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Biological-Chemical Treatment of Soils Contaminated with Exploration and Production Wastes

BHUPENDRA. K. SONI,* J. ROBERT PATEREK, SALIL PRADHAN, AND VIPUL. J. SRIVASTAVA

Institute of Gas Technology, 1700 S. Mount Prospect Road, Des Plaines, Illinois 60018

ABSTRACT

Oil-gas exploration and production (E&P) soils contaminated with total petroleum hydrocarbons (TPHs) have been tested for degradation by two different treatments: biological and chemical. Biological treatment includes the use of native microorganisms for transformation of the various hydrocarbons found in E&P soils. Degradation of TPH of 80 and 86%, was achieved for two different soils, respectively in control experiments. The effect of growth stimulants such as glucose, acetic acid, and valeric acid was examined on TPH degradation. Incorporation of inducer (valerate) enhanced the degradation up to 89 and 93%, for the two soils, respectively. A large portion (> 41%) of contaminant in one soil was comprised of compounds in the carbon range of C_{10}–C_{16} and < 7% constituted carbon range of C_{24}–C_{28}. The degradation of C_{10}–C_{16} compounds was higher (> 98%) as compared to C_{24}–C_{28} compounds (< 75%). Likewise, the degradation rate was also higher (58 mg/kg/d) for lower compounds as compared to higher carbon range compounds (6.7 mg/kg/d). Experiments conducted on chemical treatment included the effect of chelators on stabilization of H_2O_2, comparative studies between buffer and water (used for soil preparation), and the effect of pH on TPH degradation. The rate of oxygen evolution from H_2O_2 was significantly reduced with use of either chelated iron or phosphate buffer using naphthelene as a model compound. Chemical treatment demonstrated a higher degradation of TPH from contaminated soils at pH 4.0 as compared to a pH of 7.0. More degradation was obtained with slurry prepared in phosphate buffer as compared to deionized water.

Index Entries: Biological treatment; chemical treatment; total petroleum hydrocarbons (TPHs).

* Author to whom all correspondence and reprint requests should be addressed.

INTRODUCTION

Oil and Gas Exploration and Production Soils

The drilling and operation of gas-exploratory wells and the operation of natural-gas production wells generate a number of waste materials. They are usually stored and/or processed at the drilling/operations site. The waste materials can include: oil-based drilling muds and cuttings; water-based drilling muds and cuttings; site-related soil or sediments contaminated by the drilling and gas recovery activities; brines, including drilling and produced water; production pit and storage tank sludge; produced oily sands and solids; residual gas condensates; vapors and odors; and natural-gas-plant-processing wastes.

The most common contaminants associated with natural-gas wells are hydrocarbons associated with the natural-gas condensates such as: benzene, ethyl benzene, toluene, and the xylenes (para-, ortho-, meta- moieties), which are commonly designated as BTEX; total petroleum hydrocarbons (TPHs); and polynuclear aromatic hydrocarbons (PAHs) from the formation's natural gas deposits.

Institute of Gas Technology (IGT) has developed innovative technology for the treatment of several hydrocarbon wastes such as PAHs *(1)* and PCBs (polychlorinated biphenyls) *(2)*.

Biological-Chemical Treatment Process (BCT)

Bioremediation is the basis of many treatment systems under development at IGT. Microorganisms exhibit abilities under laboratory conditions to degrade nearly all contaminants examined. The rates and extent of these activities might be low as compared to the requirements of the treatment technology. The enhancements under study are designed to accelerate the rate and/or extent of degradation.

IGT has developed and is investigating the application of an integrated biological-chemical treatment (BCT) process for the remediation of soils contaminated with polynuclear aromatic hydrocarbons *(1,3–11)*. A schematic diagram of the process is presented in Fig. 1. The chemical treatment can be performed as a pretreatment before the biological degradation or can be integrated as a step between biological treatments. The process uses a mild chemical treatment with Fenton's reagent that produces hydroxyl radicals that react with the organic contaminants. The contaminants are modified to forms that are more readily degraded by native or supplemented microorganisms. Results with approx 25 MGP (manufactured gas plant) soils show that the CBT process is capable of enhancing the rate, as well as the extent, of PAH degradation. This integrated process generates environmentally benign products, that is, carbon dioxide (CO_2), inorganic salts, biomass, and water.

