Biological treatment of petroleum contaminated soils by soil slurry-sequencing batch reactors (SS-SBRs)

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Abstract

The soil slurry-sequencing bath reactor (SS-SBR) was studied to treat poorly graded sand with clay (SP-SC) contaminated by aged petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) with concentrations of 23000 mg/kg and 750 mg/kg respectively. An 8 L bioreactor was operated with a 10% solid concentration (0.1 kg dry soil/L slurry). The fill period was relatively instantaneous, and the draw period lasted approximately 1 minute so the react period comprised essentially the entire cycle time. In the draw period a fraction of slurry (10%) was removed from the SS-SBR weekly and it was replaced with untreated slurry. This volumetric replacement strategy provided 70 days hydraulic retention time (HRT). The process performance was assessed by monitoring total petroleum hydrocarbons (TPH) and PAH concentrations, pH, dissolved oxygen (DO), oxygen uptake rate (OUR) and colony forming units (CFU). Due to a high concentration of TPH, silica gel clean up was performed to specify PAH degradation. The results have shown high overall removal efficiency for TPH close to 97% whereas biodegradation of PAHs has been performed with a removal efficiency of 90%.
Keywords: petroleum contaminated soils, bioslurry, SS-SBR, TPH, PAH.

1   Introduction

For many years the soils of Azimabad, in the vicinity of the Tehran refinery plant, have been contaminated with petroleum hydrocarbons through spills, leakage of oil reservoirs, decay pipelines and refinery wastes. The intensity of

pollution has affected even groundwater quality. In addition PAHs compounds, which are classified as environmental priority pollutants, are found in this area with high concentrations.

Bioslurry treatment, which is a relatively new application to contaminated sediments, soils and sludges clean up [1], is a biological ex situ technology, offering optimal process control and high biodegradation rate [1,2] and could be operated in different modes such as batch systems tested [3,4], tanks-in-series [5], soil slurry-sequencing batch reactor (SS-SBR) [6], continuous-flow reactor (CSTR) [7]. Among the above mentioned bioreactor types, SS-SBR and CSTR are the most common in field systems. At least for soil contaminated by hydrocarbons, SS-SBRs are able to reach higher efficiencies than CSTR [8]. On the other hand SS-SBR has shown a good performance in treating PAH contaminated soils and sediments [9,10], which are relatively persistent due to their hydrophobicity and stability [11].

2 Materials and methods

2.1 The feed slurry

Soil samples used in experimental studies were collected from a region in the vicinity of Tehran refinery plant in accordance with sampling procedure, described in chapter four of Test Methods for Evaluating Solis Waste, Physical/Chemical Methods (EPA, SW-846) [12]. The soil organic matter was determined by the Walkley-Black Method [13]. The soil was poorly graded sand with clay (SP-SC) according to Unified Soil Classification System (USCS) ASTM D 2487-93 [14]. Before using, the soil was passed through a 0.5mm sieve. The sieved fraction was partially air-dried and was stored at 4°C to maintain biological activity. Prior to using in bioslurry experiments, the samples were spiked with a known concentration of PAHs including Naphthalene, Phenanthrene and Pyrene (750 mg/kg) dissolved in dichloromethane. Tap water

Table 1:   Characteristics of the soil.

Soil Classification (USCS)	SP-SC
Composition of soil	
Sand (%)	90
Silt (%)	3
Clay (%)	7
Bulk density (g/cm^3)	1.7
Soil pH (1:2 w/v)	7.5
Organic matter (%)	11
Organic carbon	6.4
Soil moisture	
Field (%)	20.1
Air dried (%)	12.3
CFU/g dry soil	9×10^4

was added to produce a solids concentration of 10% (0.1 kg dry soil/L slurry). The Mineral Salt Medium (MSM) provides a C:N:P ratio of approximately 60:2:1 by adding ammonia, nitrate and phosphate as NH_4Cl, KNO_3, K_2HPO_4. Sodium sulphate (Na_2SO_4) and Magnesium sulphate heptahydrate ($MgSO_4.7H_2O$) were added with 2000 mg/L and 200 mg/L concentrations respectively. Since the samples were collected from an aged contaminated site, the endogenous microorganisms were supposed to degrade contaminants and therefore no adapted microorganism addition (bioaugmentation) was performed. The characterization of examined soil is indicated in Table 1.

