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ORIGINAL PAPER

Effect of sulphur species on the hydrocarbon biodegradation of oil sludge generated by a gas processing facility

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Abstract Oily sludge from gas processing facilities contains components that are major environmental pollutants. Biodegradation is an alternative treatment, but can be affected by other components of the sludge, such as sulphur compounds, so it is important to evaluate the effect of these on oil biodegradation in order to prevent negative impacts. This work studied the transformation of sulphur compounds in oily sludge biodegradation systems at the microcosm level. The predominant sulphur compounds in the original sludge were elemental sulphur and pyrite (9,776 and 28,705.4 mg kg^{-1}, respectively). In the biodegradability assays, hydrocarbon concentrations decreased from 312,705.6 to 186, 760.3 mg kg^{-1} after 15 days of treatment. After this time, hydrocarbon degrading activity stopped, corresponding with a decrease in hydrocarbon degrading bacteria. These changes were related to a reduction in pH that inhibits biodegradation. During the assay, sulphur compounds were gradually oxidized and transformed. The concentration of sulphate increased from 5,096 to 64,868.3 mg kg^{-1} after 30 days in the assay, although controls were unchanged. Therefore, it is important to determine changes to the main compounds of the waste in order to assess their impact.

Keywords Hydrocarbon biodegradation · Sulphate · Elemental sulphur · Pyrite

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Introduction

Gas processing facilities generate oil sludges, which are oil wastes from purges and separation equipment (Manning and Thompson 1995). The composition of these wastes is variable but overall they contain hydrocarbons and sulphur (EPA 2000). Because it is a heterogeneous matrix of complex components, the handling and disposal of oily sludge is a serious environmental problem (Ward et al. 2003). An alternative treatment for these sludges is biological processing. The effectiveness of this method has been previously demonstrated in the biodegradation of oil sludge from different origins (Bengtsson et al. 1998; Ward et al. 2003), in which removal of 80–99 % of sludge over 60–120 days was achieved with total petroleum hydrocarbon (TPH) concentrations of 26,000–50,000 mg kg^{-1}. Other studies report the use of composting biopiles in removal of hydrocarbon from drilling mud and refinery oil sludge with TPH concentrations of 100,000–371,000 mg kg^{-1} and removal efficiencies of 31–53 % (Al-Daher et al. 2001; Ouyang et al. 2005; Marín et al. 2006). The difficulty associated with the treatment of oily sludge containing hydrocarbons is that they comprise a mixture of compounds, which may be saturated, aromatic and heteroatom compounds containing sulphur, oxygen or nitrogen (Balba et al. 1998). After carbon and hydrogen, sulphur is the most abundant element in crude oil, in which its concentration can vary from 0.05 to 5 %, but can be up to 14 % in heavier oil (Bahuguna et al. 2011). In reservoirs, sulphur can be found in inorganic forms such as hydrogen sulphide (H_2S), pyrite (FeS_2) and elemental sulphur S^o, or organic compounds such as aromatic and saturated forms of thiols, sulphides and heterocycles (Shennan, 1996). Some of these compounds, such as dibenzothiophene (DBT) and its derivatives, are considered highly recalcitrant in sulphur removal processes (Soleimani et al. 2007).

Studies on the presence of sulphur compounds and hydrocarbon biodegradation have focused on the biodesulphurization of thiophene, dibenzothiophene and its derivatives (Shennan 1996; Bressler et al. 1998). In the case of inorganic sulphur (pyrite and elemental sulphur), studies have been directed towards metal leaching (Bacelar-Nicolau and Johnson 1999; Rawlings 2004), and very few have assessed the impact of pyrite in the bioremediation of organic compounds (Sarioglu and Copty 2008).

The application of biological alternatives for the treatment oily sludge has been aimed at the removal of hydrocarbons (Ouyang et al. 2005; Marín et al. 2006). In most of these studies, no account has been taken of the effect of the presence of other pollutants on degradation, such as sulphur and compounds derived from secondary biological processes that can occur in parallel. These compounds can inhibit the activity of hydrocarbon degraders (Meyer and Steinhart 2000). Therefore, it is important to study changes in sulphurous species and their effect on biodegradation.

The aim of this work was to evaluate the effect of sulphur species on hydrocarbon biodegradation in oily sludge from a gas processing facility. The research described in this paper was performed in laboratories of Instituto Mexicano del Petróleo, Mexico City in 2010.

Materials and methods

Sludge sample

Oil sludge was generated in a natural gas processing facility located in Tabasco, Mexico. The oil sludge sample was obtained from an open pool where the wastes were deposited. The sludge sample was placed in plastic containers, transported and stored at 4 °C until its characterization and use.