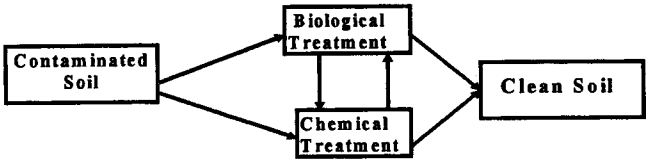

Fig. 1. TPH-REM process: different alternatives.

The application of a biological-chemical treatment to E&P-contaminated soils has been under study for 2 yr. Preliminary results indicated that this biological-chemical treatment exhibited success levels warranting further research and development *(9)*. The research presented here examined the chemical treatment on two E&P soils under pH-regulated conditions. The laboratory research falls into two major areas of IGT's chemical treatment: oxygen evolution and pH optimization.

MATERIALS AND METHODS

Soil Sample Preparation

Soil samples were collected from E&P sites by various organizations and shipped to IGT for study. These soils with PIT ID no. of 6689 and 1260 were designated as soil 2 and 3 for further reference. The samples were transported to IGT's laboratories and stored at 4°C until used. Soil was sieved (0.25-in screen) prior to use. The soil was supplemented with the nutrient medium containing the following components for biological treatment per liter: NH_4Cl,1.0 g; $KH_2PO_4$0.5 g; and K_2HPO_4 0.5 g.

Determination of Oxygen Evolution

The oxygen evolution, with chelated iron and control (no chelating compound), was conducted in glass bottles (50 mL). The glass bottles were sealed with rubber septum and aluminum crimp. The glass syringes (50 mL) were used to collect the gas produced in the head space. Sodium citrate (10 m*M*) was used for the chelation of ferrous sulfate (10 m*M*). Naphthelene (7219 PPM) was used as the sole carbon source for these studies. The test samples were prepared both in phosphate buffer and deionized water (pH 5.0). At least two different pHs, 5.0 and 7.0, were tested using phosphate buffer (0.05 *M*). The oxygen-evolution studies were started by the addition of H_2O_2 to achieve a final concentration of 2% (w/v).

Effect of pH and Buffer on Degradation of TPH Compounds

The effect of pH was tested by varying the pH in the range of 4.0 to 7.0 using phosphate buffer (0.05 *M*). A 20% soil slurry was prepared in glass bottles (160 mL) by addition of 10 g of soil in 50 mL of buffer. Sodium citrate and ferrous sulfate were each added at the final concentration of 10 m*M*. The treatment was started by addition of H_2O_2 (2% w/v). In some

microcosoms, soil slurry was prepared in water to compare the performance with the buffer used for slurry preparation.

Soil-Treatability Studies

The soil treatability studies were conducted in glass bottles (160 mL). The nutrient medium, as described above, was used for the biological treatment. Several growth inducers such as acetic acid, glucose, and valeric acid were tested for enhancement in TPH degradation. For chemical treatments, air-dried soils were weighed (4–10 g) and 20–50 mL of phosphate buffer (pH 4.0-7.0) was added to prepare a 20% soil slurry. Ferrous sulfate (10 m*M*) and sodium citrate (10 m*M*) were added in all studies. In one set of tests, deionized water was added at the initial pH of 5.0. H_2O_2 was added to achieve a final concentration of 2% (w/v). The treatment was allowed to react for 1–3 wk and liquid samples were evaporated to dryness and extracted with methylene chloride for analysis of TPHs.

Gas Chromatography

All extracts were analyzed by capillary column gas chromatography (Varian 3400 gas chromatograph with flame ionization detector, autosampler/controller). The sieved soil was dried overnight and soil extracts were prepared by shaking the soil vigorously with methylene chloride for 3–5 min. The Wisconsin DNR PUBL-SW-141 (modified DRO method) had three choices of extractant solvents: methylene chloride; hexane, and carbon disulfide. The extraction procedure was repeated three more times and all the aliquots were combined. The column used for separation was a 30 m EC-Wax (Carbowax) with an internal diameter of 0.75 mm and a 0.25 μm film thickness (Alltech, Deerfield, IL). The column temperature was kept at 32°C (1-min holding) followed by a programming of 18°C/min up to 300°C (2-min holding). The injector and detector temperatures were maintained at 270 and 290°C, respectively. The flow rate of make-up gas (nitrogen) was 32 mL/min and air flow was 300 mL/min. The split ratio was maintained at 10:1. The total peaks detected were integrated to generate a total petroleum hydrocarbon (TPH) value. The standardization was done using the external standard method with various hydrocarbon mixtures. The chromatographic parameter, extraction protocols, and standardization methods were taken from the U.S. Environmental Protection Agency's test methods for Evaluating Solid Waste, SW-846. Final concentrations were reported on a soil dry-weight basis.

