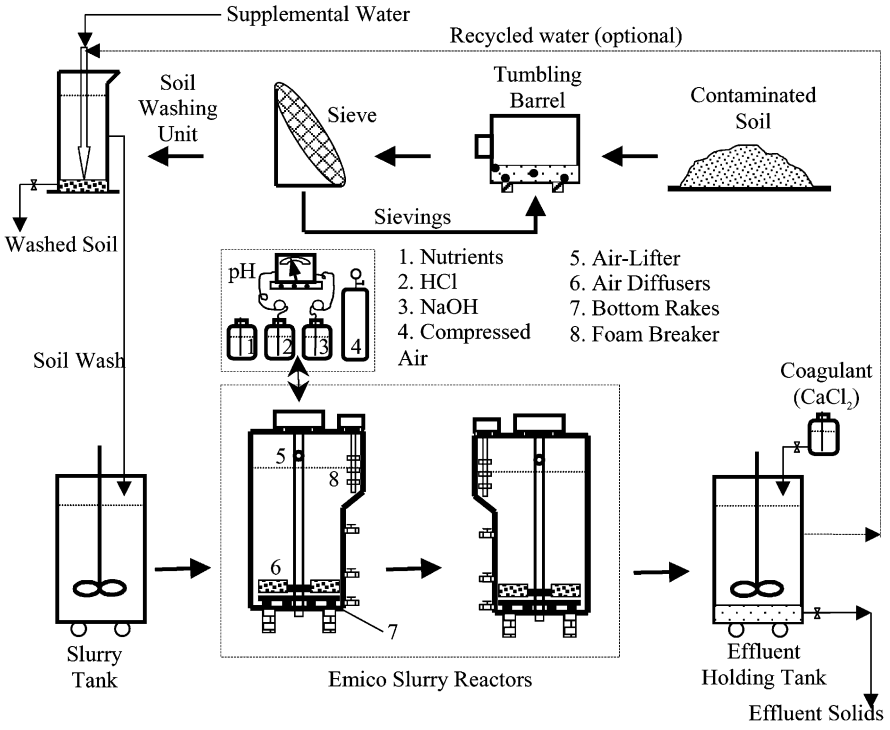

Fig. 1. Treatment scheme of pilot-scale soil washing and sequential aerobic slurry reactor system.

typically used to describe the levels of soils added to slurry reactors. However, contaminated soils were not added directly to the reactors in this study, so the actual solids concentration in a reactor depended on the amount of soil added to the soil wash unit, and the percentage (weight basis) of large soil particulates removed by the soil washing process. For this reason, the term "nominal solids loading" is used throughout this paper to reflect levels of soil treated by the overall process. For example, a nominal 10% solids loading is equivalent to 7 kg of dry soil added to the soil washing process, which became feed for fill-and-draw operation, since the operating volume of the reactor was 70 l. VAAP soil was tested at nominal solids loadings of 5, 20, and 30%, whereas BAAP soil was tested at nominal solids loadings of 5, 10, 20, 30, and 40% (Table 1). A comparison of the nominal solids loading and actual solid concentrations in reactors along with DNT concentrations in reactors is presented in Table 1.

As shown in Table 1, the actual solids concentration in the reactor was lower than the nominal solids loading. The difference was more evident for sandy soils (e.g. BAAP soil) than clay soils (e.g. VAAP soil) since a higher percentage of large soil particulates were associated with sandy soil. Note also that the suspended solids concentration is a calculated concentration based on the actual mass of soil entered into the reactor, assuming a homogeneous distribution.

Table 1
Solids loading, suspended solids, and initial DNT concentrations in the slurry reactor[a]

	Solids loading tested in this study				
VAAP soil					
Nominal solids loading (% w/v)	5	20	30		
Actual solids loading (% w/v)	4	16	25		
Suspended solid (SS) $\times 10^3$ (mg/l)	40	160	250		
2,4-DNT (μM)	2990	11960	17940		
2,6-DNT (μM)	240	960	1440		
BAAP soil					
Nominal solids loading (% w/v)	5	10	20	30	40
Actual solids loading (% w/v)	0.7	1.3	2.6	3.9	5.2
Suspended solid (SS) $\times 10^3$ (mg/l)	7	13	26	39	52
2,4-DNT (μM)	2450	4900	9800	14700	19600
2,6-DNT (μM)	130	260	520	780	1040

[a] The removal of large soil particulates was assumed to be 18% for VAAP soil and 87% for BAAP soil, based on the averaged data from experiment. Reactor volume = 70 L.

