

In-situ bioestimulation of ethyl acetate and volatile fatty acids (VFA) in industrially polluted groundwater



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Objectives

- The present study aims to assess the potential for the in situ aerobic biostimulation of the indigenous microbial population through nutrient solution injections (Environutri) and oxygen supply by oxygen release compound (ORC) and active oxygen diffusion devices in a site polluted with ethyl acetate.
- Furthermore, the acclimation time of the indigenous contaminant degrading bacteria, was studied by traditional microbiological techniques with physicochemical parameters, in order to ensure reaching the Environmental Authorities established target values in a short period of time.

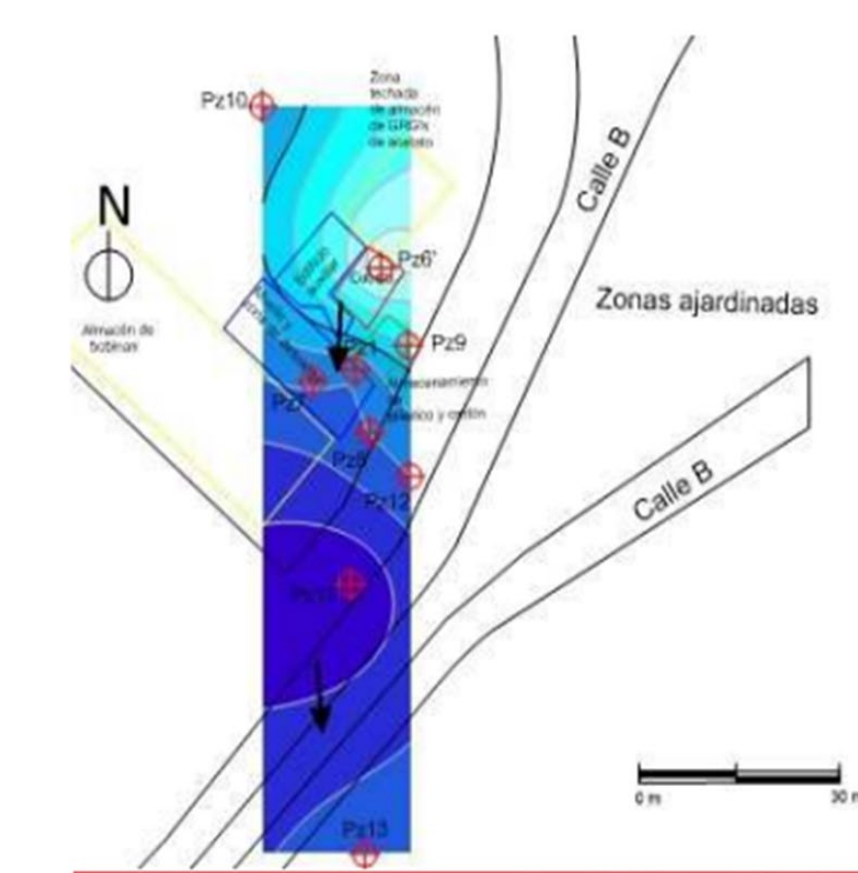


Figure 1. Groundwater contours lines (Baseline)

Background

Characterization studies in a manufacturing industry in Spain have led to the detection of an ethyl acetate plume reaching groundwater level. After the detection and decommissioning of the contamination sources related to an ethyl acetate underground storage facility, the remaining contamination plume in groundwater was reaching the factory's boundaries posing a risk to the regional aquifer and potential off-site receptors, justifying remedial actions. A total of 9 monitoring wells were installed in the area, defining a 200m² groundwater plume with a GW level between 22 and 25 meters below ground surface (bgs). Groundwater sampling resulted in the detection of ethyl acetate (range 2,900-8,100 mg/L), acetic acid (5.290 mg/l), butyric acid (bgs).