RESULTS AND DISCUSSIONS

Biological Treatment

Stimulation of Bacterial Consortia by Use of Volatile Fatty Acids and Glucose as Carbon Source

E&P soils 2 and 3 were evaluated for stimulation of indigenous microflora using glucose, acetic acid, and valeric acid (1 g/l) as additional

Table 1. Composition of Contaminants in Soil 3

Compounds	%
C_{10}-C_{16}	41.1
C_{16}-C_{20}	32.0
C_{20}-C_{24}	20.6
C_{24}-C_{28}	6.3

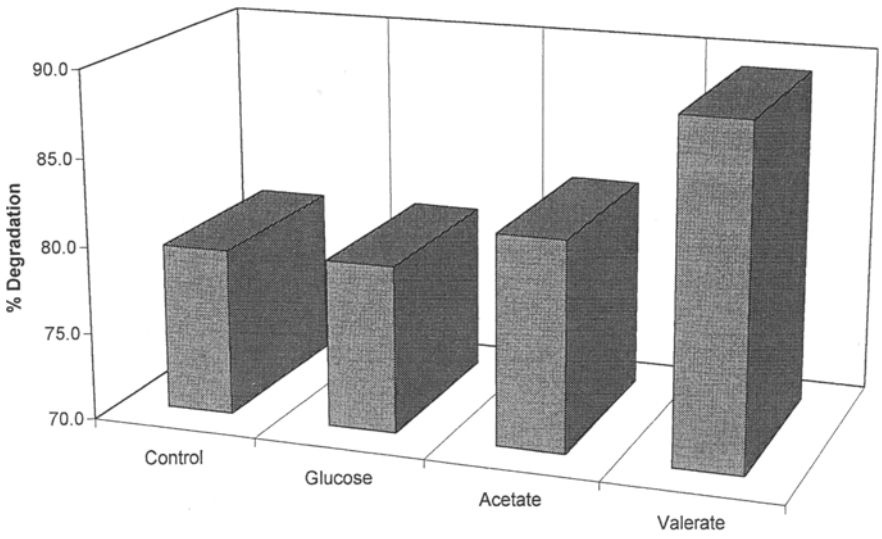

Fig. 2. Effect of various inducers on TPH degradation of soil 2.

growth factors. The studies were continued for 3 wk and samples were analyzed for degradation of TPHs. The results summarized (Figs. 2 and 3) showed that degradation of TPH was 80 and 86% for soils 2 and 3, respectively. Incorporation of the inducer, valerate, did enhance the degradation further to 89 and 93%, for soils 2 and 3, respectively. Statistically this is in the same range as noted without any inducer. Soil 3 was further analyzed for composition of individual TPHs degradation. The compositions (Table 1) of contaminants in soil 3 indicate that over 41% of contaminants fall in the carbon range of C_{10}–C_{16} and less than 7% in the carbon range of C_{24}–C_{28}. Despite the presence of higher proportion of lower-carbon-range compounds, the degradation of lower-carbon-range compounds (C_{10}–C_{16}) was higher (> 98%) as compared to higher (C_{24}–C_{28}) (Fig. 4) carbon-range compounds (> 74%). Likewise, the degradation rate (Fig. 5) was also higher in the lower-carbon-range compounds (58 mg/kg/d) as compared to higher-carbon-range components (6.7 mg/kg/d). These findings indicate that lower-carbon-range compounds are degraded to a

