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In Situ Biodegradation of a Hydrocarbon-Contaminated Landfill

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ABSTRACT

The anaerobic and/or low-aeration biodegradation of urban waste, contaminated by polycyclic aromatic hydrocarbon (PAH) compounds and a spill of tar products, is described. Before the industrial plant was designed, laboratory tests were carried out to determine the process feasibility and define the biodegradation rate of the pollutants. Preliminary tests on bacteria growth efficiency in aerobic and anaerobic conditions were carried out in Erlenmeyer flasks and showed interesting results in both cases. Following these tests, four different laboratory reactors were assembled to simulate waste treatment under different operating conditions. During 3 months of continuous treatment, the tar and PAH contents were measured in the waste and in the leachate and the bacteria population growth was registered. Treatment results show pollutant degradation of nearly 90%.

INTRODUCTION

The Sezzadio landfill in Italy is located in an inactive clay quarry and has a total surface area of approximately 8,000 m^2. About 75% of the quarry's total volume (about 22,000 m^3) was filled with urban waste and a quantity of toxic and hazardous wastes. Taking into account possible water lens pollution, a decontamination plan was finalized. The landfill area stratigraphy shows a stratum of covering ground with a mean thickness of approximately 1 m; below this stratum lies a waste mass of up to 5 m in depth. In the lower side the waste borders for the most part on a clay stratum, with the exception of a point where it is in direct contact with the alluvial stratum.

The first survey carried out in 1988 disclosed that the waste was contaminated by a PAH and tar products spill. Because the level of pollution differed according to zone, the first treatment design differentiated the treatment according to pollution level:

- Contamination levels greater than 5,000 mg/kg of tar products—wastes to external treatment (special landfill)
- Contamination levels between 200 and 5,000 mg/kg of tar products—in situ bioremediation
- Contamination levels lower than 200 mg/kg of tar products—no treatment.

This arrangement is related to Italian national rule 915/82 that defines 50,000 mg/kg as a limit concentration for tar products. Because waste contaminated by tar products can be stored indefinitely in a 2-B type landfill if pollutant is present at 1/100 of the limit concentration, a bioremediation treatment of waste containing between 5,000 and 200 mg/kg was postulated, with a biodegradation efficiency of 80 to 90%.

According to the request to the Authority in 1989, while waiting for final contract agreement definition, the waste landfill was temporarily secured. Initially, to limit pollution diffusion, clearly identifiable hazardous waste was disposed of and the remaining waste was capped to avoid leaching. A drainage system was implemented for surface water disposal.

Remediation began in March 1994, but after capping removal the pollution status was determined to be quite different from the contamination found in 1988. During 5 years the contaminant level had decreased and a diffusion phenomenon had occurred in the waste bulk. Thus, in situ anaerobic and low-aeration biodegradation using indigenous microorganisms was chosen as the optimal method for cleaning up the area. Preliminary tests on bacteria growth efficiency in aerobic and anaerobic conditions were carried out in Erlenmeyer flasks and showed interesting results in both cases. As a second step it was decided to perform in the laboratory a continuous test in pilot reactors to study the degradation phenomena at different operating conditions.

EXPERIMENTAL PROCEDURES AND MATERIALS

Laboratory Reactors

The wastes used in the laboratory tests were collected from the field, transferred to the laboratory, and manually mixed to eliminate larger plastic parts so as to obtain a sufficiently homogeneous substrate. For the experimental tests, four closed reactors with the following characteristics were used: gross volume, 20 L; waste content, 15 L; waste layer thickness, 20 cm; gravel layer thickness, 5 cm; wetting rate, 90 L/h; and air pumping rate, 80 L/h. A support grid was placed on the bottom of each reactor to allow leachate drainage. Each reactor was filled with the gravel and waste. A spray system was provided at the top of each reactor to keep the waste mass wet with recirculated leachate. A wetting rate was adopted at intervals of 4 h for a period of 6 min for each wetting action. Table 1 shows the process parameters adopted for each reactor; Figure 1 is a flowchart for the plant.

