Influence of pH on Decomposition of Total Petroleum Hydrocarbon in Soil Slurry-Sequencing Batch Reactors

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The contamination of soil and water with petroleum hydrocarbons is a widespread environmental problem. The treatment requirement and removal of this pollutant are becoming more important in these days. Total Petroleum Hydrocarbon (TPH) has been reported to be toxic, carcinogenic, and an endocrine disrupter widely used in developing countries. Various physical, chemical, and biological methods were used for removing TPH in water treatment. Soil Slurry – Sequencing Batch Reactor (SS-SBR) is one of the important in-situ or ex-situ technologies which were able to bio-remediate the soils containing high levels of organic matters. In fact, in this condition the pollutant depletion rates depend mainly on the degradation activity of the microorganisms available in the system. The results obtained generally reflect the actual biological depuration potential of the soil. The application of aerobic SS-SBR is predominant for bio-remediation of soils. A large number of successful laboratory, pilot and full-scale studies and cases of aerobic SS-SBRs have been reported for bioremediation of soils polluted with Polycyclic Aromatic Hydrocarbons (PAHs), pesticides, diesel, and explosives. Slurry-phase bioreactors (SPB) are well-stirred tanks in which soil and water are mixed with air, microbial cells, and nutrients. Soil is sieved to produce a 1mm particle, approximately, before feeding it to the reactor. Many factors influence the feasibility and effectiveness of bioremediation. Some of these are the presence of suitable microorganisms, the availability of nutrients, temperature, and pH. Consideration of these factors is critical for a successful implementation of bioremediation systems. Soil pH is an important process control parameter. The optimum pH for soil biodegradation lies between 6 and 8; however, effective biodegradation can be found outside this range. In this research, the ex-situ methods have been selected. In comparison with in-situ methods, they are faster, simpler and more controllable and can be applied for treating and removing more pollutants and soils. Among ex-situ techniques, slurry phase has been chosen, where contaminated soil is combined with water and other additives in bioreactors and then mixed. Nutrients and oxygen are added, and conditions in the bioreactor are controlled to create the optimum environment for microorganisms to degrade the contaminants. This technique offers two advantages. First, these experimental conditions maximize the contact between the solid and the aqueous phase, thus enhancing the mass transfer and, as a consequence, the biodegradation rate. In addition, slurry-phase degradation experiments give the results that can be promptly transferred to a full-scale process. The biodegradation of oils in a SPB has a higher degradation rate than other biological treatment methods. Various modes of SPB operation have been tested in laboratories and pilot-scale plants, and one of the most common and best performing modes involves an SS-SBR. This research has investigated the optimum pH that afforded best degradation of TPH in SS-SBR with a variation of pH and other fixed conditions.

Materials and methods: The HPLC grade n-hexane and dichloromethane have been used for extraction solvents. Anhydrous granular (Na_2SO_4) has been provided. Sulfuric acid and sodium hydroxide were used for pH adjustment. NH_4Cl, K_2HPO_4, and KH_2PO_4 as nutrients have been used for balancing the C:N:P ratio as 60:2:1. All of these chemicals were purchased from Merck, Germany. The soil sample has been collected from Azimabad region in the south of Tehran refinery. The soil main characteristics are shown in Table 1.

TOC and nitrogen have been measured by combustion using an NA2100 Protein Nitrogen Analyzer (Thermoquest CE Instruments, Italy). Nitrite, nitrate and phosphate have been measured in a chromatographic system equipped with a Waters 515 pumping system, a Waters IC-PAK anions column, an UV/V Kontron model 332 detector (Kontron Instruments, Italy), and a Wescan conductivity detector (Wedan Instruments, USA). The pH of slurry has been measured by Metrohm 691 pH meter (Switzerland). Heterotrophic and degrader populations have also been enumerated by the MPN technique.