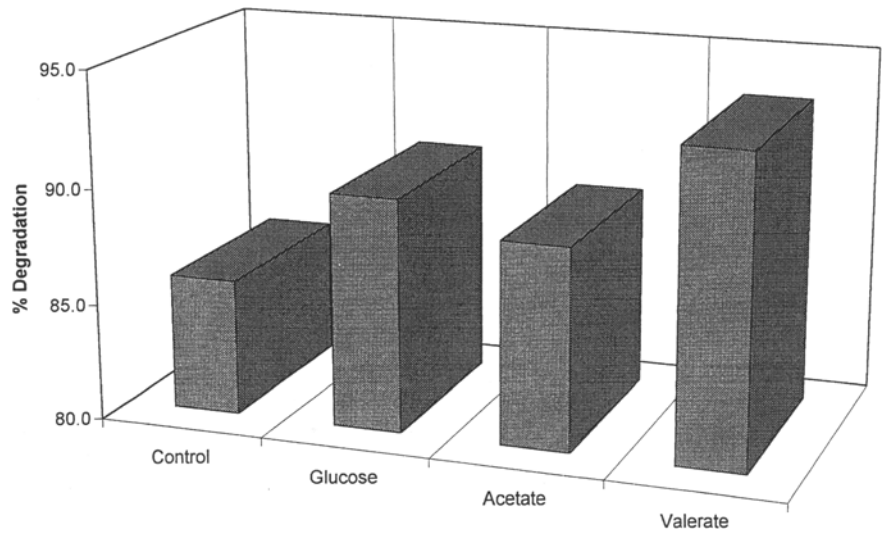

Fig. 3. Effect of various inducers on TPH degradation of soil 3.

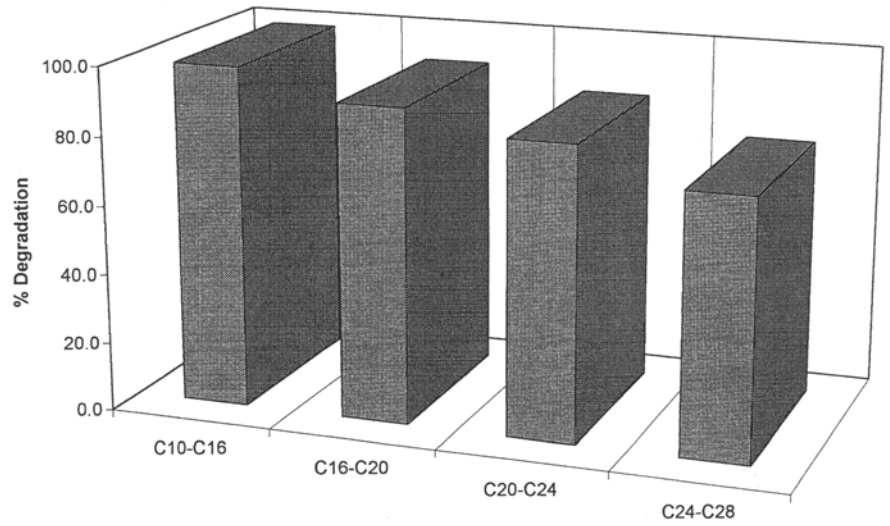

Fig. 4. Degradation of different groups of TPH compounds by biological treatment.

larger extent (> 98%) and at faster rates (58 mg/kg/d) compared to higher-carbon compounds. These experiments have suggested to us that none of the inducers were useful for significantly enhancing the degradation of TPHs. One of the reasons for this could be attributed to higher degradation of TPHs without any inducer (> 85%). These results suggest that TPH degradation does not need any externally added inducers.

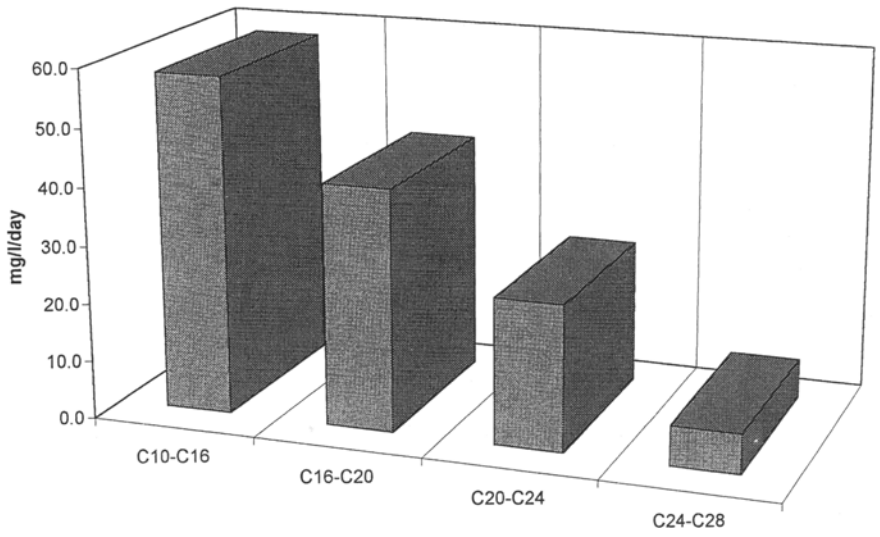

Fig. 5. Degradation rate of different TPH compounds by biological treatment.