2.4. System monitoring and sample analysis

Three sampling ports (bottom, middle, and top) were located along the side-wall of the reactor at 2, 15, and 40 cm from the bottom of the reactors. Routine samples were taken from the top sampling port of the reactor side-wall. Slurry samples taken from the reactor were transferred to a beaker and mixed vigorously with a magnetic stir plate. Sub-samples were withdrawn through a large-bore pipette tip.

To determine DNT concentrations, samples were extracted and analyzed by a Hewlett-Packard series 1050 HPLC equipped with a UV detector according to previously described methods [8]. The extraction procedure allowed for the determination of the aqueous phase concentration, the solid phase concentration (centrifugation of slurry samples, followed by the extraction of solids with acetonitrile), or the overall slurry concentration. The mass of 2,4-DNT in the reactors often exceeded its aqueous solubility, and crystalline DNT was often present at the beginning of the cycles. Therefore, the results of HPLC analysis are presented as the slurry phase concentration, which corresponds to the total amount of DNT per liter of slurry [6].

Sub-samples for nitrite analysis were centrifuged and the supernatant was immediately withdrawn and subjected to analysis using a modified colorimetric method [9]. Absorbance readings were made at 560 nm on an EL340 Automated Microplate Reader (Bio-Tek Instruments, Inc., Winooski, VT). Slurry samples taken for oxygen uptake rate analysis were placed directly in a 300 ml BOD bottle. After re-aeration at 30°C, dissolved oxygen concentrations were measured using a YSI Model 58 dissolved oxygen meter with a YSI 5905 BOD probe (Yellow Springs Instrument Co., Inc., Yellow Spring, OH). A typical oxygen consumption curve demonstrated zero-order kinetics, and the oxygen uptake rate was determined directly by linear regression.

The reactors were also routinely monitored by the measurement of temperature, pH, SS, and NaOH consumption. Treated soil wash (sludge) samples were also taken for the analyses

of residual 2,4-DNT and 2,6-DNT [10]. These samples were taken after the settling of the reactor effluent from representative runs and subsequent decanting of the supernatant. The wet sludge samples were oven-dried overnight at temperature below 55°C and subjected to homogenization prior to analysis.

3. Results and discussion

3.1. Soil washing unit performance

In an attempt to improve reactor mixing and overcome clogging problems when soils were fed directly, soil washing studies were conducted to evaluate the potential to remove contaminants from the sand with a repeated resuspension in water — simulating a soil washing procedure. Preliminary results from bench studies (data not shown) indicated that soil washing could effectively remove sandy materials while leaving most of the DNT in the slurry phase. Further studies were conducted to determine the ability to reduce the volume of water required, so that the procedure could be implemented for use as a pretreatment for both soils.

Fig. 2A shows the mass of particulates removed in soil wash. In general, soil washing was very successful in separating large particles from both soils. On a weight basis, 87% of large particles in BAAP soil were removed after soil washing. The remaining 13% were finer particles suspended in the soil slurry. For VAAP soil, the distribution after soil washing was nearly reversed, as VAAP soil was comprised primarily of fine particles. Approximately 18% of VAAP soil (weight basis) was removed after soil washing, and 82% of the soil was fine particles suspended in the slurry phase.

Fig. 2B shows the mass of DNT retained in the slurry phase for BAAP soil. The efficiency was examined at different ratios of water/soil to determine the appropriate water volume required for preparation of reactor feed. The results suggest that a water/soil ratio of 10 l/kg or greater resulted in nearly complete retention of contaminants after removal of the sands. However, a ratio of 5 l/kg or less resulted in reduced efficiency and significant DNT levels remained associated with residuals. For VAAP soil, a similar pattern was noticed (data not shown). Increasing water/soil ratio apparently improved soil washing efficiency. However, VAAP soil appeared to have higher residual concentrations when compared to BAAP soil at identical operational conditions. A water/soil ratio of 17 l/kg was necessary to maintain a 98% or higher reduction in concentration. Under the operational conditions tested in this study, an efficiency of 99.3% or greater was achieved in all soil washing steps.

