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EVALUATION OF XYLENE BIOVENTING IN A RESIDUAL GRANITIC SOIL REMEDIATION

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ABSTRACT

In the present study a residual granitic soil contaminated with xylene was submitted to bioventing tests.The most adequate range for the growth of the microbial consortia, developed from a soil sample collected in a refinery area, was determined by extensive kinetic studies in flasks, using different contaminant concentrations. The selected xylene degrader consortium of bacteria was used in custom-built soil bioventing columns, subject to a contamination level previously established by kinetic studies, a constant air flow and room temperature. Control was done simultaneously by respirometry, measuring O_2, CO_2 and moisture, by Gas Chromatography and by measuring biomass, counting colony-forming units by spreading on Petri plates. Bioventing results a mathematical model contemplating different kinetics rates for the volatilized and for the biodegraded fractions of the contaminant.

1. INTRODUCTON

There are several technologies successfully used toremediate soils contaminated with petroleum hydrocarbons in the unsaturated zones of the soil, namely soil vapour extraction (SVE) and bioventing (BV). In SVE air flow is induced for removing volatile organic compounds (VOC'S) from contaminated soils, while bioventing is a process designed to provide indigenous organisms with adequate oxygen to supply for the aerobic degradation of the target contaminants[1,2].Twenty years ago bioventing was applied to several sites contaminated with petroleum hydrocarbons as it is an effective and inexpensive remediation technology [3]. Despite, bioventing requires remediation times greater than a year, being this technology nowadays deprecated in favor to techniques with shorter residence time but often more expensive.One problem is the frequent discrepancy between laboratory tests and the conditions prevailing in the field. Bioventing efficiency is very sensitive to the air flow through the soil pores. This aspect is crucial in the scale up from laboratory to field, because soils are heterogeneous media, highly conditioned by geological characteristics of the site [3]. Published works in this theme often disregard the operating field conditions. Some authors use soil samples with high content in organic matter while others use pulsed pumping in the air extraction system [4]. In the present work, a regional representative granitic soil is tested with continuous air extraction similar to the field conditions, allowing interpret bioventing efficiency through contaminant concentration in the gas phase, oxygen consumption and carbon dioxide depletion. Mathematical modeling of biodegradation is based, although with some condensation of parameters, on Monod kineticswhich address biomass growth and substrate decrease[5], in this case the model was adapted to bioventing process including an equation for oxygen consumption in aerobic biodegradation of the contaminant.

2. METHODOLOGY

2.1. Preliminary tests

Preliminary tests were used to develop the selected microorganism's consortium, adapt it to the contaminant and study its capability to biodegrade xylene in a residual granitic soil (Srγ).Srγ is very common in the north Portugal as it is the result of "Granite Rocks" weathering. It was collected in a clean site on a recent slope excavation.The consortium of

microorganisms was obtained from a crude contaminated soil (BSoil) sample collected from the protection area of crude storage tanks in a refinery.

The studies were performed in three different stages: initially in mineral liquid medium (MMA) [6] in sterilized Erlenmeyer flasks, afterwards in a Srγsample in sterilized Erlenmeyer flasks and finally in a Srγsample in steel columns.

The tests in liquid phase (MMA) were made in order to develop the selected microorganismsconsortium and adapt it to the contaminant; successive transfers (T1, T2 and T3) in enrichment cultures (EC) were carried out. Various contaminant levels of xylene (i = 3.4, 6.9, 13.8, 17.2, 20.6, 27.5 and 34.4 mg added to 100mL of inocula) were tested to select the most adequate working concentration range [6].

The studies in Srγ, first performed in sterilized flasks (500 mL) closed by Mininert valves, were made with 200g of wet Srγ with 20% of moisture content (inocula obtained in the second transfer, T2, of the enrichment cultures). Different xylene supplements (i = 70, 86 and 103 mg per kg of wet Srγ) and two different temperatures (t = 20 and 28°C) were used in these tests [6]. Non inoculated media was used for "Blank" tests.

Studies in bioventing columns were made using a lab-scale reactor with a 3.9 liter capacity [6]. Each column was loaded with 2000g of wet Srγ, inoculated with the second transfer of the enrichment culturesand contaminated with 206 mg of xylene. Non inoculated media was used for two types of "Blank" tests, onewith previously sterilized Srγ and the other without sterilization. These bioremediation tests were carried out at temperature rangefrom 22 to 25ºC.

