Block 6

WASTE AND SOIL TECHNOLOGIES In situ remediation technologies













SPIN® INJECTION TECHNOLOGY OR HOW TO PERFORM ACCURATE INJECTIONS FOR AN OPTIMAL REMEDIATION RESULT, EVEN IN LOW PERMEABILITY OR HETEROGENEOUS SOILS. EXPLANATIONS THROUGH THE CASE OF LINDANE

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Summary

Lindane, (γ -HCH, an isomer of HCH), widely used as an insecticide in agriculture since the 1930s, is a resistant and persistent molecule and now considered hazardous to human health and has harmful effects on the environment. As former HCH production sites are reported worldwide, lindane - and HCH in general - has become of global concern. The treatment techniques and possible degradation pathways are beginning to be well known, whether biological, under aerobic or anaerobic conditions, or chemical - oxidation (ISCO) or reduction (ISCR) - or even physical to allow the extraction of the DNAPL (Dense Non-Aqueous Phase Liquid). Most studies and experiments on the treatment of lindane are relatively well known but still largely at the laboratory scale where all conditions are controlled.

The main challenges for the treatment of HCH pollutions are the very high concentrations, the high sorption affinity to the soil organic matter and the occurrence at great depths. In-situ techniques, especially remediation by injection of reagents, seems to be a promising way to efficiently and sustainably remediate and degrade HCH into non-toxic molecules.

But a critical requirement for successful in situ soil remediation is getting reagents in contact with the pollutants to be treated, especially in case of heterogeneous and low permeability soils.

To overcome the limitations of traditional injection techniques (direct push or injection on wells), Injectis has developed and patented the SPIN® injection technique. Combining the best in situ degradation pathway, the most suitable reagent(s) and an accurate injection technique might bring a new light in HCH darkness. Before full scale application, a series of pilot tests under real field conditions could help to evaluate the feasibility of in situ degradation reactions and reagents demonstrated in the lab.

Lindane, (γ -HCH, an isomer of HCH), widely used as an insecticide in agriculture since the 1930s, is a resistant and persistent molecule. It is now considered hazardous to human health and has harmful effects on the environment, due to its generally lipophilic and bio-accumulative nature. Due to the high persistence of lindane and HCH isomers, their indiscriminate and uncontrolled release has become a global concern, with heavily HCH-contaminated sites reported worldwide. In Europe, the former lindane production sites were located especially in Germany and Spain, with Sabiñanigo as a sad reference for maybe the highest concentrations (Waclawek et al., 2019). Lindane is currently banned by the European Union since 1991. It is classified as a Persistent Organic Pollutant (POP) under the Stockholm Convention (2009) and is listed in Group 1 of the WHO (World Health Organization) list of most hazardous substances.

Faced with this global problem, extensive research has been carried out to find the best treatment techniques. Especially since the early 2000s, the number of studies on HCH isomers and its degradation potential has increased. Given the nature of lindane and the other HCH isomers, which are easily dispersed to greater depths, the remediation should best be addressed by in situ degradation or sorption processes induced by injection of reagents.

Biological degradation

Many research studies have been published focusing on the biological degradation of lindane and other HCH-isomers. Both aerobic and anaerobic bacteria have been found to be able to degrade these contaminants (Srivastava et al. 2019). The crucial reaction during the microbial degradation of halogenated organic molecules is the removal of a halogen atom. During this dechlorination step, the halogen atom - which is usually responsible for the toxic and xenobiotic properties of the chemical compound – is usually replaced by a hydrogen atom or a hydroxyl group. During aerobic biodegradation of HCH isomers, several intermediate degradation products like penta- and tetrachlorocyclohexenes (PCCH and TCCH), tri- and dichlorobenzenes (TCH and DCB), and can be mineralized completely (Srivastava et al. 2019; Lal et al., 2010). The anaerobic biodegradation of HCH-isomers usually results in the formation of benzene and chlorobenzenes, mostly monochlorobenzene (MCB) as end product (Lal et al., 2010). The complete degradation of these intermediate products to CO2 and/or methane is significantly faster under aerobic conditions, which explains their frequently observed accumulation under anaerobic conditions.

As dechlorination of halogenated compounds is more favorable under anaerobic than under aerobic conditions, the degradation of lindane and other HCH-isomers is essentially presumed to be an anaerobic process; the so-called reductive dechlorination.

Several factors influence the biodegradation rates and pathways under field conditions. The optimal biogeochemical conditions (pH, redox, T...), availability of a suitable electron donor, the presence of the degrading bacterial strains... determine the natural attenuation potential, but can be adapted by biostimulation or bio-augmentation operations. The highly lipophilic/hydrophobic properties of HCH-isomers result in the low bioavailability for biological degradation. On the other hand, the high concentrations found on lindane production and waste sites might be of toxic levels for the microbial biota.