Without the use of soil washing pretreatment, clogging of the airlift in the slurry reactor occurred even at a 5% solids loading. The ability to effectively remove DNT in a soil wash process to improve the reliability of slurry phase bioremediation is an important concern in application. Residual levels of DNT in coarse materials may require some additional level of treatment before disposal; however, the biodegradation potential of trace levels of residual DNT was not evaluated.

3.2. Slurry reactor performance and monitoring for 2,4-DNT degradation

Samples taken from the slurry reactor immediately after feeding were analyzed by HPLC and compared to the DNT concentration that should have resulted based upon the known

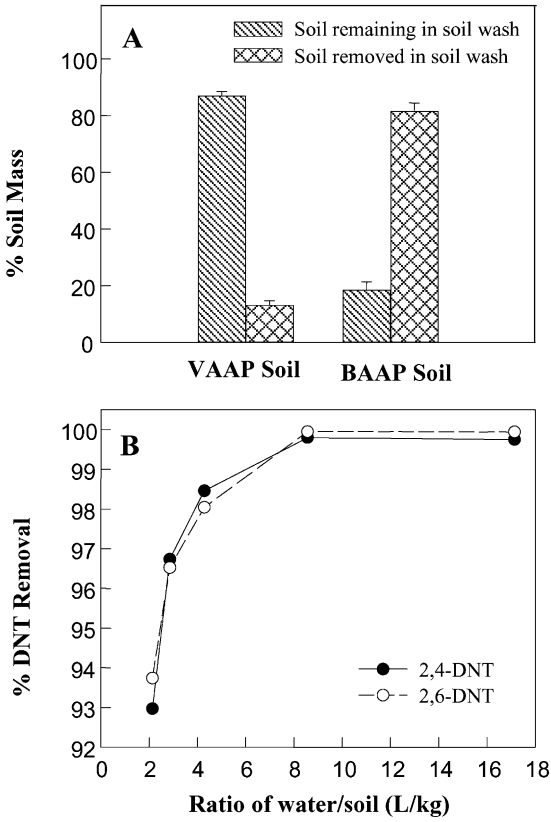

Fig. 2. (A) Soil mass distribution after soil washing process: VAAP soil vs. BAAP soil. (B) Effects of water/soil ratio on soil washing efficiency (BAAP soil).

mass of DNT in the feed slurry (analyzed by HPLC). Results are presented in Fig. 3A at different solids loadings of BAAP soil (5, 10, 20, 30 and 40%). These results show a significant discrepancy between the measured DNT concentrations and the calculated DNT concentrations in the slurry reactors (the known mass of DNT added to the reactor divided by the reactor volume). A similar discrepancy was observed in VAAP soil (Fig. 3B). For both soils, the discrepancies increased as the solids loading increased, suggesting that sampling procedures did not take into account the heterogeneous nature of the reactor. This hypothesis is supported by the observation of DNT crystals floating as a mat in the reactors shortly after feeding, which disappeared as degradation proceeded.

The implications of this finding are of consequence to the ability of the operation and monitoring of the reactor. In terms of reactor operation, the inability to measure true levels of DNT in the system can lead to an underestimation of the nutrient or electron acceptor requirements. In terms of monitoring, the inability to measure actual levels of contamination reduces the ability to assess the extent to which biodegradation is, or is not, occurring.

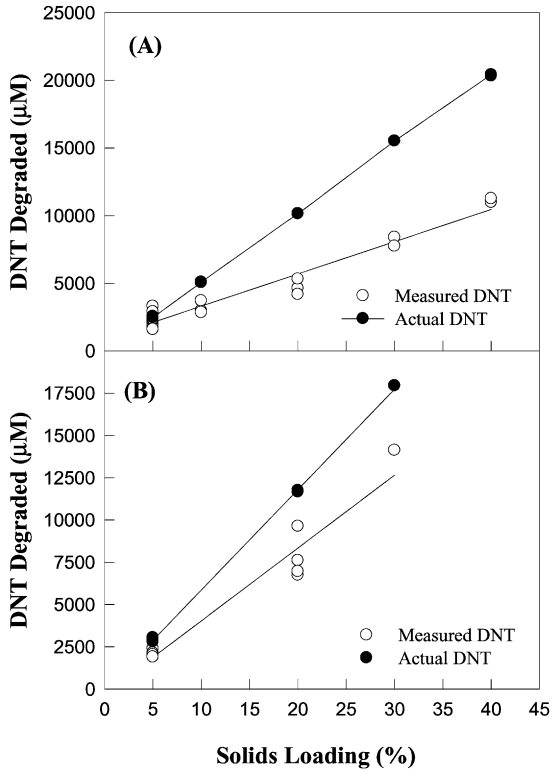

Fig. 3. Measured DNT degradation vs. actual 2,4-DNT degradation at different solids loading: (A) BAAP soil; (B) VAAP soil.