The xylene concentration was monitored by gas chromatography (GC) [6] and the incubation period ended when the xylene concentration in the gas phase reached 0.5 mg per liter of air. At the end of the experiments spread-plate technique was used for Colony Forming Units (CFU) counting [6].

2.2. Bioventing tests

The selected xylene degrader consortium of bacteria was used in custombioventing columns, with air circulation created by vacuum extraction. In respirometry circuit the air was pushed by a small diaphragm pump, controlled by a massicflowmeter with valve controller (Sierra 840 Auto-Trak); it was then dried in a Drierite tube; CO_2 was measured in a Sablesys CA-1B carbon dioxideanalyzer, and scrubbed from the air flow by an Ascarite tube; finally, O_2 was measured by an Sablesys FC-1B oxygenanalyzer. Data collection from thermometers, flowmeter and gas analyzers was made by custom developed computer routines, using both analogic and digital data sources. The amount of data gathered is configurable, although it tends to be larger [7].

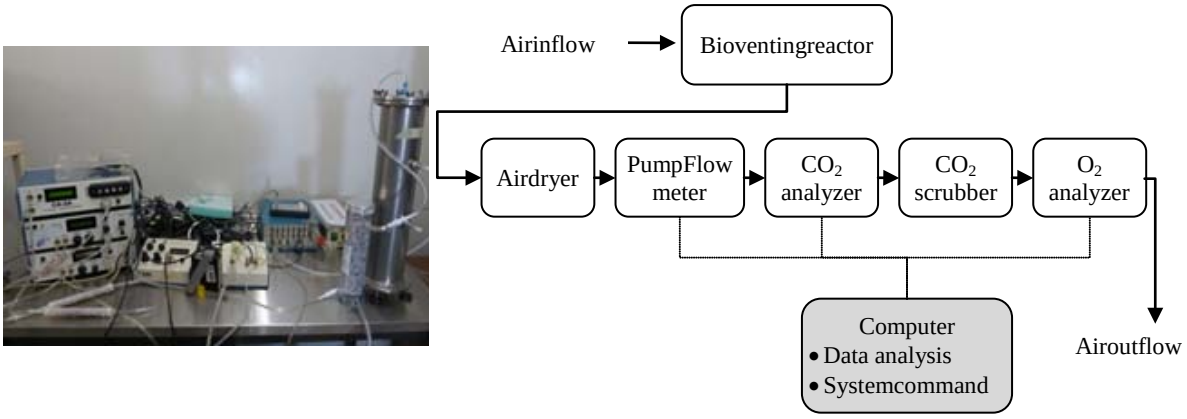

Fig. 1 - Bioventing experimental design - respirometric circuit.

The custom bioventing reactor isa steel column cylinder with internal diameter of 100 mm and a height of 500 mm, closed by bottom and top air – tight lids, with four ports: the inflow in the bottom, the outflow in the top and two sampling ports in the side wall. Bioventing control was made simultaneously by respirometry with a continuous measurement of O_2, CO_2 and daily xylene quantification by gas chromatography.

In each test, the columns were loaded with 2000 grams of wet Srγ(20% of moisture content). In the inoculated tests the soil was moistened with 400 mL of the second transfer of the enrichment cultures. Control tests used Srγ soil wetted with sterile water. In order to evenly distribute xylene (206 or 309 mg), the columns were loaded and contaminated bylayers. Two flow rates were tested in these trials, 13 and 3.6 liter per hour (table 1). These tests were carried out at temperature range from 22 to 25 ºC.

Table 1 - Parameters (flow rate, xylene and inocula) used in studies with 2000g wet Srγ

Test	Soil	Inocula	Xylene Mass	Flow Rate
BV_13	2000g wet Srγ	Second transfer	206 mg	13 L/h
BV_3.6	2000g wet Srγ	Second transfer	309 mg	3.6 L/h
Blank	2000g wet Srγ	Sterile water	206 mg	13 L/h