Two soil-slurry circular reactors made by plaxy glass have been designed and equipped in laboratory-scale with 6 liters volume which its diameter and height is 19 and 30cm, respectively (Fig. 1). In each

reactor 600gr of sieved and dried soil has been added with NH_4Cl, K_2HPO_4, and KH_2PO_4, in order. During the research, the pH is adjusted in a range of 5-10 (Table 2). The reactors are continuously mixed and aerated through a fine bubble diffuser from the bottom to provide 5mg/l DO. The reactors have been started with 10% (w/v on a dry weight basis) TPH contaminated soil in sterile tap water. The SBRs have also been started as a batch growth for 14 days pro start up and then carried out six runs by two month retention time. The volumetric feed rate is a function of the desired hydraulic residence time.
Dried soil sample has been mixed with 3x20ml CH_2Cl_2 and n-hexane (1:1) and measured by an Power Sonic 420 (Korea) ultrasonic cleaning system for 5 min in three times. Then, the samples have been poured through sodium sulfate and concentrated in a Kuderna-Danish (KD) concentrator under a gentle steam of nitrogen to nearly 2ml for GC-FID analysis. Before GC analysis, liquid phase has been filtered through 0.45 m cellulose filter paper and LLE with 1 liter sample with 3x15ml dichloromethane/n-hexane (1:1) which added to a decanter and shaken for 10 minutes, strongly for three tomes. The three extracts have been combined and evaporated under a gentle steam of nitrogen to 2ml for GC-FID analysis. TPH in soil samples were analyzed by GC. For GC analysis, 2µL of the sample was injected into a gas chromatograph UNICAM 610 series equipped with a FID. The column was used in the analysis is DB-5 with 30m length, 0.25mm internal diameter, and 0.2 µm film thickness. Nitrogen is as carrier gas. Injector and FID detector temperatures are 280°C and 340°C, respectively. The column initial temperature was 50°C for 5 min, and then increased to 250°C with 10°C/min slope and remained at 250°C for 40 minutes. The calibration curves have been prepared with weathered diesel standards in concentrations of 1000 to 4000 ppm as shown in Figure 2.
Results and discussion: Initial experiments on this soil shows that the type of pollutant is weathered diesel as the chromatograms obtained after soil extraction (Fig. 3). The time zero chromatograms for all conditions are similar to the initial chromatogram and clearly illustrated the large number of compounds present in weathered diesel fuel. In day14 of the reactor operation, the bacterial counts have been numerated suitable, as DO in the reactors is 5mg/l. This study has showed that aerobic soil slurry reactor can effectively remediate TPH contaminated soil. The performance of reactors in TPH remediation in each run is shown in Table 3. SBR1 in second run encompass 88.3% degradation efficiency in pH=7. However, both reactors in first run and SBR1 in third run have to some extent similar results, so, the best pH has occurred on natural pH. Therefore, this is optimum pH for such applications and would be used in farther studies. Figure 4 shows TPH removal percent and results of trend line. TPH solubility of contaminated soil in liquid phase in the reactors is shown in Table 4. According to Table 4, at the end of all runs the amount of pollutants remained in the liquid phase has been less than 1%. Thus, it is clear that in large scales liquid phase could be used in further runs, because the amount of TPH in this phase has been a little. Previous studies by various investigators were focused on the bioremediation of TPH and very few reports on partial degradation of TPH in sequencing batch soil slurry reactor. The aerobic SS-SBR system is promising. The advantage of the slurry reactor is its simple operating conditions; only mixing, aeration, and a carbon source.
Conclusion: To reduce costs and increase efficiency, the operating parameters should be optimized. Soil pH is an important process control parameter. In this study we have investigated optimum pH that had the best degradation of TPH in SS-SBR with variation of pH and other fixed conditions. TPH concentration have also been analyzed by GC equipped with a FID and defined optimum pH for bioremediation of TPH-contaminated soil in SS-SBRs in nearly normal pH, i.e., 7.

Keywords: bioremediation, Flame Ionization Detector (FID), Gas Chromatography (GC), pH, Soil Slurry – Sequencing Batch Reactor (SS, SBR), Total Petroleum Hydrocarbon (TPH)