Therefore, parameters other than slurry-phase DNT were tested for monitoring reactor performance.

Fig. 4A presents the production of nitrite in 20 feeding cycles of BAAP soil wash during the course of 2,4-DNT degradation. As expected, the pattern of the nitrite production corresponded to the disappearance of dinitrotoluene, and concentrations of nitrite produced increased proportionally with increases in solids loading. Fig. 4B presents the oxygen uptake rate obtained in each feeding cycle (data not available for the first cycle). Oxygen uptake rates appear to correlate with the overall 2,4-DNT degradation activity in the reactor, with peak oxygen uptake rates increasing with increasing solids loading. A maximum oxygen uptake rate ($\approx$2.0 mg/l min) was observed when the nominal solids loading reached 20%.

Fig. 5A presents 2,4-DNT and nitrite concentration profiles in VAAP soil slurry reactors. The maximum nitrite concentrations were approximately 35,000 μM at a 20% nominal solids loading. As with BAAP soil, the pattern of nitrite production corresponded to the disappearance of dinitrotoluene. (Note that the maximum concentrations at a 30% loading rate remained about the same as the concentrations at a 20% loading rate because a fill-and-draw was initiated prior to the complete degradation of 2,4-DNT.) Fig. 5B presents

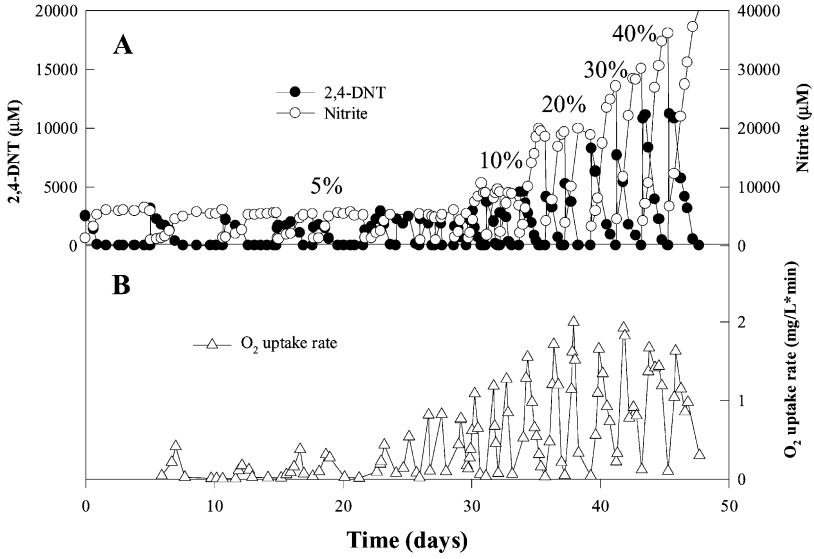

Fig. 4. Temporal concentration profiles of (A) 2,4-DNT and nitrite (data for 2,4-DNT concentration previously reported in [8]) and (B) oxygen uptake rate with BAAP soil (% are nominal solids loading).