Biodegradability assays

Aerobic biodegradation assays were performed as follows: 15 g of oil sludge at 70 % moisture were placed in 125 ml serum bottles, and nitrogen (N) and phosphorus (P) were added as NH_4Cl and K_2HPO_4 in order to biostimulate the native microbiota. Bottles were sealed with acrylonitrile rubber stoppers and aluminium seals and incubated at 30 °C at 100 rpm in an orbital shaker (New Brunswick Scientific, model C-25) for a 30 day period. The systems were opened under sterile conditions once per day for 30 min to ensure an adequate oxygen supply. Samples were measured at the beginning of the experiment and at 15 and 30 days. Six bottles were prepared for each assay (*M*1, *M*2 and *M*3) with C/N ratios of 8.3, 14.3 and 33.3 and C/P ratios of 200, 200 and 100, respectively. Two bottles per assay were analysed at each sampling time.

The controls (*C*0) were prepared without the addition of nitrogen and phosphorus and were sterilized by autoclaving. During sampling, an entire bottle of each treatment was taken, and the total content was measured for analysis. Moisture content, pH, heterotrophic and hydrocarbon degrading bacteria, TPH content, sulphur, sulphates and pyrite were quantified in the sludge.

Analytical methods

Enumeration of heterotrophic bacteria (HB) and hydrocarbon degrading bacteria (HDB) was performed in selective media, by means of the plate-count method, according to Fernández et al. (2006). To determine TPH, sludge samples (1 g) were taken from each bottle and extracted following a modified shaking/centrifugation method using dichloromethane (Arce et al. 2004). The organic extracts were free asphaltenes, purified by hexane precipitation. Concentrated samples (1 µl) were analysed by FID-gas chromatography (Agilent Technologies, model 6890) under the conditions described by Rojas-Avelizapa et al. (2006), but increasing the duration of the last step (290 °C for 25 min). Helium was used as the carrier gas at a flow rate of 1.4 ml min^{-1}. The temperature of the injector and detector was set at 250 °C. Total nitrogen was measured by the Kjendahl method according to Fernández et al. (2006); total sulphur was measured according to ASTM-D1552-08 (2008); soluble sulphate was extracted with distilled water using a fraction of previously dried sludge, and analysis was performed on the supernatant using a capillary ion analyser (Waters Corp.). Elemental sulphur was analysed in a sludge sample according to Bartlett and Skoog (1954). Pyrite analysis was carried out by Mössbauer spectroscopy with a constant acceleration by Wissel instruments, model MRG-500, complemented by X-ray diffraction (Simens, model D-5000) according to Nava et al. (2006).

Analysis of organic sulphur compounds was carried out using a gas chromatograph (HP-6890) with a Sievers 355 Sulphur Chemiluminescence Detector (SCD) (Castorena et al. 2002). Metals were analysed using the EPA-6010C (2007) technique; pH was analysed with a pH meter Cole Parmer, model Accument AR50, and moisture content was measured according to Fernández et al. (2006). All analyses were carried out twice.

Results and discussion

Sludge characterization

Sludge characterization showed high concentrations of TPH (312,705.6 mg kg^{-1} dry matter d.m.), iron (60,200 mg kg^{-1} d.m.) and total sulphur (26,928.7 mg kg^{-1} d.m.), where 36.6 % of total sulphur was as elemental-S, 6.3 % as sulphate-S, 56.6 % as pyrite-S (FeS_2) and less than 0.5 % was detected as other organic sulphur compounds (Table 1). Figure 1a shows the chromatogram of organic sulphur compounds, with dibenzothiophene as reference standard in a gas-oil sample. The same conditions were used to analyse an organic extract of oily sludge and detected a single organic sulphur compound at a low concentration (Fig. 1b).

Enumerations of heterotrophic and hydrocarbon degrading bacteria in oily sludge confirmed the presence of native microbiota (Table 1), which is indicative of microorganism viability and the biodegradation potential of the system (Bossert and Kosson 1997; Mishra et al. 2001).

Hydrocarbon removal, pH and moisture behaviour

In the biodegradation systems (*M*1, *M*2 and *M*3), hydrocarbon biodegradation was observed in contrast to the control; however, no significant differences between the systems were detected. In these systems, the TPH content decreased on average by 40.3 % after 30 days of treatment while in the control the decrease was 9.3 % (Fig. 2). Some studies report the biodegradation of oil sludge with high hydrocarbon content (Ouyang et al. 2005). Marín et al. (2006), using a biopile composting process with the addition of a texturing agent, report a removal efficiency of 60 % over 3 months of treatment in an oily sludge from a refinery with an initial concentration of 250,000–300,000 mg TPH kg^{-1} d.m. The estimated removal rate was 2,000 mg TPH kg^{-1} d.m. day^{-1}. However, neither the metal nor the sulphur content were reported. These elements are known to impact negatively hydrocarbon degradation (Benka-Coker and Ekundayo 1998; Sandrin and Maier 2003).