Chemical Treatment

Determination of Oxygen Evolution With and Without Chelating/Stabilizing Agents at Different pHs

Hydrogen peroxide decomposes readily to water and oxygen at room temperature. The decomposition of H_2O_2 can be minimized by the use of stabilizing agents. The evolution of oxygen from H_2O_2 was studied under different conditions: water at pH 7.0 and 5.0; sodium citrate as chelator (10 m*M*); phosphate buffer (0.05 *M*) at pH 5.0 and 7.0. The objective was to determine the stabilization/chelation obtained by addition of sodium citrate and phosphate buffers. Naphthalene was used as model substrate for these studies at the initial concentration of 7219 mg/L. The results (Fig. 6) suggested a significant amount of oxygen production at pH 7.0 using deionized water alone with H_2O_2 and $FeSO_4$ (10 m*M*) addition. Incorporation of sodium citrate (10 m*M*) resulted in a marked reduction in oxygen production. Experiments conducted at a lower pH of 5.0 did not show oxygen production with or without addition of chelator (results not shown). In other studies with phosphate buffer (pH 5.0 and 7.0), no oxygen was produced at the lower pH of 5.0. The overall degradation of naphthalene was between 6 and 24%. It may be concluded from these experiments that loss of hydrogen peroxide for unproductive oxygen can be minimized by use of different stabilizers/chelators such as citrate or phosphate salts. It is important to mention here that soluble form of iron is important for Fenton's reaction. This soluble form is essentially achieved either at lower pH (< 4.0) or alternatively by using chelators. Our results have suggested that addition of either sodium citrate or phosphate buffer has stabilized the decomposition of H_2O_2 even at higher pH as evidenced by lower oxygen

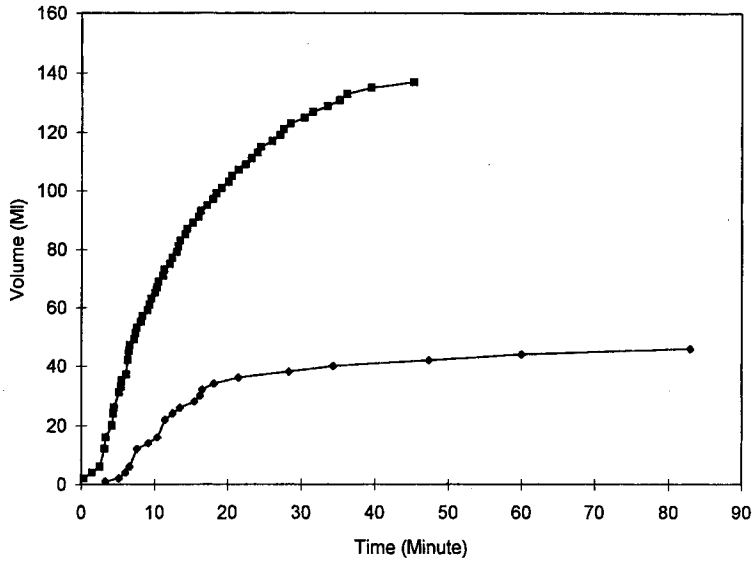

Fig. 6. Evolution of oxygen with and without sodium citrate in naphthelene-added reactor. (—◆— sodium citrate, —□— control).

evolution. However, at lower pH (5.0), the oxygen evolution was lower suggesting a stabilization without addition of external compounds. Fenton's reaction involves several series of reactions. The production of oxygen from HO_2 radical is dependent on pH. It was suggested that the rate constant for oxygen production from HO_2 is pH dependent with a value of 2×10^4 at lower pH (< 3.0) to a value of 1×10^6 L/mole-sec at higher pH (near neutral) *(12)*.