2.3. Mathematical model

The main variables to evaluate the efficiency of the bioventing are the followingoutput variables: contaminant content (C), microorganism population (M)and the oxygen availability (O) (measured in percentage and transformed in mass per volume). The timedependent decrease of the contaminant (equation 1) is due to two different processes: biodegradation and volatilization [8, 9]. Itislimited by the asymptote representing the recalcitrant fraction of the contaminant. Microorganism population (or biomass)(equation 2) follows a logistic law incorporating a positive term proportional to contaminant content (or substrate), biomass and oxygen content, and a negative term representing inhibitory growing or massive killing episodes proportional to the square of biomass. Oxygen decreasing (equation 3) is proportional to the biomass present at any instant (t) of time. The following equationsdescribe time evolution of these three variables:

$$\frac{dC}{dt} = -k_1 M.C - k_3 C + C_f \qquad (1)$$

$$\frac{dM}{dt} = k_2.M.C.O - k_4 M^2 \qquad (2)$$

$$\frac{dO}{dt} = -k_0.M \qquad (3)$$

where:
C is contaminant concentration (mg of xylene /L of air), t is time (days), M is biomass (CFU), C_f is the remaining contaminant concentration (mg of xylene / L of air), O is the oxygen concentration (mg / L) and k_0, k_1, k_2, k_3 and k_4 are kinetics parameters.

This system of three ordinary differential equations (1), (2) and (3) was numerically integrated by a fourth order Runge-Kutta method implemented in Matlab.

3. RESULTS AND DISCUSSION

3.1. Preliminary tests

Liquid medium tests allowedto select the contaminant concentrations for the soil tests. It showed that only concentrations ranging from 3.4 up to 27.5 mg of xylene per 100 mL of inoculum were suitable for the bacterial consortium used, revealing similar extent of xylene degradation and high efficiencies of remediation [6]. For this range the biomass quantification showed that bacterial growth increases with xylene concentration. The observation of xylene biodegradation in several different tests of sequential transfers of the same enrichment cultures showed that the achieved remediation was identical in all trials but the second transfer (T2) was the fastest [6], thus it was chosen as inoculum in subsequent soil tests.

The bioremediation tests in Srγ (in flasks) exhibited identical results for all contaminant levels of xylene. The highest bacterial growth was obtained with 103 mg of xylene per kg of wet Srγ. The remediation time, considering different incubation conditions, showedthat temperature does not substantially affect the global efficiency[6].

The results for the column tests indicated identical xylene degradation comparatively with those obtained in flasks with a time span varying from 7 to 13 days. Both “Blanks” displayed similar results, which show that the endogenous microorganisms of Srγ are not able to degrade xylene [6].

The results obtained in these preliminary tests showed that the remediation period is longer for the soil (Srγ) but the final remediation efficiency was the same. The consortium developed was, therefore, able to degrade xylene in both media at the tested scale, and as such, selected for usage in the subsequent bioventing tests.

3.2. Bioventing tests

Respirometric bioventing tests produced anomalous data points as CO_2 and O_2 were analyzed continuously, forcing an a posteriori data processing. Oxygen and carbon dioxide present natural cyclical fluctuations. In order to compare the blank test to the bioventing test for each flow rate, the differences between the measured and the mean value for the blank assay was calculated for $O_2$and CO_2, as showed in the following figures (figures 2 and 3).Biodegradation isn’t visible on the results plotted on figure 2. This fact emphasizes that the flow rate was high prevailing the volatilization of

xylene. Decreasing the air flow rate to 3.6 L/hclearly pointed to the beginning of biodegradation between the seventh and eighth days.This is confirmed by oxygen consumption and carbon dioxide production computations (figure 4),integrating the differential measured variables.

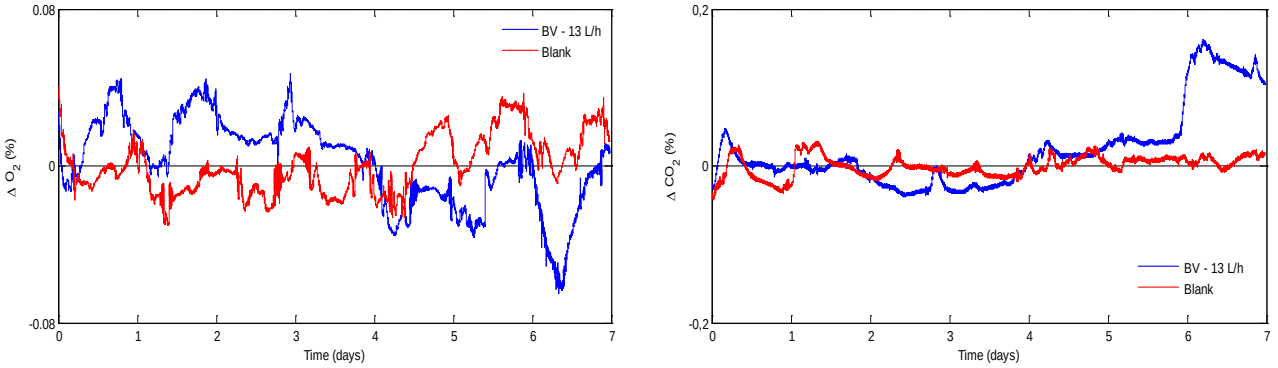

Fig. 2 – O_2 and CO_2results for bioventing test (inoculated and blank) with an air flow rate of 13 L/h. Zero corresponds to the mean value of the blank test.