All the reactors were provided with recycled leachate; in three reactors aerobic conditions were improved by continually aerating the leachate in an

TABLE 1. Reactor process parameters.

PARAMETERS	Leachate recycle	Leachate aeration	Nutrients	Specific bacteria
Reactor 1 (R1)	X			
Reactor 2 (R2)	X	X		
Reactor 3 (R3)	X	X	X	
Reactor 4 (R4)	X	X	X	X

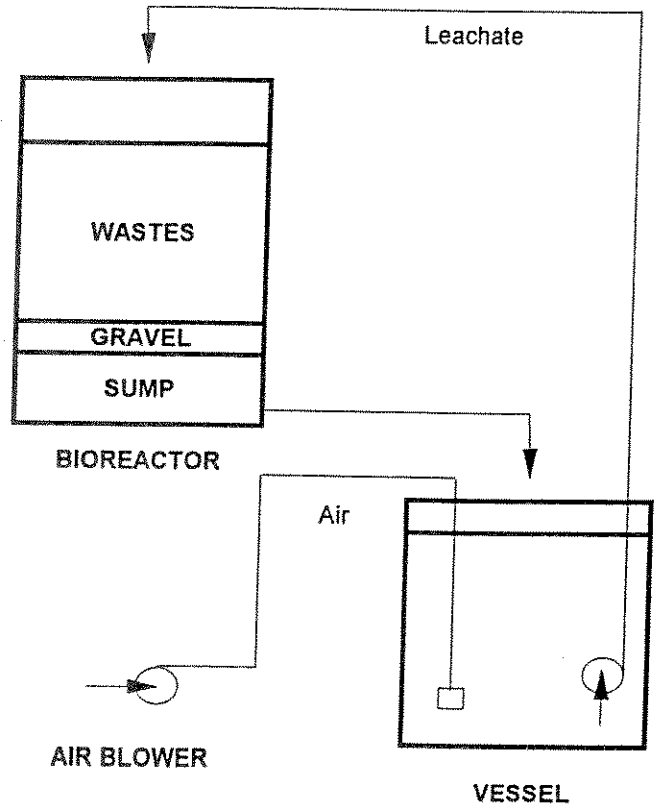

FIGURE 1. Pilot plant flowchart.

external collection vessel by means of submerged ceramic diffusers, making it possible to obtain leachate oxygen saturation. In two reactors, after 45 days of treatment, nutrients were added as NH_4NO_3 to obtain a nitrogen level of 20 mg/L. Specific hydrocarbon-degrading bacteria were added to one reactor only. The tests were carried out at a temperature of 18 to 24°C for approximately 3 months.

The hydrocarbon-degrading bacteria were furnished by a specialized firm and were representative of microorganisms from contaminated areas that are capable of degrading polluted contaminants such as hydrocarbon compounds, PAHs, etc. These bacteria belong to the genera *Pseudomonas, Acinetobacter,* and *Arthrobacter.* Because the indigenous microorganisms had not been taxonomically identified, it was not possible to distinguish them from the laboratory-selected bacteria. The commercial bacteria were added to the one reactor at the beginning of the study and at intervals of 77, 86, and 91 days from startup.

Sampling

The analytical parameters listed in Table 2 were measured to determine the rate of biodegradation. The frequency of sampling for both waste and leachate was weekly up to day 49 and every 15 days after day 49.

Considering that the startup analysis showed low concentrations of anthracene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene, only the behavior of the other aromatic compounds, listed in Table 2, was examined.

As far as the sampling method is concerned, the waste was randomly collected from each bioreactor in four subsamples at different depths into the soil using a small corer.

The four subsamples were then carefully mixed together, and a single sample was collected as representative of the bioreactor itself.