Table 1 Characterization of oily sludge

Parameter	Concentration
Total petroleum hydrocarbons, TPH (mg kg^{-1} d.m.)	334,700 (±7,020)
Total sulphur (mg kg^{-1} d.m.)	26,928.7 (±40.4)
Elemental sulphur, S^o (mg kg^{-1} d.m.)	9,776 (±1,147)
Sulphate, SO_4 (mg kg^{-1} d.m.)	5,096 (±121)
Iron sulphide, FeS_2 (mg kg^{-1} d.m.)	28,705.4 (±2,149)
Organic sulphur compounds (mg kg^{-1} d.m.)	124
Organic nitrogen (mg kg^{-1} d.m.)	6,275 (±318)
pH	7.82 ± 0.15
Chromium (mg kg^{-1} d.m.)	207.28(±8.5)
Zinc (mg kg^{-1} d.m.)	8,265 (±110)
Iron (mg kg^{-1} d.m.)	60,200 (±179)
Heterotrophic bacteria, HB (CFU g^{-1} d.m.)	1.81.1 × 106
Hydrocarbon degrading bacteria, HDB (CFU g^{-1} d.m.)	7.08 × 104

d.m. dry matter

In our study, in addition to high hydrocarbon concentrations, we also found a high metal and sulphur content, which increased the difficulty of the biodegradation process. The initial TPH concentration was 334,700 mg kg^{-1} d.m., and the system achieved a removal of 143,921 mg kg^{-1} d.m over 30 days at a rate of 11,156 mg TPH kg^{-1} d.m. day^{-1}. The TPH removal rate was 5.6-fold higher than that obtained in the work reported by Marín et al. (2006).

In the first 15 days of the biodegradation process, the HB and HDB microbial population increased by about three orders of magnitude (Fig. 3). Between 15 and 30 days, it was observed that TPH degradation was inhibited (Fig. 2), which matched the decrease in HB and HDB bacterial populations (Fig. 3).

The decrease in the bacterial population was related to decreased pH (from 7.9 to 5.3) after 15 days of treatment (Fig. 4a). Kästner et al. (1998) found that, in most cultures, the growth and degradation rates decrease dramatically when the pH drops below 5.0. The maximum values of the hydrocarbon degradation rate and bacterial growth occurred when the initial pH was between 7.5 and 8.5, suggesting that the maximum degradation rate is related to microbial activity (Mutai 2009).

The pH of the control system was unchanged, but decreased in the biodegradation systems; therefore, this change could be attributed to biological factors. It is known that some acidophile microorganisms have the ability to obtain energy from sulphur and iron (Ghauri et al. 2007; Johnson 2009), such as *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* species, which can catalyze sulphide or elemental sulphur by oxidation to sulphuric acid (Kuenen et al. 1992; Chazal and Lens 2000).

Other microorganisms, such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Gallionella ferruginea*, have the ability to oxidize pyrite (FeS_2) in the presence of water and oxygen, according to Eq. 1 (Johnson and Hallberg 2005; Chockalingam and Subramanian 2006). The oxidation of elemental sulphur is described in Eq. 2.

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 \downarrow + 2\ SO_42^- + 4H^+ \quad (1)$$

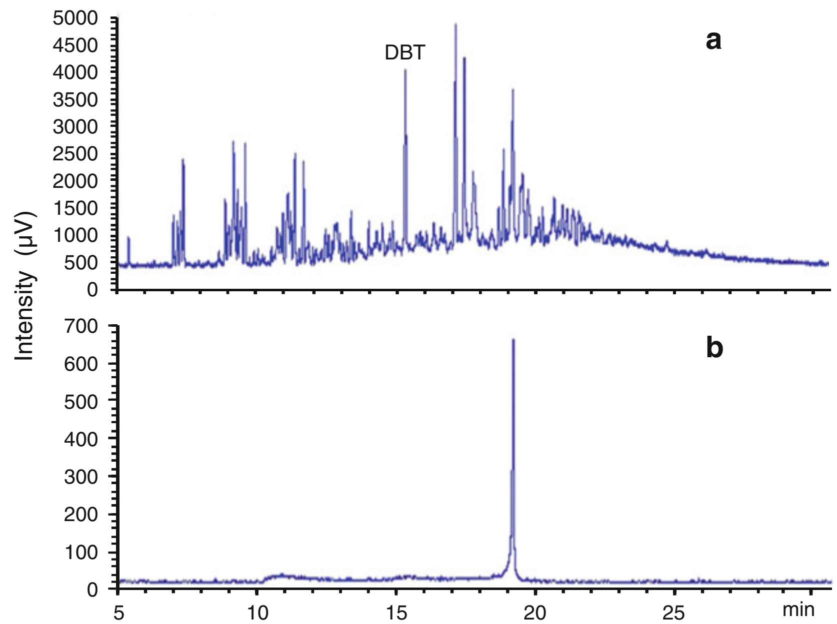

Fig. 1 GC-SCD chromatograms of organic-sulphur compounds. **a** gas-oil sample, **b** oil sludge. DBT (Dibenzothiophene) was used as reference standard