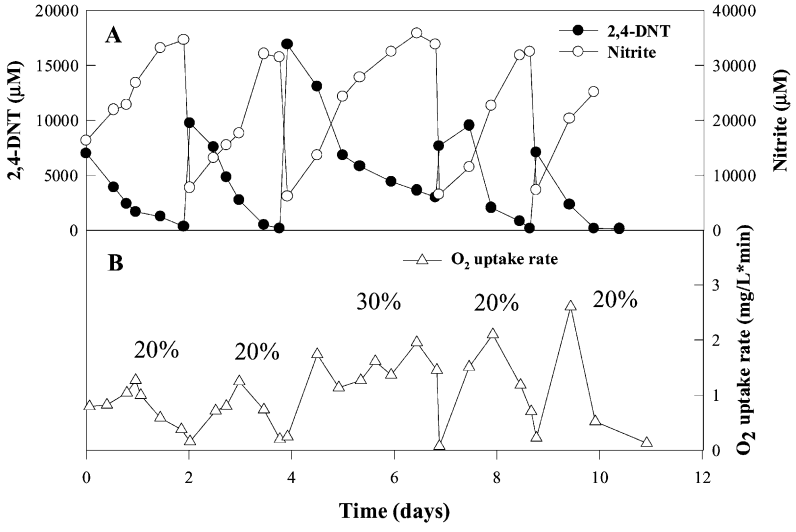

Fig. 5. Temporal concentration profiles of (A) 2,4-DNT and nitrite (data for 2,4-DNT concentration previously reported in [8]) and (B) oxygen uptake rate with VAAP soil (% are nominal solids loading).

the oxygen uptake rate in the same soil, and again oxygen uptake rates appear to correspond with microbial DNT degradation activity in the reactor. The peak oxygen uptake rates ranged between 1.3 and 2.6 mg/l min, as compared to the observed maximum oxygen uptake rate of 2.0 mg/l min for BAAP soil.

NaOH data was collected as volume (ml) of 12.5N consumed per feed cycle (data not shown). For the BAAP soil, the NaOH consumption was consistent with the degradation pattern of DNT. At 5, 10, 20, 30 and 40% nominal solids loading, average NaOH consumption was 26, 42, 92, 142 and 186 ml, respectively. The NaOH consumption for VAAP soil was also consistent with the DNT degradation pattern. The average NaOH consumption at a 20% nominal solids loading was 94 ml.

The nitrite production, oxygen uptake rate, and NaOH consumption data can be used to calculate the molar ratio of each compound produced or consumed to DNT degraded. These molar ratios can then be compared to the molar ratio predicted from the stoichiometry of the biodegradation of DNT. The oxidation of DNT to CO_2 and nitrite results in the consumption of oxygen and the production of H^+. A balanced reaction for complete DNT oxidation is shown in Eq. (1):

$$C_7H_6N_2O_4 + 8O_2 \rightarrow 7CO_2 + 2H_2O + 2NO_2{}^- + 2H^+ \quad (1)$$

However, this reaction does not consider biomass synthesis. To obtain the stoichiometry of the reaction with biomass synthesis considered, bioenergetic calculations for the biodegradation of DNT were performed. These calculations were completed using the procedure developed by McCarty [11,12]. First, the half reaction of DNT was developed:

$$\tfrac{1}{32}C_7H_6N_2O_4 + \tfrac{7}{16}H_2O \rightarrow \tfrac{7}{32}CO_2 + \tfrac{1}{16}NO_2{}^- + \tfrac{17}{16}H^+ + e^-, \quad \Delta G_f^0 = -0.234\,\text{kcal/eq}. \quad (2)$$

The free energy of formation values published by Mavrovouniotis [13] and Brock and Madigan [14] were used to calculate the standard free energy of formation of the DNT half reaction. The free energy of formation for DNT is not a published value; it was calculated using the group contribution method developed by Mavrovouniotis [13] with the NO_2 contribution determined by Shelly et al. [15]. The efficiency of energy transfer, the transferring of energy from the carrier to synthesis, by dinitrotoluene degraders was assumed to be 60% [16] because a value has not been determined experimentally. The bioenergetic calculations resulted in the following stoichiometry that includes biomass synthesis:

$$C_7H_6N_2O_4 + 5.62O_2 \rightarrow 5.17CO_2 + 1.63NO_2{}^- + 1.63H^+ + 0.90H_2O + 0.37C_5H_7O_2N \quad (3)$$

The stoichiometry appears to be different from a previous study reported by Lendenmann et al. [17]. In this fluidized-bed reactor study, 9 mol of oxygen were required for 1 mol of DNT. However, this value was derived solely on chemical oxidation (i.e. no biomass synthesis) and included the impact of nitrite-oxidizing bacteria that were present in the fluidized-bed reactor. In the slurry reactors, nitrate production was not detected at any significant levels.

Assuming that the stoichiometry in Eq. (3) is predictive of the biological activity in the reactor (i.e. degradation of other organic material is an insignificant contribution to the consumption/production of constituents in the aforementioned reaction) it is possible to use oxygen consumption, nitrite release, and acid neutralization as control parameters. Of these three, only the analysis of oxygen demand is complicated by heterogeneous solids profiles, as our method for oxygen demand required the monitoring of oxygen uptake by a slurry sample taken from the reactor.