Analytical Methods

The analytical methods applied to determine the various parameters are as follows: (1) total hydrocarbon samples are extracted with Freon 113 and the organic phase is purified, concentrated, and analyzed by Fourier-transform infrared (FTIR) analyses between 3200 and 2700 cm^{-1}; (2) PAH samples are extracted with methyl chloride, dehydrated, concentrated, transferred in acetonitrile, and analyzed by high-performance liquid chromatography (HPLC) using an ultraviolet (UV) diode array and fluorimeter; (3) NO_2,NO_3, and PO_4 are analyzed through ionic chromatography; (4) total Kjeldahl N is analyzed through the Kjeldahl method; and (5) organic carbon is oxidized with potassium dichromate and titrated with ferrous iron.

RESULTS

Pollutant content reduction is reported in Figures 2 to 7. For the total hydrocarbon content, the final pollutant reduction in the four reactors was 93%

TABLE 2. Analytical parameters.

Parameters	Waste	Leachate
Total Hydrocarbons	X	X
Naphthalene	X	X
Phenanthrene	X	X
Anthracene	X	X
Fluoranthene	X	X
Benzo(a)anthracene	X	X
Chrysene	X	X
Benzo(k)fluoranthene	X	X
Benzo(a)pyrene	X	X
Benzo(ghi)perylene	X	X
Indeno(1,2,3-cd)pyrene	X	X
Microbial population		X
N	X	
C	X	
P (total)	X	
NO_2		X
NO_3		X
pH		X

(mean value). Taking into account the different reactor process conditions, the first consideration that can be made is that in reactors 2, 3, and 4 the hydrocarbon concentration was reduced to one-half of the initial concentration in 8 days. Specifically, the pollutant contents decrease from 2,297 to 414 mg/kg dry weight for R2, from 1565 to 514 mg/kg dry weight for R3, and from 2263 to 262 mg/kg dry weight for R4. In reactor 1, where the leachate was not aerated,

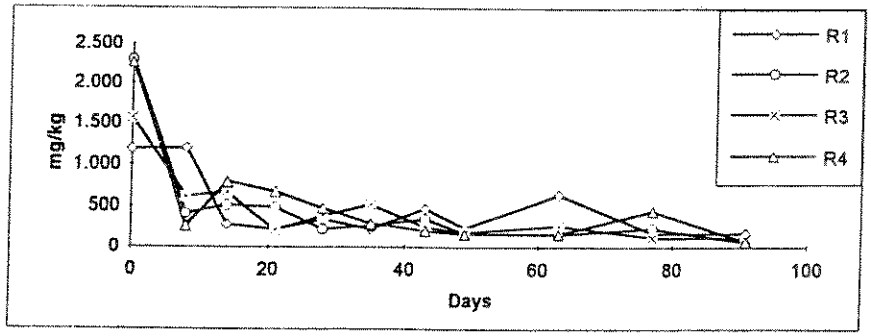

FIGURE 2. Tar products content reduction.

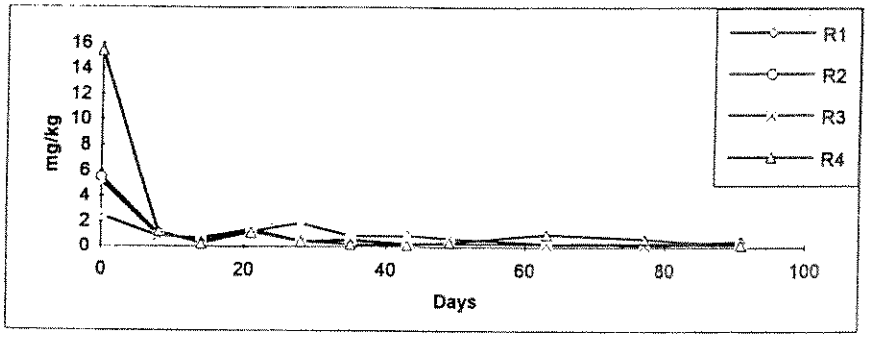

FIGURE 3. Naphthalene content reduction.