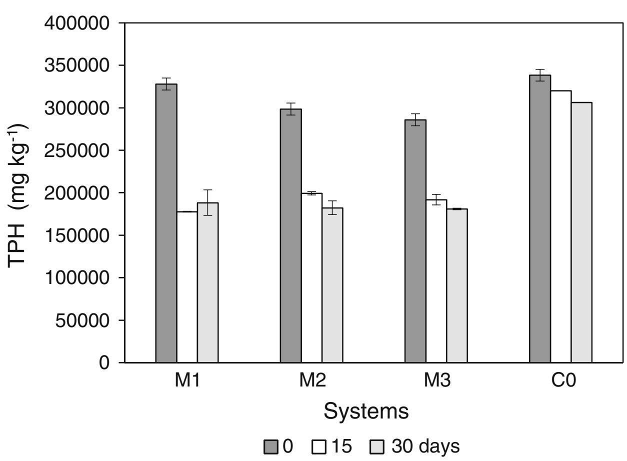

Fig. 2 HTP content in the biodegradation systems (*M*1, *M*2, *M*3) and sterilized control (*C*0)

$$S^{o} + 3/2O_2 + H_2O \rightarrow H_2SO_4 \quad (2)$$

In the conditions of the biodegradation system, the conversion of pyrite and elemental sulphur to sulphate was stimulated by water, aeration and microorganisms. The initial sulphate (SO_4) content of 5,081 mg kg^{-1} increased up to 67,110 mg kg^{-1} after 30 days of incubation (Fig. 5a), indicative of sulphuric acid (H_2SO_4) production.

In the biodegradation systems, the moisture content was 73.5 % at the start of the experiment (Fig. 4b). After 15 days, the system recorded an increase in moisture content of 4 % and, at 30 days, this decreased by approximately the same percentage (4 %). This implies that the moisture content was unchanged over the duration of the experiment. Moisture plays an important role because it catalyzes the degradation processes through hydrolysis and

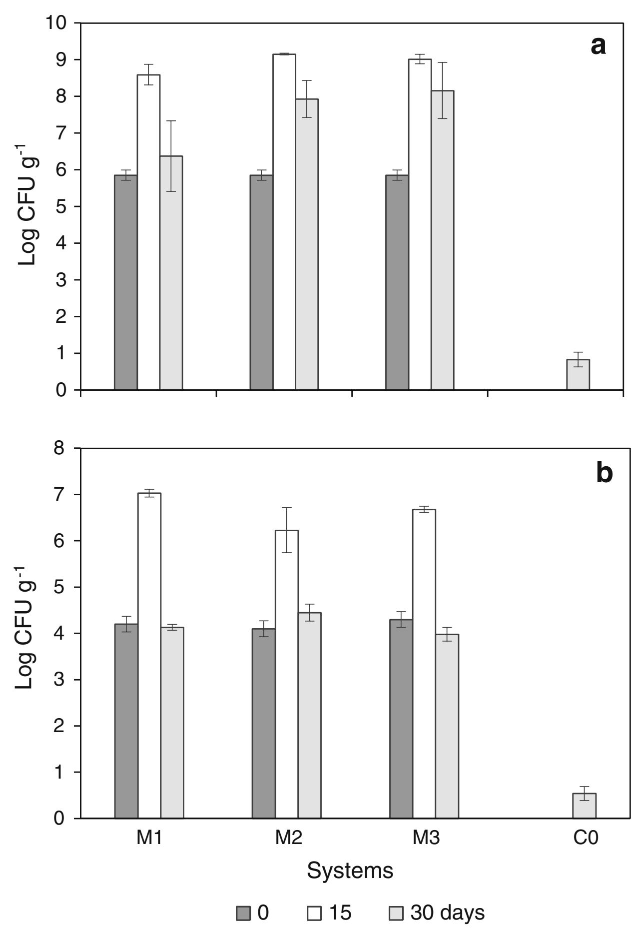

Fig. 3 Enumeration of bacterial population. **a** Heterotrophic bacteria, **b** Hydrocarbon degrading bacteria, in the biodegradation systems (*M*1, *M*2, *M*3) and sterilized control (*C*0)

