Bioresource Technology 100 (2009) 5671–5677

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Microcosm assays and Taguchi experimental design for treatment of oil sludge containing high concentration of hydrocarbons

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ARTICLE INFO

Article history:
Received 6 February 2009
Received in revised form 10 June 2009
Accepted 12 June 2009
Available online 26 July 2009

Keywords:
Oil sludge
Hydrocarbons
Microorganisms
Taguchi design

ABSTRACT

Microcosm assays and Taguchi experimental design was used to assess the biodegradation of an oil sludge produced by a gas processing unit. The study showed that the biodegradation of the sludge sample is feasible despite the high level of pollutants and complexity involved in the sludge. The physicochemical and microbiological characterization of the sludge revealed a high concentration of hydrocarbons (334,766 ± 7001 mg kg^{-1} dry matter, d.m.) containing a variety of compounds between 6 and 73 carbon atoms in their structure, whereas the concentration of Fe was 60,000 mg kg^{-1} d.m. and 26,800 mg kg^{-1} d.m. of sulfide. A Taguchi L_9 experimental design comprising 4 variables and 3 levels moisture, nitrogen source, surfactant concentration and oxidant agent was performed, proving that moisture and nitrogen source are the major variables that affect CO_2 production and Total petroleum hydrocarbons (TPH) degradation. The best experimental treatment yielded a TPH removal of 56,092 mg kg^{-1} d.m. The treatment was carried out under the following conditions: 70% moisture, no oxidant agent, 0.5% of surfactant and NH_4Cl as nitrogen source.

1. Introduction

The petroleum-related activities in México, such as the hydrocarbon extraction, refining and production processes, have a significant impact on the environment due to air pollution, dust, gas emissions, waste waters and solid discharges. Recent surveys have unveiled that around 22% of the overall emissions and discharges accumulated in the country are hazardous residues produced by the oil industry operations. Specifically, the residues that the gas processing units generate are oil sludge, exhausted catalyst and waste oil (PEMEX, 2001). Oil sludge containing solid material and drag oil is regarded as a dangerous residue according to México's environmental regulations (SEMARNAT, 2006). As a consequence, a need arises as to develop and to implement efficient low-cost technologies for oil sludge treatment.

Biological technologies are based on the use of microorganisms able to live in sites containing pollutant compounds (i.e. hydrocarbons) which could be used as carbon source. Technologies for soil bioremediation can be adapted to suit oil sludge treatment requirements. The main parameters that influence the efficiency of biological technology applications are: temperature, pH, nutrient and oxygen availability, C/N and C/P rates, moisture and contaminant availability for microorganisms.

The molecular structure of the contaminant determines its chemical properties and hence its biodegradability. The latter is affected by properties such as the solubility, concentration of the contaminant, recalcitrance and toxicity (Semple et al., 2001). Many publications concerning hydrocarbon removal are focused on the biodegradation of specific oil fractions using isolate microorganisms. However, in contaminated systems (sludge, soils and sediments) the scenario is more complicated because of the existence of various hydrocarbon species at elevated concentrations. As a result, these systems are more toxic and complex and their treatment becomes more intricate as well.

Ouyang et al. (2005) applied a composting technique to remediate oil sludge with concentrations ranging from 327,700 to 371,200 mg TPH kg^{-1} d.m. The analysis was carried out at room temperature during 56 days. At the end of the test period the hydrocarbon removal was 31%.

Marín et al. (2006) used a compost system to reduce the hydrocarbon concentration from refining oil sludge. The initial TPH concentration was 250,000–300,000 mg TPH kg^{-1}. The sludge sample was under treatment for three months using a biopile system. In this experiment, the hydrocarbon removal was 60% and the control of moisture was the key parameter. Rojas-Avelizapa et al. (2007) utilized a series of biopiles and a compost system for the remediation of a site polluted with drilling mud. The capacity of the biopiles was 1 ton of soil and it was added with straw as texturing agent. Moisture was maintained at 30–35%. The concentra-

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doi:10.1016/j.biortech.2009.06.050

Nomenclature

45 $P(t)$	CO_2 cumulative production at time t (mg CO_2)	47 P	CO_2 potential production (mg CO_2)
46 λ	time of lag-phase (h)	48 r_m	Gas production rate (mg CO_2 h^{-1})

tion of hydrocarbons decreased from 99,300 (±23,000) to 5500 (±770) mg TPH kg^{-1} in the soil; the experiment lasted 180 days.

The results of the investigations as described above disclose that the use of biological systems to remediate polluted sites containing high TPH concentrations is feasible. In spite of this, the lack of an accurate tendency observed in the results of TPH removal uncover that each sludge (or soil) owns properties and contaminants characteristic of the site. Hence, the nature and the amount of contaminants must be taken into account in every application to estimate whether the biological remediation is viable. For practicality reasons, exhaustive biodegradation assays should be performed in the laboratory prior to any field application.