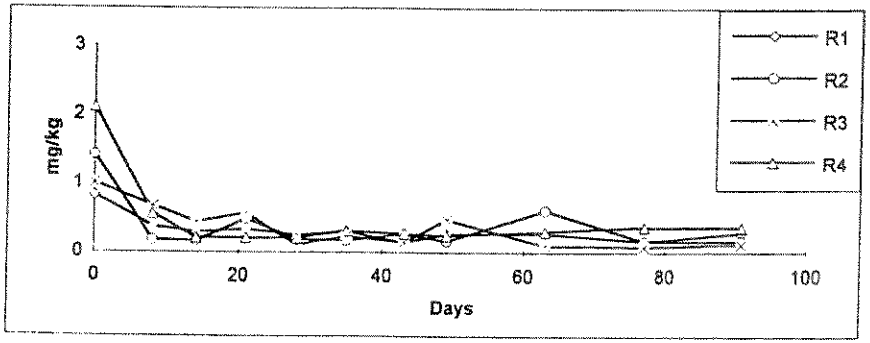

FIGURE 4. Phenanthrene content reduction.

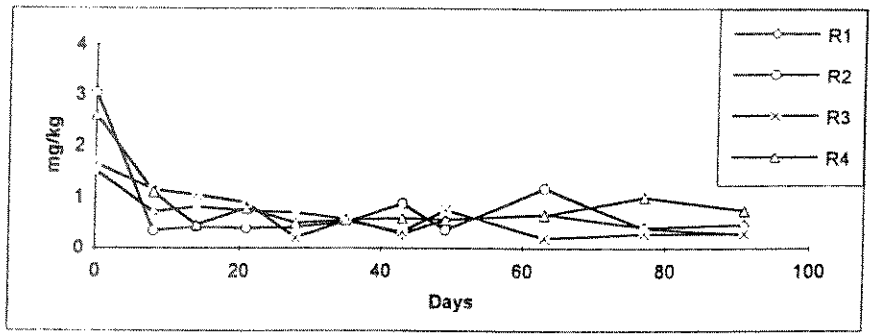

FIGURE 5. Fluoranthene content reduction.

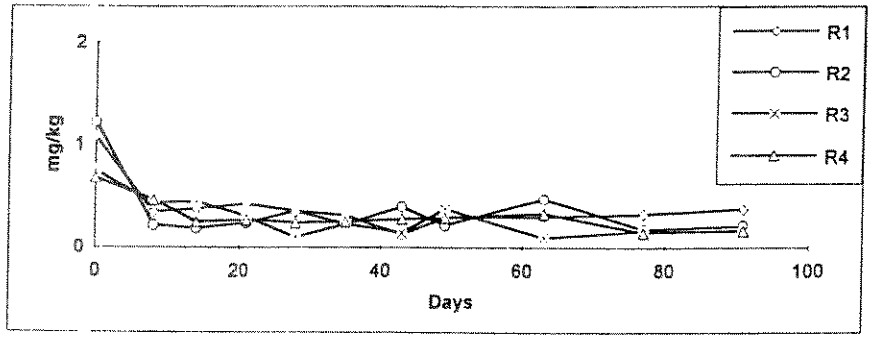

FIGURE 6. Chrysene content reduction.

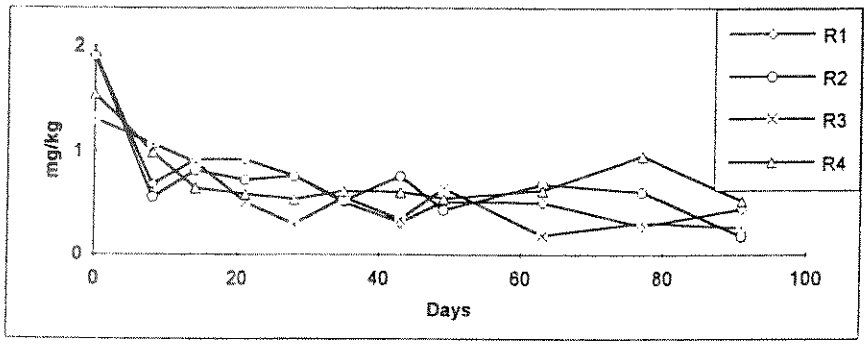

FIGURE 7. Benzopyrene(a) content reduction.