2.2 Bioreactor configuration

The soil slurry-sequencing batch reactor (SS-SBR) consisted of sealed 8 L rounded bottom Plexiglas vessel with a working volume of 6 L (7 cm free board). The reactor was equipped with a 400 rpm speed mixer. Oxygen was supplied through a fine-bubble diffuser at the bottom. Two ports were provided in the lid for housing dissolved oxygen (DO) and pH probes. A granular activated carbon (GAC) trap was used to collect volatile organics in effluent air. Since foaming is a common problem in bioslurry treatment, which is attributed to biosurfactant production [15,16] and considering that foam production was reported in previous bioslurry SBR investigations [8], a siphon was provided in reactor to discharge probable foams. The reactor used for the experiments is shown schematically in Fig. 1. During studies, the reactor was maintained at relatively constant temperature (23–25°C).
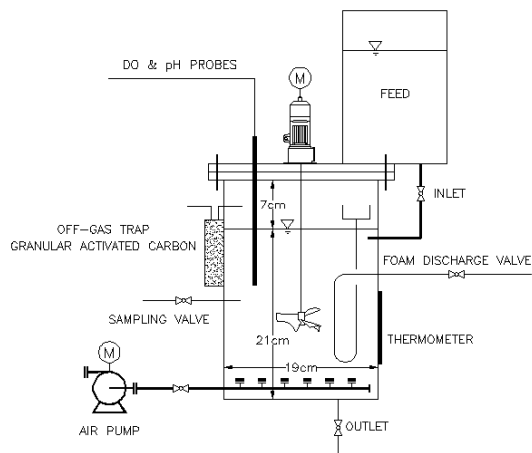

Figure 1:   Reactor configuration.

2.3 Bioreactor operation

6 L of prepared slurry was fed to reactor through the feed reservoir by gravity. The reactor was operated in sequencing batch mode. Fill period was relatively instantaneous, and draw period lasted approximately 1 minute so the react period

comprised essentially the entire cycle time. In draw period a fraction of slurry (10%) was removed from the SS-SBR weekly and it replaced with untreated slurry. This volumetric replacement strategy provided a 7 days solid retention time (SRT) and 70 days hydraulic retention time (HRT). A certain volume of slurry (the recycle fraction) remained in the reactor to provide acclimated microorganism for the next batch of untreated slurry.

2.4 Analytical methods

Fed and treated slurry were sampled during each treatment cycle for biological and physicochemical properties measurement.

2.4.1 Physicochemical analysis
The bioreactor was monitored regularly for slurry phase pH, using pH meter (model 51935, HACH, USA) and dissolved oxygen (DO) using DO probe (model 51970, sensION6, HACH, USA). The Oxygen uptake rate (OUR) was evaluated for slurry samples decanted from bioreactor in duplicate according to Standard Methods (SM 2710 B) [17].

2.4.2 Microorganism quantification
After extraction of microorganisms from soil [18], pour plate method described in Standard Methods (SM 9215B) [17] was used to enumerate heterotrophic bacteria in quadruplicate. Dilutions were plated on plate count agar (Merck) and incubated for 48 hours at 37°C. Colony forming units (CFU) were counted and reported as CFU g^{-1} dry soil.