Taguchi method based on orthogonal arrays (OA) can be used to analyze a large number of variables with a small amount of experiments. By using this method, the number of experimental arrays can be significantly decreased (Mohan et al., 2007). This procedure determines the relationship between variables by focusing on those interactions that are thought to affect the functional characteristics under study.

The aim of this work was to accomplish microcosm assays and Taguchi experimental design to evaluate, as a first approach, the feasibility of the biodegradation of an oil sludge containing considerable concentration of hydrocarbons.

2. Methods

The sludge sample used in the experiments was obtained from the waste oil pool of a gas processing unit in México. Physicochemical and microbiological tests of the sample were done to determine: total petroleum hydrocarbons (TPH), metals, sulfide compounds, nitrogen, carbon, phosphates, heterotrophic and hydrocarbon-degrading bacteria (Table 1).

Taguchi L_9 (orthogonal array) experimental design covered 4 variables at 3 levels: moisture, nitrogen source and C/N rate, and addition of a surfactant (Tween 40) and an oxidant agent (CaO_2) (Table 2). Those levels were selected based on previous works reported in the literature on bioremediation: C/N rate (Huesemann, 1994); nitrogen source (Brook et al., 2001) moisture (Antizar-Ladislao et al., 2006; Rojas et al., 2006) oxidant agent (Cassidy Daniel and Irvine Robert, 1999) and surfactant (Márquez et al., 2000).

Biodegradation assays were made at the microcosm level in 1 L sealed bottles that were loaded with 60 g of dry sludge. The systems were kept at 30 °C and under continuous orbital shaking at 150 rpm. They were also aerated daily for 1 h. CO_2 production was evaluated by gas chromatography using a Gow Mac thermal conductivity detector.

To determine TPH, sludge samples (1 g) were taken out of each bottle and extracted following a modified shaking/centrifugation method using dichloromethane (Arce-Ortega et al., 2004). The organic extracts were free asphaltenes purified by hexane precipitation. Concentrated samples (1 μL) were analyzed by FID-gas chromatography (Agillent Technologies, model 6890) under the conditions described by Rojas et al. (2006) and increasing the time in the last step (290 °C for 25 min). Helium was used as the carrier gas at 1.4 mL min^{-1} flow rate. The temperature of the injector and detector were set at 250 °C. All experiments were carried out twice. Two controls – a positive control with no addition of nutrient, surfactant or oxidant agent, and a negative control sterilized with sodium azide were run simultaneously. The analysis of results (data) was accomplished by utilizing the STATISTICA V. 6.0 software.

2.1. Analysis of results (experimental data)

The cumulative CO_2 production curves vs. time were fitted by using the modified Gompertz model (Eq. 1) (Van Ginkel et al., 2001).

$$P(t) = P \cdot \exp\left\{-\exp\left[\frac{r_m \cdot e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

where, $P(t)$, CO_2 cumulative production at time t (mg CO_2); λ, time of lag-phase (h); P, CO_2 potential production (mg CO_2); r_m, gas production rate (mg CO_2 h^{-1}).

These parameters were estimated by minimizing the square sum of errors (SSE) between the experimental data and the estimated values from the models. The "Solver" function of Microsoft Excel 2003 was used to reach a solution. The significance of the calculated parameters was tested according to an analysis of variance.

Table 1
Methods applied for physicochemical and microbiological characterization of oil sludge.

Parameter	Method
pH	Potentiometric
Moisture (% v/w)	Gravimetric
Total hydrocarbons (mg kg^{-1} d.m.)	Method 8015 EPA (1996) and Arce et al. (2004)
Boiling point distribution for size distribution	ASTM D-7169-05
SARA analysis	ASTM-D 2007-03
Phosphorous available (mg kg^{-1} d.m.)	Bray method Muñoz et al. (2000)
Total organic carbon	Total oxidation by IR Shimadzu Rojas-Avelizapa et al. (2007)
Total sulfide (mg kg^{-1} d.m.)	ASTM-D4294-03
Total nitrogen, organic and ammonium (mg kg^{-1} d.m.)	Kjendahl
Metals	EPA-6010C
Heterotrophic bacteria and hydrocarbon-degrading bacteria (CFU g^{-1} d.m.)	Plate-count method

d.m.: Dry matter.

Table 2
Taguchi L_9 (orthogonal array) experimental design.

Treatment no.	Moisture (%)	Oxidant agent (%)	Surfactant (%)	N source (C/N)
Factor				
1	50	0	0	Urea (15)
2	50	0.1	0.1	NH_4Cl (18)
3	50	0.5	0.5	w/a
4	60	0	0.1	w/a
5	60	0.1	0.5	Urea (15)
6	60	0.5	0	NH_4Cl (18)
7	70	0	0.5	NH_4Cl (18)
8	70	0.1	0	w/a
9	70	0.5	0.1	Urea (15)

Oxidant agent: calcium peroxide, surfactant: Tween 40 and w/a: without addition.