The overall stoichiometric relationship obtained between nitrite production and total dinitrotoluene degraded (based on soil washing efficiency) in BAAP soil at five different loading rates is presented in Fig. 6A. The mole ratio of $[NO_2^-]$/[DNT] was 1.61 based on DNT degraded. Fig. 6B shows a similar stoichiometric relationship for VAAP soil at three different solids loadings. Although data were slightly more scattered for VAAP soil, a similar mole ratio of 1.85 $[NO_2^-]$/[DNT] was obtained.

Fig. 7A is the stoichiometric relationship between NaOH consumption and the amount of total dinitrotoluene degraded in BAAP soil at five different loading rates. The mole

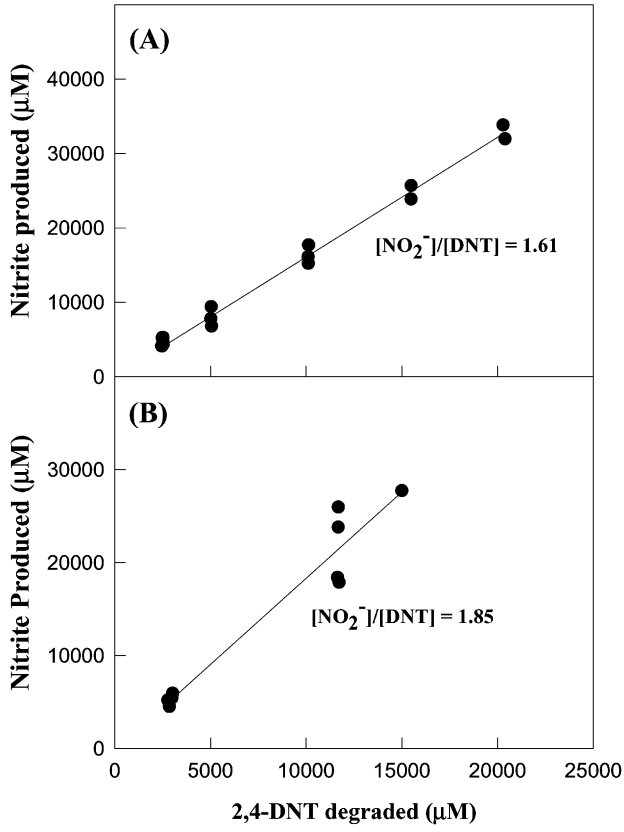

Fig. 6. Stoichiometric relationships between 2,4-DNT degradation and nitrite production at various test loading rates: (A) BAAP soil; (B) VAAP soil.

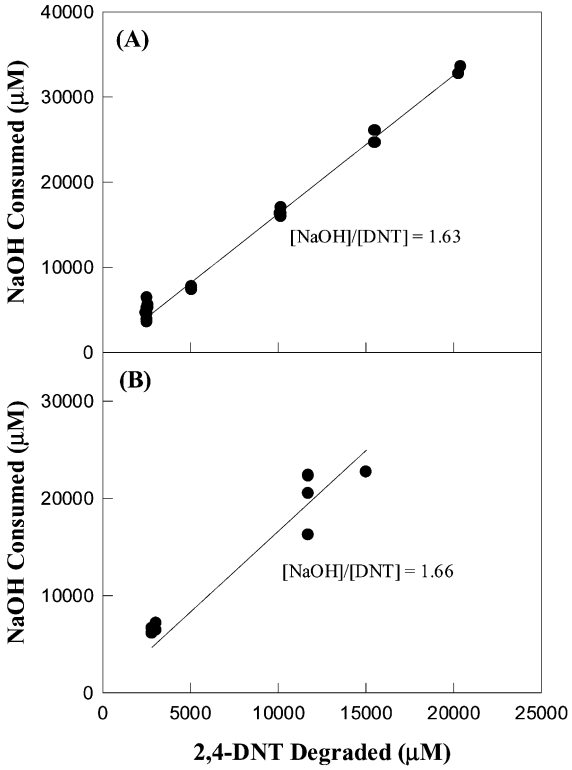

Fig. 7. Stoichiometric relationships between 2,4-DNT degradation and NaOH consumption at various test loading rates: (A) BAAP soil; (B) VAAP soil.

ratio of [NaOH]/[DNT] was 1.63 based on actual DNT degraded. Fig. 7B is the same stoichiometric relationship for VAAP soil at three different solids loadings. The mole ratio of [NaOH]/[DNT] obtained was 1.66.