this period increased to 14 days (from 1,187 to 1,200 to 280 mg/kg dry weight). For the PAH concentration, the following percentage reductions (mean value) were registered: naphathalene, 93%; phenanthrene, 81%; fluoranthene, 74%; chrysene, 69%; benzo(a)pyrene, 78%.

The analysis of concentration versus time curves does not show substantial differences among the four reactors; in particular, the nutrients added and the specific bacteria did not improve degradation efficiency, demonstrating the efficiency of the indigenous bacteria. The bacterial activity, tested by plate count, was high during the entire treatment period, with bacteria concentrations changing from 9×10^4 cell/mL to 8×10^7 cell/mL.

The waste and leachate characteristics at the beginning of the experiment and during the treatment are reported in Tables 3 and 4. As shown in Tables 5 and 6, there is no evidence of the presence of total hydrocarbons and PAHs in the leachate and in the waste collected from deep in the soil. These results signify that autochthonous microorganisms were able to carry out the biodegrading activity.

TABLE 3. Waste parameters.

Parameters	Reactor 1		Reactor 2		Reactor 3		Reactor 4	
	T_0	T_{28}	T_0	T_{28}	T_0	T_{28}	T_0	T_{28}
pH	7.2	7.0	7.6	7.9	7.6	8.2	7.5	8.4
N Kjeldhal (mg/Kg_{SS})	2311	2100	1988	2048	1790	1954	2028	1981
C organic (% ss)	2.1	2.6	1.7	3.4	1.5	1.2	1.7	2.6
P (PO_4^{3-}) (mg/Kg_{SS})	1682	1321	1155	920	1399	666	1606	1158

TABLE 4. Leachate parameters.

Time	NO_2 (mg/L)				NO_3 (mg/L)				pH			
	P1	P2	P3	P4	P1	P2	P3	P4	P1	P2	P3	P4
T_0	2.07	2.14	2.20	2.02	4.02	4.92	6.29	4.92	7.58	8.27	8.26	8.32
T_8	1.80	2.05	2.80	1.95	4.38	2.54	3.96	2.91	7.67	8.32	8.39	8.39
T_{14}	<0.5	1.25	2.32	2.88	106	136	200	220	7.96	8.39	8.44	8.44
T_{21}	0.86	1.29	1.36	1.34	28.9	41.8	64.0	41.6	8.10	8.50	8.56	8.56
T_{28}	<0.5	<0.5	<0.5	<0.5	29.8	17.4	23.0	31.1	8.41	8.64	8.61	8.61
T_{35}	<0.5	<0.5	<0.5	-	4.77	7.52	11.51	-	8.09	8.54	8.57	-
T_{49}	<0.5	<0.5	136	148	5.15	8.56	477	577	8.00	8.56	8.49	8.53
T_{63}	<0.5	<0.5	<0.5	<0.5	6.14	6.48	148.8	106.7	-	-	-	-
T_{77}	<0.5	<0.5	<0.5	<0.5	4.87	4.77	69.6	104.4	8.32	8.65	8.48	8.48
T_{91}	<0.5	<0.5	<0.5	<0.5	5.32	-	63.8	52.3	-	-	-	-

TABLE 5. Total hydrocarbon (mg/L) and PAHs (μg/L) in the leachate.