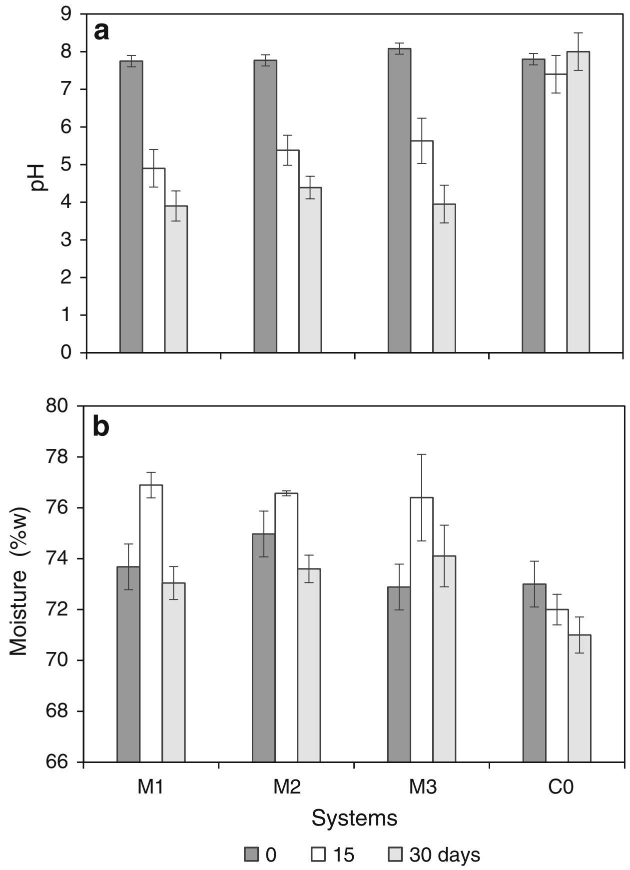

Fig. 4 Evolution of **a** pH and **b** moisture in the biodegradation systems (*M*1, *M*2, *M*3) and sterilized control (*C*0)

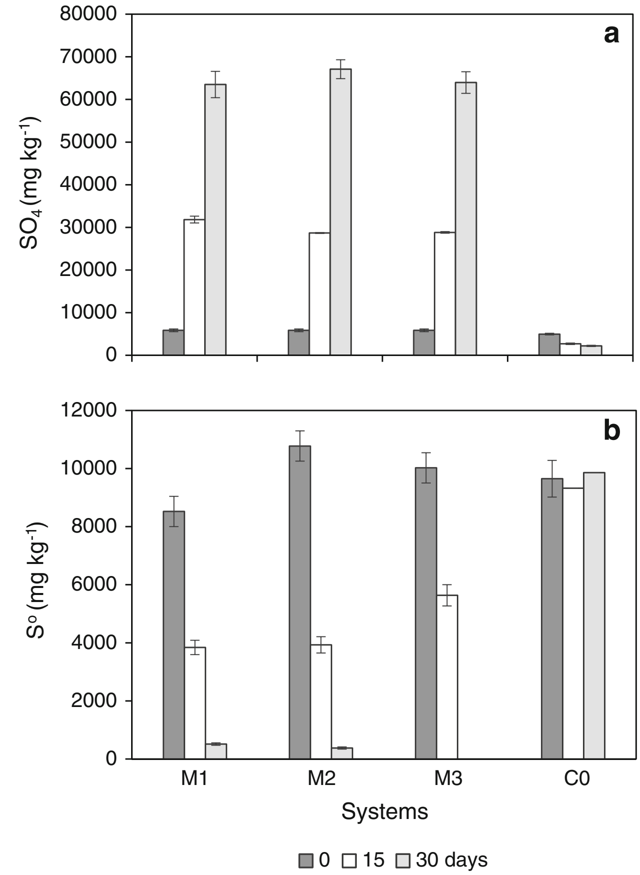

Fig. 5 Evolution of **a** Sulphate (SO_4) production and **b** Consumption of elemental sulphur (S^o), in the biodegradation systems (*M*1, *M*2, *M*3) and sterilized control (*C*0)

dissolution of organic and inorganic compounds. The sterile control showed a slight decrease in moisture content.