Oxygen consumption was calculated using the sum of the average rate of oxygen uptake over discrete time intervals, and the DNT degradation that occurred during that time interval. Fig. 8A presents observed oxygen consumption during the degradation of dinitrotoluene in BAAP soil, and Fig. 8B presents observed oxygen consumption for VAAP soil. (Note data in Fig. 8A and B were from a single feeding cycle.) The molar ratio of oxygen consumption to DNT degradation was 6.82 for BAAP soil and 5.64 for VAAP soil.

The values of nitrite production, NaOH addition, and oxygen consumption compare favorably with what is predicted by stoichiometry. NaOH addition was the most accurate and least variable of all parameters assessed. Cumulative oxygen consumption was the most difficult parameter to evaluate because it is extrapolated from instantaneous oxygen uptake rate data. Also, cumulative oxygen uptake has the potential interference of metabolism of organics other than DNT in the reactor. For example, BAAP soils had a noticeable fuel odor prior to soil washing. Presumably, some of these fuel-related organics were degraded

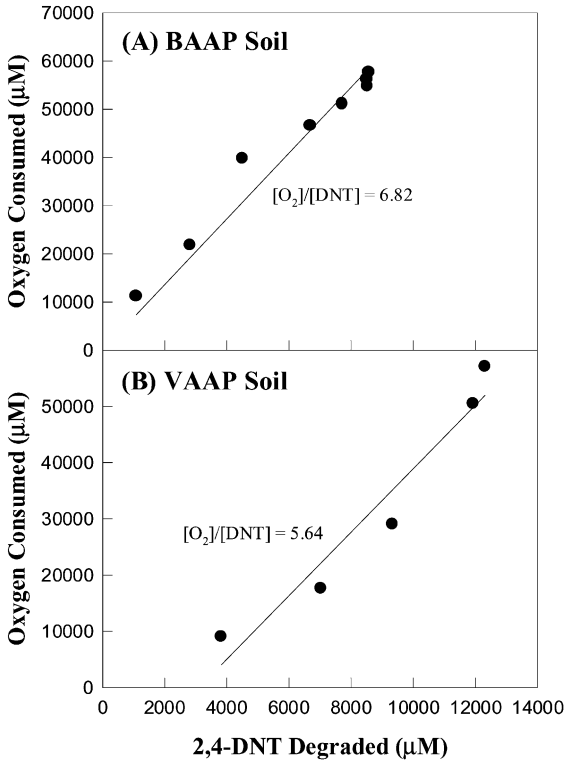

Fig. 8. Stoichiometric relationships between 2,4-DNT degradation and oxygen consumption.

(a parameter not measured directly) in the reactor, which would explain the higher molar O_2/DNT ratio observed.

Beyond the overall reaction stoichiometry observed, the use of surrogate parameters to determine reactor performance overcame the difficulties in assessing activity through the measurement of 2,4-DNT concentrations in the slurry reactor. Fig. 9 presents the relationship between 2,4-DNT degradation and two related monitoring parameters: nitrite production and oxygen uptake rate. Data shown is from a single feeding cycle of BAAP at 5 (Fig. 9A), 10 (Fig. 9B) and 20% (Fig. 9C), and of VAAP at 20% (Fig. 9D), respectively. In all feeding cycles, the initially measured levels of DNT in the reactor do not indicate rapid biodegradation activity; however, nitrite production and oxygen uptake rates clearly demonstrate the microbes are active and that DNT degradation is taking place. As time progresses, the onset of complete 2,4-DNT degradation corresponds with a decrease in oxygen uptake and constant nitrite concentrations. Thus, the use of surrogate parameters was important in the understanding of 2,4-DNT degradation — both at the beginning, and at the end of a feeding cycle.