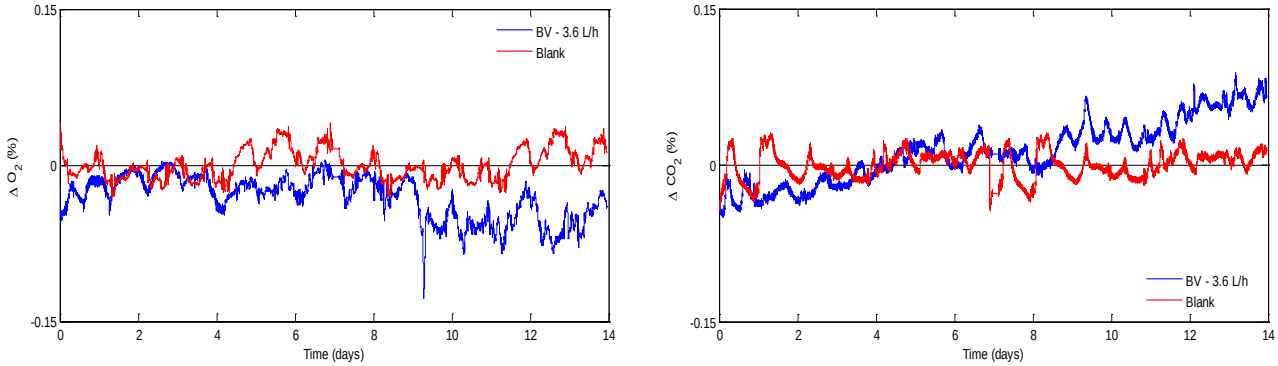

Fig. 3 – O_2 and CO_2results for bioventing test (inoculated and blank) with an air flow rate of 3.6 L/h. Zero corresponds to the mean value of the blank test.

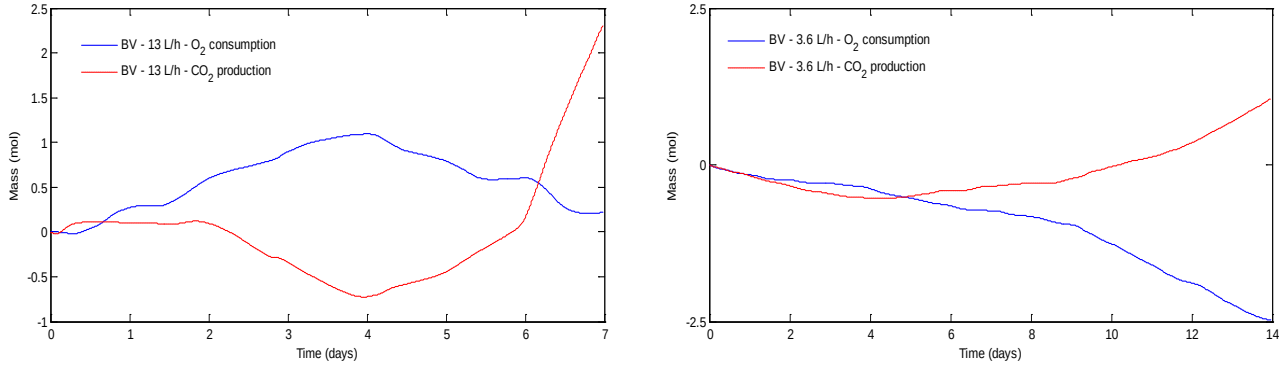

Fig. 4 – O_2 consumption and CO_2production for bioventing test with air flow rates of 13 and 3.6 L/h.

Daily measured xylene concentrations allowed to calibrate the model describedabove (figure 5). The parameters controlling xylene decrease, k_1, k_3 were lower in the bioventing test with 3.6 L/h air flow rate. In the same test $C_{f,}$ the final xylene concentration, was higher.