Chemical degradation (ISCO, ISCR)

In situ chemical oxidation (ISCO) is a commonly used soil and groundwater remediation reaction to reduce the concentrations of organic pollutants in aquifer systems. ISCO reactions are induced by the injection or mixing of a chemical oxidant in the aquifer to chemically destroy the contaminant of concern to CO2, H2O and eventually salts. This chemical oxidation reaction is used to remediate a variety of organic compounds, mostly those who are resistant to natural degradation or where the naturally occurring aquifer properties are too oxidative to achieve a strong reductive degradation conditions. The oxidants that are most commonly used for in situ chemical oxidation are sodium or potassium permanganate, Fenton's reagent (a mixture of ferrous iron salts and hydrogen peroxide) and sodium or potassium persulfate. The latter might need – depending on the oxidation potential for complete oxidation of the chemical of concern - a prior activation. Lab tests have demonstrated that an ISCO treatment of soil samples highly polluted with liquid wastes from lindane was successfully accomplished using alkaline activated persulfate (García-Cervilla et al.,2019). This indicates that chemical oxidation might be one of the useful degradation reactions for the in situ treatment of HCH-pollutions. A high natural oxidant demand (NOD) and typically high pollutant concentrations at lindane-sites might necessitate high stoichiometric amounts of oxidants, making it technically and/or economically not feasible.

Chemical reduction (In situ chemical reduction, ISCR) of HCH is also well reported in scientific literature based on laboratory experiments. Given the advances and good results obtained in the treatment of soil and groundwater pollution by chemical reduction, zerovalent iron (ZVI) is the reductant with the greatest potential for use in in situ soil and groundwater remediation (Elliot et al., 2009). The metallic iron (Fe0) particles have a strong tendency to release two or three electrons

and hence to be oxidized into ferrous (Fe2+) or ferric (Fe3+) iron atoms. In presence of halogenated compounds, the electrons are used to remove the halogen from the organic compound and replace it by hydrogen. As for all chemical reactions, the finer distributed the reagent, the more reactive it is and the faster and more intense the chemical reaction. Nano-scale ZVI (nZVI) has been reported to be more efficient than microscale ZVI (mZVI). The advantage of chemical reduction with ZVI is that nearly no chlorinated intermediates are being formed. Besides the pollutant mass, the redox conditions and the concentration of electron acceptors (oxygen, nitrate and sulfate) in the aquifer strongly determine the stoichiometric amount of ZVI to be supplied to the aquifer material.

As currently frequently applied for the in situ remediation of chlorinated ethanes and ethenes in soil and groundwater, the combination of stimulated anaerobic biodegradation and chemical reduction could be applied to optimize the in situ lindane treatment (Aparicio et al., 2021).

Physical process

As HCH-isomers are characterized by a strong lipophilic nature, physical remediation techniques are also possible with sorption as the main process. Sorption of lindane and the other HCH isomers on activated carbon during pump and treat remediation of polluted groundwater is probably the best known technique. Also, for in situ soil remediation, sorption on activated carbon is a more and more used technique the last years by using colloidal activated carbon.

The sorption reaction can be used on its own or can be combined with a biological or chemical degradation process which reactivates the activated carbon by removing the sorbed pollutants.

Closing the gap between lab and field

Most of the research done so far has been carried out under controlled laboratory conditions. Besides excluding influx of (polluted) groundwater and controlling biogeochemical properties, the ideal homogeneous and thorough mixing of the soilgroundwater slurry with the added reagents might be the factor that is farthest from realistic field conditions. After all, the intensity and success rate of an in situ remediation reaction is determined by the degree of contact between the pollutant molecules and the reagent molecules within the latter's life span. Hence, in order to be able to reproduce the results obtained during lab experiments on field-scale, more effort should be done to bring reagents into close contact with the pollution in natural aquifers.

Choosing the most appropriate injection technique for the given aquifer material, is the key to close the gap between lab and field experiments. Based on the currently available information, only a limited number of pilot scale tests on in situ remediation of lindane and HCH isomers have been performed. Within the European Life-discovered project, a pilot test was performed at the HCH contaminated site – Bailín. The pilot test existed of the injection of activated persulfate in order to test the in situ chemical oxidation of lindane and its isomers. The results of another pilot test were reported in the Interreg Central project of AMIIGA. This pilot test was performed at the Jaworzno site (Poland), where a bio-reactive barrier was implemented for the removal of HCH and chlorobenzenes from the groundwater passing this barrier (B. Kończak et al., 2022).