3.3. Slurry reactor performance and monitoring for 2,6-DNT degradation

Stoichiometric relationships could not be established in the second reactor treating residual 2,6-DNT from either soil. This is due to several factors including, the high nitrite carried

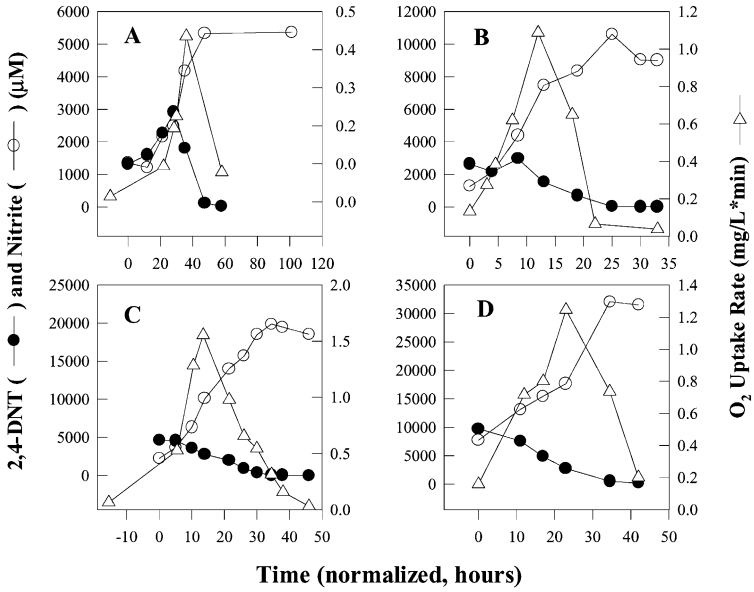

Fig. 9. Temporal concentration profiles of 2,4-DNT and nitrite and oxygen uptake rate of BAAP soil at 5% (A), 10% (B), 20% (C) and of VAAP soil at 20% (D) solids loading.

over from the first reactor and the low levels of DNT degradation occurring in the second reactor. For instance, the second reactor treating BAAP soils had initial nitrite concentrations ranging between 5,000 and 10,000 μM as nitrite was carried over from the first reactor. Any additional nitrite production from the degradation of low 2,6-DNT concentration was difficult to detect. Similarly, NaOH consumption was minimal in the second reactor. The theoretical consumption (based on 1.65 mol NaOH/mol DNT) of 12.5N NaOH is very small (3.0 ml) for 250 μM of 2,6-DNT, and NaOH addition was often not needed to keep pH above 6.75. Oxygen uptake in the second reactor was also minimal, and correlation with DNT degradation could not be established. The maximum oxygen uptake rates observed in the second reactors were 0.7–0.75 mg O_2/l min, which were approximately 20 times lower than that in the first reactor. Interestingly, this ratio was comparable to the relative concentrations of 2,4-DNT to 2,6-DNT degraded in the separate reactors.

4. Conclusions and implications

The main problem that was encountered in process monitoring for these slurry reactors was the heterogeneous nature of the DNT distribution in the systems, which in turn led to a non-representative analysis of contaminant levels. Without the ability to directly determine contaminant levels, the ability to determine nutrient or electron acceptor requirements can become complicated. Also, this difficulty in analysis decreases the ability to accurately assess the rates at which degradation is occurring, particularly in the early stages of the feed cycles.

Since monitoring 2,4-DNT concentrations was not always indicative of degradation activity, oxygen consumption, nitrite production and NaOH consumption were tested as surrogate monitoring parameters. It was determined that oxygen consumption is a less reliable indicator of reactor performance because of the difficulty in obtaining samples and the possibility of other organics being present in the soil that could contribute to the oxygen consumption. Nitrite production and NaOH consumption were determined to be the best surrogate monitoring parameters. Nitrite production can be used to accurately assess the microbial activity and NaOH consumption can be used to correctly predict the amount of DNT degraded. Therefore, nitrite production and NaOH consumption are both inexpensive monitoring parameters that can be used for accurate routine process control.

The use of surrogate monitoring parameters did not extend to the second reactor in series. Low levels of 2,6-DNT were the main reason for the lack of correlation between 2,6-DNT degradation and surrogate monitoring parameters in the second reactor. In addition, carry over from the first reactor caused difficulty in detecting some parameters. For example, nitrite production from the degradation of 2,6-DNT was masked by the high levels of nitrite that carried over from the first reactor. Therefore, monitoring reactors with low concentrations of 2,6-DNT could only be conducted by direct measurement of 2,6-DNT concentrations by HPLC. If the 2,6-DNT concentrations were higher, the use of surrogate monitoring parameters may have become an accurate test in predicting reactor performance.

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