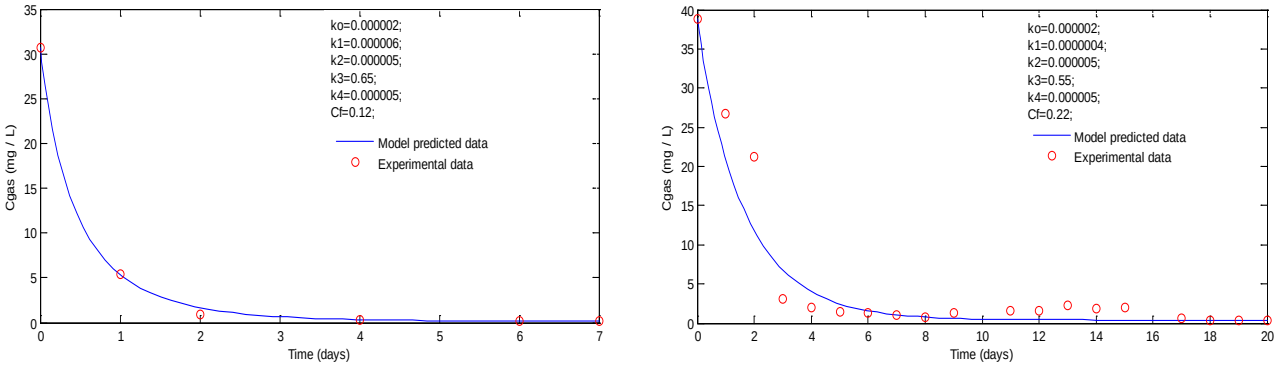

Fig. 5 – Measured *versus* model predicted xylene concentration for bioventing tests (left: 13 L/h, right: 3.6 L/h).

4. CONCLUSIONS

Air extraction flow rate is a critical issue in bioventing, as it is difficult to maintain a continuous and constant low flow rate for several days. Thedecreasingof the flow rate increases the remediation time, as it promotes the microorganism's activity, minimizing the transport of the contaminant to the atmosphere by volatilization.

The model proposed constitutes a robust tool to predict the behavior of the main output variables in bioventing. Flow rates, as well as biodegradation yield coefficient, are condensed in the kinetics parameters, which also implicitly include other relevant bioventing properties related to the soil and to the contaminant.

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REFERENCES

[1] Hu, G. J. "The effect of barometric pumping on field determined respiration rate for bioventing process". *www.containment.fsu.edu/cd/content/pdf/343.pdf*. (Retrieved 26.04.11).

[2] Diele, F., Notarnicola, F., Sgura, I., (2002) "Uniform air velocity field for a bioventing system design: some numerical results". International Journal of Engineering Science, 40, 1199–1210.

[3] Sayles, G., Leeson, A., Trizinsky, M., Rotstein, P., (1997) "Field test of nonfuel hydrocarbon bioventing in clayey-sand soil". BioremediationJournal, 1:2, 123–133.

[4] GarcíaFrutos, F.J., Escolano, O., García, S., Babín, M., Fernández, M. D., (2010) "Bioventing remediation and ecotoxicity evaluation of phenanthrene-contaminated soil", Journal of Hazardous Materials, 183, 806-813.

[5] Ostendorf, D. W., Schonberg, T. H., Hinlein, E. S., Long, S. C., (2007) "Monod kinetics for aerobic biodegradation of petroleum hydrocarbons in unsaturated soil microcosms", Environ. Sci. Technol., 41, 2343-2349.

[6] Carvalho, M., Vila, M.C., Soeiro de Carvalho, J., Domingues, V., Delerue-Matos, C.M., Oliva-Teles, M.T. and Fiúza, A. (2010) "Extensive methodology for preliminary bioventing tests – Application to a residual granitic soil contaminated with xylene". Paper in *11th International UFZ- Deltares/TNO Conference on Management of Soil, Groundwater and Sediment - ConSoil 2010*, Salzburg, Austria.Published on CD.

[7] Vila, M.C. and Fiúza, A. (2005) "Signal Treatment Applied To Environmental Biological Systems". Paper in 9th *International UFZ- Deltares/TNO Conference on Management of Soil, Groundwater and Sediment - ConSoil 2005*, Bordeaux, France. Published on CD.

[8] Vila, M.C., Nunes, O. P., Fiúza, A., (2001) "A model of biodegradation of crude oil in soils", Proceedings of the First Bioremediation Conference, Chania, Greece, 1-4.

[9] Nakhla, G., Liu, V., Bassi, A., (2006) "Kinetic modeling of aerobic biodegradation of high oil and grease rendering wastewater". Bioresource Technology, 97, 131-139.