AGUAS SUBTERRÁNEAS	Unid.	Objetivo de Calidad	Pz1	Pz6'	Pz7	Pz8	Pz9	Pz10	Pz11	Pz12	Pz13	BC-A
Acetatos	Acetato de Etilo	mg/l	<1.0	1600	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Alcoholes	Etilo	mg/l	<1.0	5.7	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Acido acético	mg/l	-	1.12	5290	<1.0	<1.0	31.5	<1.0	0.66	<1.0	<1.50
	Acido láctico	mg/l	-	<0.5	<250	<0.5	<0.5	<5	<0.5	<0.5	<0.5	<0.5
Acidos grasos volátiles	Acido propiónico	mg/l	-	<0.5	<250	<0.5	<0.5	<5	<0.5	<0.5	<0.5	<0.5
	Acido	mg/l	-	<0.5	1590	<0.5	<0.5	<5	<0.5	<0.5	<0.5	<0.5
	butírico/isobutírico	mg/l	-	<0.5	<250	<0.5	<0.5	<5	<0.5	<0.5	<0.5	<0.5
	Acido valérico	mg/l	-	<0.5	<250	<0.5	<0.5	<5	<0.5	<0.5	<0.5	<0.5
Acido isovalérico	mg/l	-	<0.5	<250	<0.5	<0.5	<5	<0.5	<0.5	<0.5	<0.5	
Acido caproico	mg/l	-	<0.5	<500	<0.5	<0.5	<5	<0.5	<0.5	<0.5	<0.5	

Table 1. Analytical results of the groundwater (Baseline sampling)

Site data and Remediation approach

The remediation project was performed in a heavily ethyl acetate and volatile fatty acids (VFA)-polluted site. From the hydrogeological point of view and on a local scale, the site is located on some upper terraces of the Ebro River that are considered to be of Pleistocene age. The flow direction of groundwater in the site is from North to South. The remediation approach has considered:

In situ bioremediation

- Baseline sampling: Carried out to ascertain the environmental situation of the site
- Nutrient application: A study is carried out in piezometers to define adequate physicochemical conditions of C:N:P 100:10:1. Bioactivator solution (Environutri) was applied
- Oxygen supply: Prior to the O₂ injection, equipment was installed which consisted of equipment for the storage and mixing of nutrients, and an O₂ supply system.
- Control and monitoring of key parameters (physicochemical and microbiological).
- Final sampling: After 6 months, the equipment was stopped, with a month of rest and then sampling of the entire network was carried out.

Soil Vapor Extraction (SVE)

Installation of vapor extraction module. This installation consists in a vacuum pump, a compressed air tank, a drop separator, an ATEX transfer pump and an automation panel.

Methodology

Lab studies were performed with groundwater samples from the site (Pz-6 and Pz-9) in order to determine the potential of indigenous microbial population to degrade ethyl acetate and volatile fatty acids (VFA). Physicochemical characterization of the groundwater included de analysis of Total COD, ethyl acetate, acetic acid, ammonia (NH₄), anions (NO₃, NO₂, PO₄), electric conductivity and pH. Microbial characterization included total viable aerobic heterotrophs and ethyl acetate degraders by means of MPN.

The remedial plan for this site was conducted at the highly contaminated section of the plume, with an area of 200 m². Two emitters for pure oxygen diffusion were installed in remediation wells Pz-6 and Pz-9, coupled with the use of ORC in 3 additional wells (Pz-1, Pz-7, Pz-8,). Nutrient supplementation was applied through injections of a solution containing urea(CO(NH₂)₂) and diphosphate (K₂HPO₄) to keep optimal conditions for the microbial population.

A 6-month monitoring plan was designed to assess bioremediation performance and nutrient conditions. On-site field determination of pH, temperature, redox potential, electric conductivity and dissolved oxygen was combined with lab determination of the following parameters: contaminant concentrations (ethyl acetate, ethanol, and volatile fatty acids), DQO, nutrients (NO₃, NO₂, NH₄, PO₄) electron acceptors, MPN total heterotrophs and MNP acetate degraders.