		T14	T28	T43	T49	T63	T77	T91
R1	total HC	0.61	0.11	3.50	0.16	<0.10	0.91	<0.10
	naphthalene	0.02	0.166	-	0.06	0.08	0.03	0.02
	phenanthrene	0.05	0.10	-	0.02	0.16	0.01	<0.01
	fluoranthene	<0.01	0.04	-	<0.01	0.04	<0.01	<0.01
	chrysene	<0.01	<0.01	-	<0.01	0.01	<0.01	<0.01
	benzo(a)pyrene	<0.01	0.03	-	<0.01	0.07	<0.01	<0.01
R2	total HC	9.12	<0.10	1.80	0.09	0.11	0.12	<0.10
	naphthalene	-	-	0.05	0.10	0.05	0.05	0.05
	phenanthrene	0.04	0.019	0.016	0.04	0.12	0.02	0.01
	fluoranthene	<0.01	<0.01	<0.01	0.03	0.03	<0.01	0.01
	chrysene	<0.01	<0.01	<0.01	0.01	0.01	<0.01	<0.01
	benzo(a)pyrene	0.01	0.01	0.026	0.04	0.05	<0.01	<0.01
R3	total HC	0.61	<0.10	<0.10	0.31	0.22	0.22	<0.10
	naphthalene	-	-	0.05	0.08	0.04	0.05	0.05
	phenanthrene	0.04	<0.01	0.08	0.03	0.09	0.03	0.02
	fluoranthene	<0.01	0.01	0.02	0.01	0.01	<0.01	0.01
	chrysene	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01
	benzo(a)pyrene	<0.01	0.013	0.043	0.01	0.01	0.01	0.02
R4	total HC	0.72	0.43	<0.1	0.1	0.27	0.47	<0.1
	naphthalene	0.02	-	0.04	0.08	0.04	0.03	0.05
	phenanthrene	0.04	<0.01	0.07	0.03	0.09	0.01	<0.01
	fluoranthene	<0.01	0.02	0.01	0.02	0.02	<0.01	<0.01
	chrysene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	benzo(a)pyrene	<0.01	<0.01	0.014	0.02	<0.01	<0.01	0.01

TABLE 6. Total hydrocarbon (mg/kg$_{SS}$) and PAHs (mg/kg$_{SS}$) in the waste at T49.

	R 1		R 2		R 3		R 4	
	up	bottom	up	bottom	up	bottom	up	bottom
total HC	231	234	484	171	174	181	153	159
naphthalene	0.29	0.67	0.18	0.23	0.32	0.28	0.27	0.33
phenanthrene	0.25	0.27	0.14	0.16	0.27	0.47	0.08	0.24
fluoranthene	0.54	0.56	0.38	0.36	0.61	0.76	0.19	0.57
chrysene	0.20	0.29	0.18	0.22	0.31	0.37	0.10	0.29
benzo(a)pyrene	0.43	0.51	0.30	0.43	0.60	0.64	0.23	0.54

CONCLUSIONS

The data analysis shows that the indigenous bacteria present in the contaminated soil are capable of degrading organic compounds such as PAHs and total hydrocarbons. This might be due to the evolution of microorganisms that in the past 5 years had adapted to the presence of the pollutants (Galli 1989). Therefore, the right environmental conditions may be the only requirement for microbial degradation.

Our data are comparable to those determined by other researchers. As an example, we cite the experiment carried out by De Kreuk and Annokkèe (1988), who used a bioreactor containing semiliquid soil contaminated by other hydrocarbons and PAH continuously mixed. After 43 days of treatment at ambient temperature, naphthalene and phenanthrene were degraded 99%, fluoranthene 75%, chrysene 82%, and benzo(a)pyrene 77%. In a similar study, Werner (1991) carried out PAH biodegradation experiments using trickling filters. Field bioremediation of oil-contaminated soil also requires several months. Bourquin (1991) reported a 97% decrease of total hydrocarbons in 56 days (from 4,000 mg/kg to 100 mg/kg).

The overall experience in biodegradation of PAH and total hydrocarbons in contaminated waste indicates that biological treatment could be a valid technology for land reclamation. It is often sufficient to improve the environmental conditions to stimulate the biodegradation activity of indigenous microorganisms.

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