Optimization of pH for Degradation of TPHs in Contaminated Soils

The objective of this study was to determine the pH for maximum degradation of TPHs. The optimization of pH was done by using phosphate buffers at several different pH (4.0–7.0). The results (Fig. 7) showed that at the lower pH of 4.0, TPH degradation of greater than 64% was achieved. The degradation was significantly reduced at the higher pH of 7.0. Replacing the buffer with deionized water resulted in lower degradation of TPHs in soil-slurry system. The degradation of TPH in buffer was twice as compared to deionized water used for preparation of slurry (Fig. 8).

CONCLUSIONS

The research conducted to-date has successfully demonstrated the removal of TPHs in soils by biological and integrated approaches. The degradation of up to 93% was achieved by biotreatment when valerate was used as a growth inducer. The major proportion (> 41%) of the contaminants were in the carbon range of C_{10}–C_{16}. The degradation of over

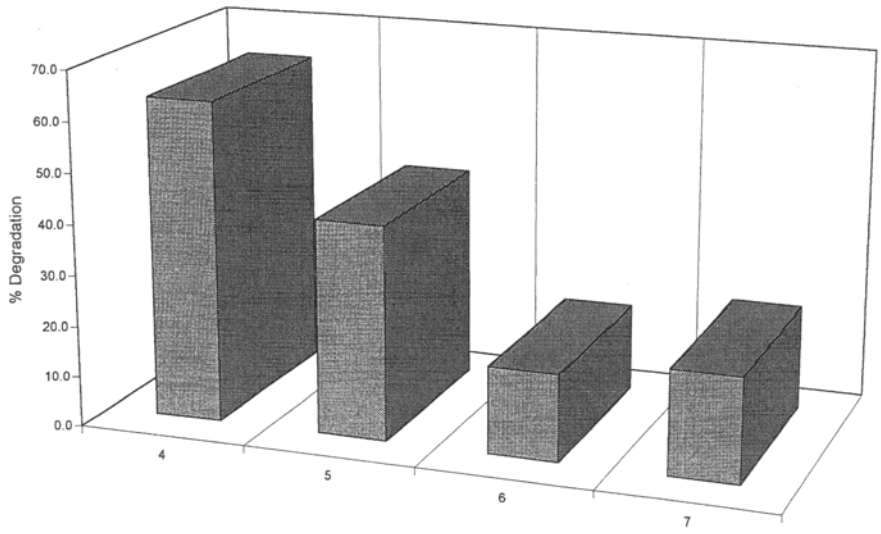

Fig. 7. Effect of pH on degradation of TPHs from soil slurry.

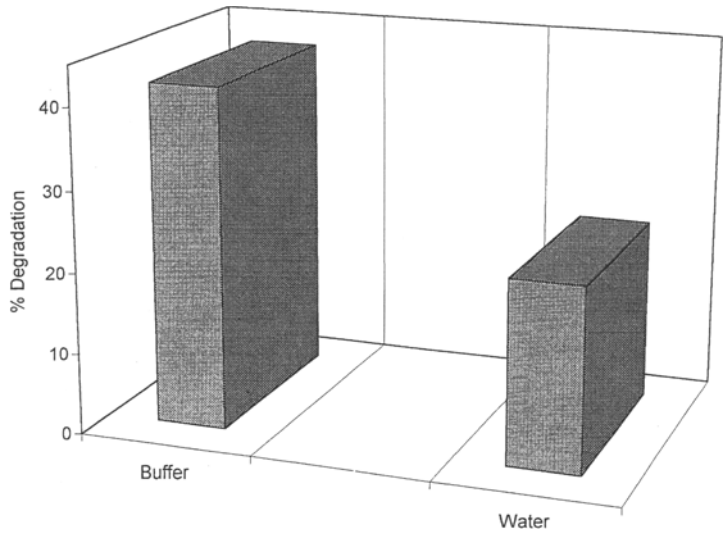

Fig. 8. TPH degradation: a comparison of buffer and water used for preparation of soil slurry.

98% was achieved for the lower-carbon compounds (C_{10}–C_{16}) as compared to 75% for higher-carbon-range compounds (C_{24}–C_{28}). Likewise, the degradation rate was also higher for degradation of lower-carbon-range compounds (58 mg/kg/d) as compared to high carbon compounds (6.7 mg/kg/day). Lower pH range of 4.0–5.0 is more effective for chemical oxidation of TPH components. Use of phosphate buffer has shown better degradation as compared to deionized water.

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