Sulphur balance

Sulphur balance in the systems was based on the quantification of total sulphur, inorganic sulphur species such as sulphate-S, elemental-S^o, pyrite-S, and organic sulphur compounds-S (osc-S) (Table 2). The initial concentration of elemental sulphur was 9,776 ± 1,147 mg kg^{-1} which decreased by over 50 % after 15 days in the biodegradation systems (Fig. 5b). The inorganic compound with the highest sulphur content in the oily sludge was pyrite (FeS_2), with a concentration of 28,705.4 mg kg^{-1}. At the end of the assay, it was found that the FeS_2 content decreased to 9,047.7 ± 1,241 mg kg^{-1} in the biodegradation systems. The elemental sulphur content decreased by over 96 % of its initial value, and the sulphate-S content increased to 21,622.7 ± 651 mg kg^{-1} (Table 2). This last value is formed by the initial sulphate-S, plus sulphate-S from the elemental-S and pyrite (FeS_2) oxidation reactions. The final value of sulphate-S was 12.7 times higher than the value at the start of the experiment. The changes in pH confirmed that the sulphate ion was present as sulphuric acid (H_2SO_4). The formation of SO_4 as sulphuric acid from pyrite and elemental sulphur occurs according to Eqs. 1 and 2, respectively. Organic sulphur content in the oily sludge was less than 0.05 %; therefore the contribution of this compound to sulphate production was negligible. The sterile control was unchanged and elemental sulphur content remained at 9,756.7 ± 148.9 mg kg^{-1} over the entire experimental period. The study of sulphur and iron oxidation systems is important for understanding their effect in the biodegradation process of hydrocarbons, in which the oxidation of sulphur to sulphate leads to sulphuric acid production, thus changing the pH of the system and negatively affecting the hydrocarbon degrading activity of microbial groups (Leahy and Colwell 1990; Sarioglu and Copty 2008). Microorganisms that oxidize sulphur under acidic conditions may obtain their energy from sulphur and iron (Kuenen et al. 1992; Chazal and Lens 2000).

Figure 6 shows the correlation between pH and the sulphate concentration described by Eq. 3, with $r^2 = 0.96$.

Table 2 Sulphur species content in biodegradation systems (*M*) and control (*C*0) before and after 30 days of incubation

	Systems			
	*M*1	*M*2	*M*3	*C*0
Initial balance				
Elemental-S° ($mg\ kg^{-1}$)	8,524.0	10,778.0	10,026.0	9,651.4
Sulphate-S ($mg\ kg^{-1}$)	1,680.0	1,745.0	1,671.0	1,694.0
Pyrite-S ($mg\ kg^{-1}$)	16,582.0	14,328.0	15,080.0	15,454.6
osc-S ($mg\ kg^{-1}$)	124	124	124	124
Total-S ($mg\ kg^{-1}$)	26,910.0	26,975.0	26,901.0	26,924.0
Final balance				
Elemental-S° ($mg\ kg^{-1}$)	514.1	377.1	0.0	9,862.0
Sulphate-S ($mg\ kg^{-1}$)	21,173.1	22,369.6	21,325.6	1,340.0
Pyrite-S ($mg\ kg^{-1}$)	5,028	4,093.3	5,374.4	15,598.0
osc-S ($mg\ kg^{-1}$)	124	124	124	124
Total-S ($mg\ kg^{-1}$)	26,839.2	26.964.0	26,824.0	26,924.0

osc-S: sulphur of organic sulphur compounds

The values are mean of two measures with a variation coefficient (CV) < 10 %

The pH value decreased while the sulphate concentration increased. This indicates that sulphate was present as sulphuric acid (H_2SO_4), as has been reported for the metabolism of some sulphur oxidizing microorganisms (Espejo et al. 1988; Sugio et al. 1989; Suzuki et al. 1990).

$$pH = -1.5\mathrm{Ln}(SO_4 - 2) + 20.86 \quad (3)$$

Biological activity promotes conditions suitable for sulphate production, high acidity and dissolution of metal ions from oily sludge. pH control can mitigate the impact of inorganic sulphur compound oxidation, including pyrite and elemental sulphur, and thus may increase the efficiency of the bioremediation process. The conventional treatment for aqueous systems characterized by high acidity and a high concentration of sulphate and dissolved metal ions is neutralization through the addition of calcium compounds, such as limestone or quicklime, and sodium components, such as caustic soda and soda ash, which result in an increase in pH and precipitation of metal ions. Biological sulphate reduction by sulphate reducing bacteria has also been proposed as an alternative; under anaerobic conditions, the process can remove metals from solution as metal sulphide precipitates (Chockalingam and Subramanian 2006).

Bioremediation processes of organic contaminants containing pyrite have demonstrated that oxygen is a limiting factor for biodegradation, as most of the oxygen is consumed through ferrous oxidation, while pH also affects the process but can be controlled (Sarioglu and Copty 2008). This is one of the first studies to analyse the effect of inorganic sulphur compounds on the oil sludge biodegradation process. Although the addition of air and moisture stimulated the activity of HDB, unwanted side effects, such as changes in pH or the dissolution of metals, may result, interfering with remediation (Chockalingam and Subramanian 2006). This work serves to highlight the importance of biodegradation microassays in the detection of problems before the scaling-up of the process for field application.