Results: Physic-chemical and microbial monitoring

Groundwater samples within the plume (Pz-6 and Pz-9) showed peak concentrations of COD, ethyl acetate and a VFA mixture concentrated in well Pz-6. Regarding nutrient concentrations, the results showed deficits of nitrogen and phosphorus (they were both non detectable in laboratory testing) that meant that both must be supplemented to balance the C:N:P ratio in order to ensure microbiological processes, due to the high content of organic compounds. Furthermore, the microbiological characterization indicated that viable ethyl acetate degrading populations were present, although in low populations (1,2x10² cfu for Pz-6 and 1,2x10² cfu for Pz-9) due to unbalanced conditions for growth under aerobic conditions.

The bioremediation strategy enhancing aeration and nutrient supply (urea and diphosphate) led to a significant depletion of ethyl acetate in target well Pz-6 well, reaching concentrations below the detection limit (<1,0 mg/l) after 75 days. Both acetic and butyric acids showed significant reductions in the same period of 59% and 52 % respectively. The pH conditions remained stable in the monitoring wells during the field work with values in the range of 6,0 and 7,8.

In parallel with the reduction of the contamination levels in the aquifer, heterotrophic bacteria and ethyl acetate degraders showed a significant increase, especially in Pz-6, with an increase of heterotrophs from 5,10x10⁵ (T=0) to 6,8x10⁶ (T=180 days) and ethyl acetate degraders from 4,1x10² (T=0) to 6,8x10⁵ (T=180 days), with a maximum percentage of degraders at 120 days (72,73%).

Table 3. Evolution microbial population

Heterótrofos Totales (NMP/ml)	Degrad. Acetato etilo (NMP/ml)	Degradadores (%)		
Pz6 10	5.10E+05	4.10E+02	0.08	
Pz6 1168h	4.60E+03	3.10E+03	67.39	
Pz6 1360h	5.60E+03	1.80E+03	32.14	
Pz6 1720h	6.80E+03	3.10E+02	4.56	
Pz6 11080h	1.80E+04	3.10E+02	1.72	
Pz6 11440h	7.70E+04	1.80E+03	2.34	
Pz6 12160h	5.60E+06	5.60E+05	10.00	
Pz6 12880h	120	7.70E+04	5.60E+04	72.73
Pz6 13600h	150	4.10E+04	1.20E+04	29.27
Pz6 14320h	180	6.80E+06	6.80E+05	10.00

Table 2. Analytical results of the groundwater (Final sampling)

AGUAS SUBTERRÁNEAS	Unid.	Objetivo de Calidad	Pz1	Pz6'	Pz7	Pz8	Pz9	Pz10	Pz11	Pz12	Pz13	BC-A
Acetatos	Acetato de Etilo	mg/l	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Alcoholes	Etilo	mg/l	-	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Acido acético	mg/l	-	<5	3140	<5	<5	<5	<5	<5	<5	<1.0
	Acido láctico	mg/l	-	<5	<250	<5	<5	<5	<5	<0.5	<0.5	<0.5
Acidos grasos volátiles	Acido propiónico	mg/l	-	<5	<250	<5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	Acido	mg/l	-	<5	829	<5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	butírico/isobutírico	mg/l	-	<5	<250	<5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	Acido valérico	mg/l	-	<5	<250	<5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Acido isovalérico	mg/l	-	<5	<250	<5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Acido caproico	mg/l	-	<5	<250	<5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	