2.4.3 Quantification of TPH and PAH
Total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH) concentrations were determined in the whole slurry and filtered slurry. Briefly, ultrasonic extraction was carried out on 2-5 g soil samples and 10 mL slurry filtered samples passed through the 0.45μm filter according to EPA 3550B method [17]. 1 μL of concentrated samples by Kuderna-Danish (K-D) concentrator was injected to GC (ATI, UNICAM, 610 series) equipped with FID detector for TPH quantification. Injection block and detector cell temperatures were 340°C and 280°C respectively. Concentration of PAH was supposed to be estimated by high performance liquid chromatography (HPLC) (Agilent, 1100 series) according to method described in EPA 8310 [17]. But due to high concentration of TPH, aspired separation of the aromatic and aliphatic could not completely be achieved. Hence silica gel clean up was performed based on method described in EPA 3630C [17] prior to injection.

3   Results and discussion

The SS-SBR was operated with a 7 day cycle. Hydraulic retention time of 70 days was achieved by replacing 600 mL of the slurry volume weekly. TPH concentration at the end of each cycle is shown in Figure 2. TPH concentrations were reduced from 23.0 g/kg in the feed slurry to 0.75 g/kg after treatment in the

SS-SBR. This represents a removal efficiency of 97% (Fig. 3). Rates of TPH removal in SS-SBR showed a considerable decrease at first two weeks of operation.
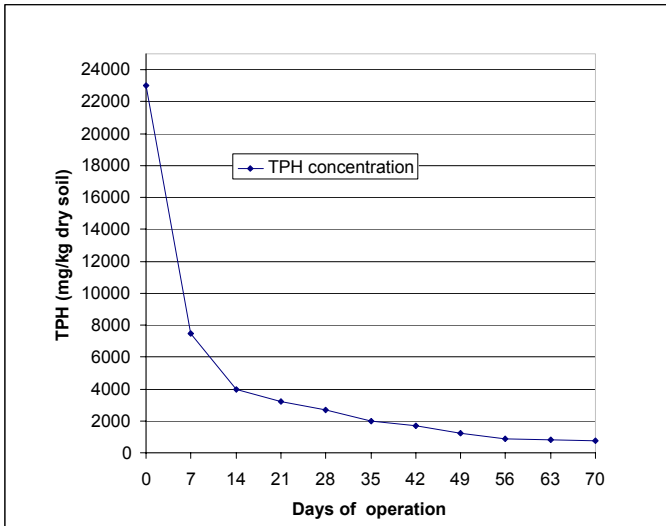

Figure 2:   TPH concentration during 70 day HRT.
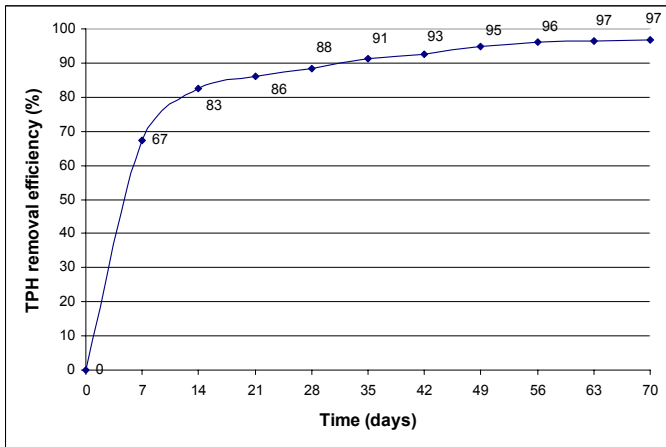

Figure 3:   TPH removal during 70 day HRT.