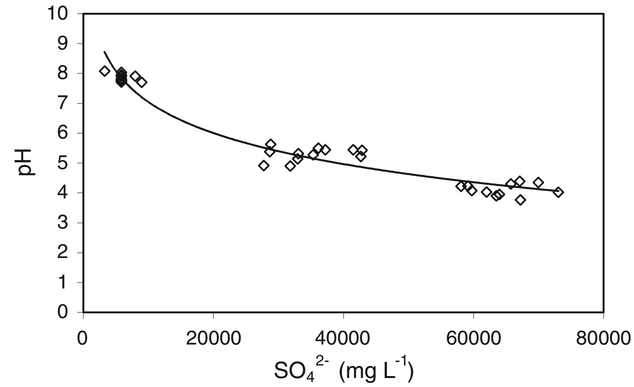

Fig. 6 Correlation between pH and sulphate concentrations in biodegradation systems

Conclusion

The results show that hydrocarbon biodegradation of oil sludge by the native microbiota is feasible. However, the biodegradation process was affected by oxidation of inorganic sulphur compounds that increase sulphate content in the form of sulphuric acid.

In order to eliminate these undesirable effects and to gain better control of the treatment of oil sludge, it is important to monitor changes of sulphur compounds in the hydrocarbon biodegradation process.

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References

Al-Daher R, Al-Awadhi N, Yateem A, Balba MT (2001) Compost soil piles for treatment of oil contaminated soil. Soil Sedim Contam 10(2):197–209

Arce OJM, Rojas ANG, Rodríguez VR (2004) Identification of recalcitrant hydrocarbons present in a drilling waste-polluted soil. J Environ Sci Health Part A 39(6):1535–1545

ASTM-D1552-08 (2008) Standard test method for sulfur in petroleum products (High-Temperature Method). American society for testing and materials, USA. doi:10.1520/D1552-08

Bacelar-Nicolau P, Johnson BD (1999) Leaching of pyrite by acidophilic heterotrophic iron-oxidizing bacteria in pure and mixed cultures. Appl Environ Microbiol 65(2):585–590

Bahuguna A, Lily MK, Munjal A, Singh RN, Dangwal K (2011) Desulfurization of dibenzothiophene (DBT) by a novel strain Lysinibacillus sphaericus DMT-7 isolated from diesel contaminated soil. J Environ Sci 23(6):975–982

Balba MT, Al-Awadhi N, Al-Daher R (1998) Bioremediation of oil contaminated soil: microbiological methods for feasibility assessment and field evaluation. J Microbiol Methods 32:155–164

Bartlett JK, Skoog DA (1954) Colorimetric determination of elemental sulphur in hydrocarbons. Anal Chem 26(6):1008–1011

Bengtsson Å, Quednau M, Haskå G, Nilzén P, Persson A (1998) Composting of oily sludges-degradation, stabilized residues, volatiles and microbial activity. Waste Manag Res 16(3): 273–284

Benka-Coker MO, Ekundayo JA (1998) Effects of heavy metals on growth of species of *Micrococcus* and *Pseudomonas* in a crude oil/mineral salts medium. Bioresource Technol 66(3): 241–245

Bossert ID, Kosson DS (1997) Methods for measuring hydrocarbon biodegradation in soils. In: Hurst CJ, Knudsen GR, McInerney MJ, Stetzenbach MV (eds) Manual of environmental microbiology. ASM Press, Washington, DC, pp 738–745

Bressler DC, Norman JA, Fedorak PM (1998) Ring cleavage of sulfur heterocycles: how does it happen? Biodegradation 8:297–311

Castorena G, Suarez C, Valdez I, Amador G, Fernández L, Borgne S (2002) Sulfur selective desulfurization of dibenzothiophene and diesel oil by newly isolated *Rhodococcus globerulus* strains. FEMS 215(1):157–161

Chazal M, Lens PNL (2000) Interactions between the sulfur and nitrogen cycle: microbiology and process technology. In: Lens PL, Hulshoff P (eds) Environmental technologies to treat sulfur pollution principles and engineering. IWA, London

Chockalingam E, Subramanian S (2006) Studies on removal of metal ions and sulphate reduction using rice husk and *Desulfotomaculum nigrificans* with reference to remediation of acid mine drainage. Chemosphere 62(5):699–708

EPA (2000) Associated waste report: dehydration and sweetening wastes. Office of solid wastes. United States Environmental Protection Agency, Washington, DC. http://www.epa.gov/osw/nonhaz/industrial/special/oil/sd.pdf

EPA 6010C (2007) Inductively coupled plasma-atomic emission spectrometry. United States Environmental Protection Agency, Washington, DC. http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/6010c.pdf

Espejo RT, Escobar B, Jedlicki E, Uribe P, Badilla-Ohlbaum R (1988) Oxidation of ferrous iron and elemental sulfur by *Thiobacillus ferrooxidans*. Appl Environ Microbiol 54(7): 1694–1699

Fernández LL, Rojas AN, Roldán CT, Ramírez IM, Zegarra MH, Uribe HR, Reyes AR, Flores HD, Arce OJ (2006) Manual of soil analysis techniques applied to the remediation of contaminated sites. (Original text in Spanish). http://www2.ine.gob.mx/publicaciones/download/509.pdf