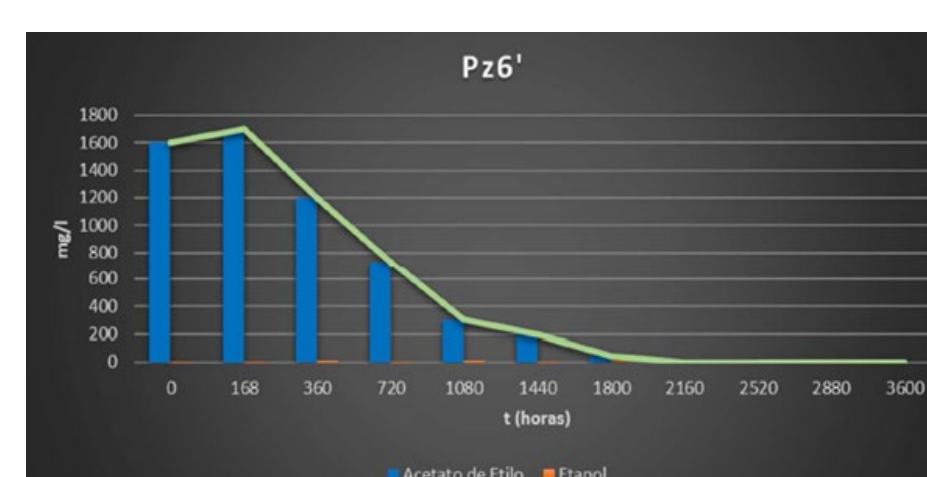


Figure 2. EtAc and EtOH Evolution in Pz6

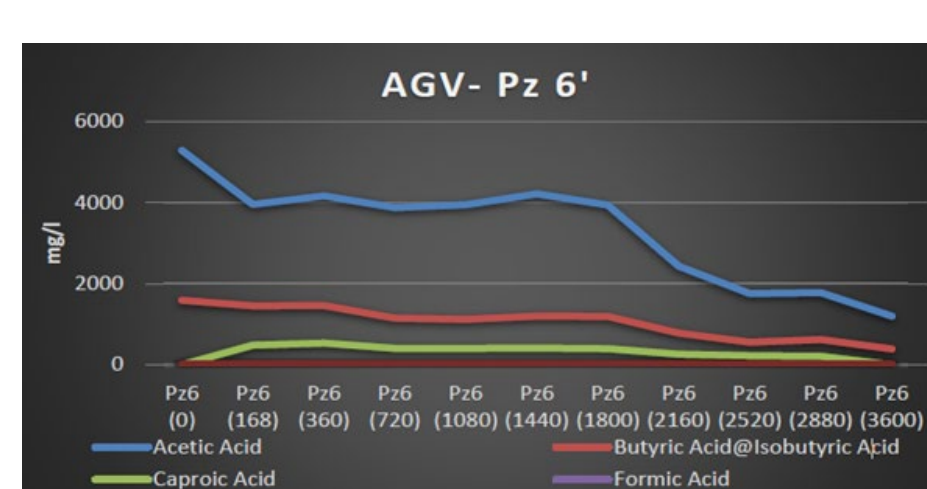


Figure 3. AGV Evolution in Pz6

Conclusions

- The study shows the effectiveness of the **biostimulation** process in achieving the clean-up standards on an industrial site contaminated mainly with a groundwater plume with ethyl acetate (range 2,900-8,100 mg/L), acetic acid (5.290 mg/l), butyric acid (1.590 mg/l).
- Initial laboratory studies showed the presence in the aquifer of indigenous microbial populations capable of degrading ethyl acetate and VFA under aerobic conditions. After the biostimulation strategy, the monitoring of the field work after 75 days indicated a significant concentration decrease for ethyl acetate and its main degradation product (ethanol) significant concentration decrease when optimal nutritional and aerobic conditions were maintained.
- The degradation of contaminants was coupled with a population increase of heterotrophic bacteria (> 10⁶ MPN/mL) and ethyl acetate degrading bacteria (> 10⁵ MPN/mL) in the monitoring wells Pz-6 and Pz-9, proving the removal of contaminants in the groundwater due to the **biostimulation** process.
- The results are indicative that the naturally present microbial populations that degrade ethyl acetate have been favourably biostimulated, starting on day 45 and reaching the maximum on day 90, in both piezometers (Pz-6 and Pz-9), even with different physicochemical conditions.