   PAHs biodegradation was investigated in the SS-SBR simultaneously. The results are shown in Figure 4.
   Time profile of oxygen uptake rate (OUR), used as a surrogate measure of biological activity in bioreactor is shown in Figure 5 during operation period. OUR increased in the SS-SBR from approximately 1.78 mg/L/hr to 8.3 mg/L/hr.
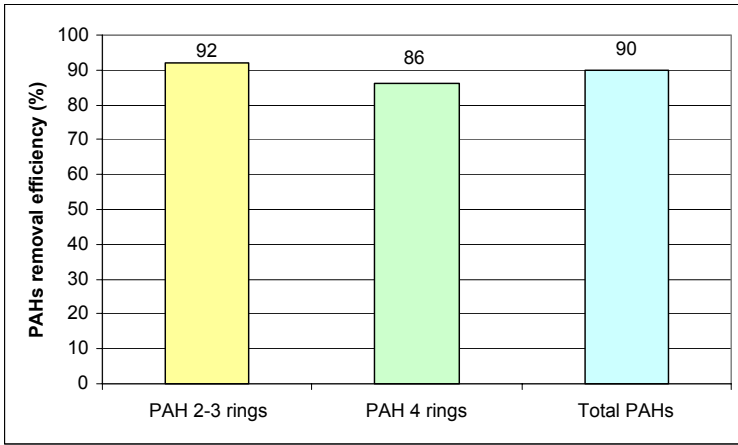
Figure 4:   PAHs removal efficiency during bioreactor operation.
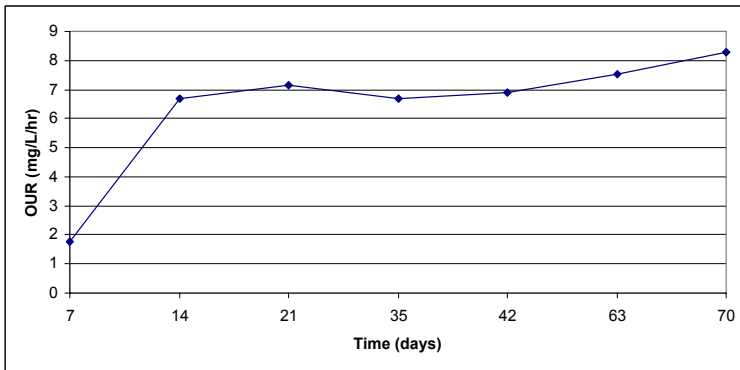

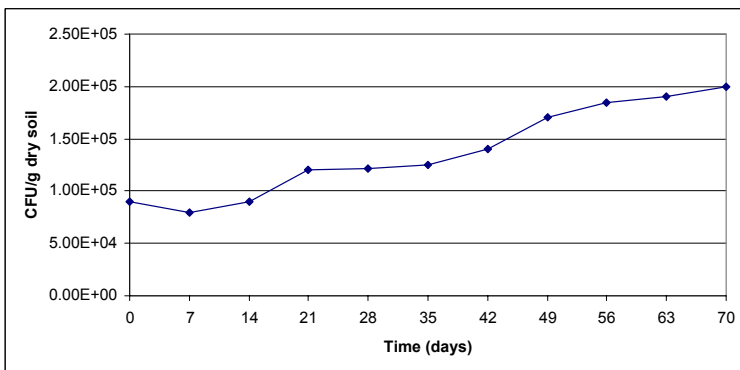Figure 5:   OURs for the SS-SBR during 70 day HRT.

Figure 6:   CFU versus time during bioreactor operation.

Results from microorganisms are shown in Figure 6. During the first week after fill, CFU did not increase. While after one week, bacterial counts began to grow up.

Table 2 lists the results of measurements made in the feed and effluent from the SS-SBR at the end of operation.

Table 2:   Results of measurements from the feed slurry and the SS-SBR effluent.

Parameter	Feed	Effluent
TPH (mg/kg soil)	23000	750
PAHs (mg/kg soil)	750	75
OM (%)	11.0	3.9
OC (%)	6.4	2.3
pH	7.6	7.3
CFU $\times 10^4$ /g dry soil	9	20

4   Conclusions

The experiments demonstrated that TPH was reduced in the SS-SBR from a concentration of 23 g/kg in the feed slurry to 0.75 g/kg in the reactor effluent at the last cycle of operation. Successful degradation of stable and hydrophobic compounds such as PAHs were also accomplished. Indeed an overall removal efficiency of 90% was achieved in 70 days HRT. However the removal efficiency was higher for 2-3 rings PAH (removal efficiency of 92%) rather than 4 rings PAH (removal efficiency of 86%).

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