Ghauri MA, Okibe N, Johnson DB (2007) Attachment of acidophilic bacteria to solid surfaces: the significance of species and strain variations. Hydrometallurgy 85(2–4):72–80

Johnson DB (2009) Extremophiles: acidic environments. In: Schaechter M (ed) The desk encyclopedia of microbiology. Elsevier Academic Press, San Diego

Johnson DB, Hallberg KB (2005) Acid mine drainage remediation options: a review. Sci Total Environ 338(1–2):3–14

Kästner M, Breuer-Jammali M, Mahro B (1998) Impact of inoculation protocols, salinity, and pH on the degradation of polycyclic aromatic hydrocarbons (PAHs) and survival of PAH-degrading bacteria introduced into soil. Appl Environ Microbiol 64(1): 359–362

Kuenen JG, Robertson LA, Tuovinen OH (1992) The genera *Thiobacillus*, *Thiomicrospira*, and *Thiosphaera*. In: Balows A, Truper HG, Dworkin M, Harder W, Schleifer K-H (eds) The prokaryotes. Springer, Berlin

Leahy JG, Colwell RR (1990) Microbial degradation of hydrocarbons in the environment. Microbiol Rev 54(3):305–315

Nava N, Sosa E, Espinosa Medina MA, Llanos ME (2006) Identification of corrosion products by Mössbauer spectroscopy (Original text in Spanish). Memorias XLI Congreso Mexicano de Química. Soc. Mex. de Química, 24–28 septiembre. http://www.quimicanuclear.org/pdf_memorias2006/simposio/NOE_%20NAVA.pdf

Manning FC, Thompson RE (1995) Oilfield processing, crude oil, vol 2. PennWell, Tulsa

Marín JA, Moreno JL, Hernández T, García C (2006) Bioremediation by composting of heavy oil refinery sludge in semiarid conditions. Biodegradation 17(3):251–261

Meyer S, Steinhart H (2000) Effects of heterocyclic PAHs (N, S, O) on the biodegradation of typical tar oil PAHs in a soil/compost mixture. Chemosphere 40(4):359–367

Mishra S, Jyot J, Kuhad RC, Lal B (2001) Evaluation of inoculum addition to stimulate in situ bioremediation of oily-sludge-contaminated soil. Appl Environ Microbiol 67(4):1675–1681

Mutai B (2009) Bioremediation of marine oil spills by hydrocarbon degrading microorganisms on laboratory-scale. In: IOC/WESTPAC international training workshop on monitoring technique and emergency response of marine oil spills, Qingdao, China, 20–23 April

Ouyang W, Liu H, Murygina V, Yu Y, Xiu Z, Kalyuzhnyi S (2005) Comparison of bioaugmentation and composting for remediation of oily sludge: a field-scale study in China. Process Biochem 40(12):3763–3768

Rawlings DE (2004) The microbially-assisted dissolution of minerals and its use in the mining industry. Pure Appl Chem 76(4): 847–859

Rojas-Avelizapa NG, Roldán CTG, Arce OJM, Ramírez IME, Zegarra MH, Fernández LLC (2006) Enhancement of hydrocarbon removal in a clay and drilling-waste polluted soil. Soil Sediment Contam 15(4):417–428

Sandrin T, Maier M (2003) Impact of metals on the biodegradation of organic pollutants. Environ Health Persp 3(8):1093–1101

Sarioglu MS, Copty NK (2008) Modeling the enhanced bioremediation of organic contaminants in pyrite-containing aquifers. Transp Porous Med 75(2):203–221

Shennan JL (1996) Microbial attack on sulphur-containing hydrocarbons: implications for the biodesulfurization of oils and coals. J Chem Technol Biotechnol 67(3):109–123

Soleimani M, Bassi A, Margaritis A (2007) Biodesulfurization of refractory organic sulfur compounds in fossil fuels. Biotechnol Adv 25(6):570–596

Sugio T, Katagiri T, Inagaki K, Tano T (1989) Actual substrate for elemental sulfur oxidation by sulfur: ferric ion oxidoreductase purified from *Thiobacillus ferrooxidans*. Biochim Biophys Acta 973(2):250–256

Suzuki I, Takeuchi TL, Yuthasastrakosol TD, Oh JK (1990) Ferrous iron and sulfur oxidation and ferric iron reduction activities of

Thiobacillus ferrooxidans are affected by growth on ferrous iron, sulfur, or a sulfide ore. Appl Environ Microbiol 56(6): 1620–1626

Ward W, Singh A, van Hamme J (2003) Accelerated biodegradation of petroleum hydrocarbon waste. J Ind Microbiol Biotechnol 30(5):260–270