Accurate injection technique

For in situ soil remediation, in addition to a welldefined conceptual site model (CSM) and the appropriate choice of degradation process and reagents, a critical requirement for successful remediation is getting reagents in contact with the pollutants to be treated. Moreover, an optimal and prolonged contact between reagents and pollutants will ensure the success of the remediation, regardless of the type of soil concerned. This contact will be optimal if the reagents are injected into the natural porosity of the soil.

However, when the permeability of the soil decreases, in sandy-loamy or clayey soils or when the soil is very heterogeneous with less permeable horizons, traditional injection techniques do not yield convincing results. Insufficient degradation compared to the amount of reagents injected or rebound are commonly observed problems in heterogeneous aquifers. Scientific literature continues to pretend that remediation techniques based on injection of reagents are not recommended in this kind of heterogeneous or low permeability geologies.

Faced with the problem of lack of crucial contact between reagents and pollutants, Injectis has developed and patented the SPIN® injection technique. With this technology, the injection rig is equipped with a continuous recording system for the injection pressure, flow rate and injected volumes, and generates an instantaneous measurement of the hydraulic conductivity of the geology drilled. This makes it possible to adapt the injection pressures as a function of soil texture and hence allows homogeneous injection, despite the heterogeneity of the soil. As a result, this innovative technique overcomes the limitations of traditional injection techniques (direct push or injection on wells) on which the scientific literature is still based. As this new technology allows

accurate injection of all kind of reagents in most challenging geologies, it largely closes the gap between lab experiments and pilot or full-scale remediation projects.

In this presentation we will explain in detail the concept of the SPIN® technology, the limitations of traditional techniques, their advantages, but also some of their limitations. The presentation will focus on the case of lindane and HCH isomers, the in situ reactions that might be applicable in what conditions and how the injection technique plays a crucial role to make the lab results work in the field.

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INNOVATIVE HCH IN-SITU REMEDIATION USING POLYMER GEL AS A REAGENT CARRIER – RESULTS AT FIELD SCALE

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Abstract

Assessing a sufficient contact time between injected reagents and contaminants is one major problem associated with in-situ remediation. Hence, the present work aimed at finding and evaluating at field-scale an innovative technique for the in-situ remediation of source zones contaminated by chlorinated compounds in high velocity aquifers. The field evaluation of the developed technique was done at a major French chemical plant, where the remediation of lindane contaminated source zone (\sim 200 mg/kg in soils, \sim 0.5 mg/l in groundwater (GW)) using classical techniques is hindered by the velocity of the GW (10+ m/d).

The field work relies on the injection of a jellified reagent to ensure a sufficient contact time despite the high velocity groundwater (GW). 150 m³ of viscous reactive gel was prepared and injected in 6 wells to target vadose and saturated zone (-8 to -15 m depth, GW table: 10 m). A comprehensive monitoring was conducted during and after injection (gel injectivity, 3D imaging using electrical resistivity tomography (ERT), reagent and dissolved lindane monitoring in GW, GW level ...) aiming at gaining knowledge over gel propagation, influence, and persistence in the aquifer. Finally, the technique efficiency was assessed on the comparison of lindane concentration in soil samples before and one month after the end of the injection of gel. The gel could be injected with very little pressure, and thanks to its high viscosity it propagated homogeneously in every direction, including upward and upstream. Radius of influence was higher than expected (> 8 meters), increasing the volume of soil treated beyond the 500 m³ planned. ERT proved to be a very efficient tool to monitor gel propagation and persistence in-between monitoring wells. It proved that gel was still massively present in the treated area one month after the end of the injection. GW monitoring showed lindane concentrations downstream quickly dropped below LOQ after gel was injected, because of its degradation and the reduction of local permeability in the treated volume. Finally, soil sampling 1 month after the end of the injection showed excellent lindane degradation (up to 99%) in the treated area. All results acquired show that gel is a powerful fluid to homogeneously deliver reagent, increase contact time by orders of magnitude, and reduce local permeability.

Keywords

Lindane, high velocity aquifers, jellified reagent, lindane degradation

INSTALLATION, COMMISSIONING AND OPERATION OF AN INJECTABLE *IN* SITU PERMEABLE REACTIVE BARRIER TO PREVENT THE ADVECTION OF PER-AND POLYFLUOROALKYL SUBSTANCES AT A EUROPEAN AIRPORT

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Summary

An airport in Europe is divesting an area at the edge of their site for residential housing. The historic fire training area is located in the tranche of land to be divested. At this location, aqueous film forming foams containing per- and polyfluoroalklyl substances (PFAS) had been used for many years. PFAS contamination was identified in the groundwater at levels exceeding guidelines (PFOS at 320 ng/L and PFOA up to 6,320 ng/L). A remedial options appraisal concluded the residential development precluded the use of active extraction of contamination to the surface, and the long-term costs were considered prohibitive. It was determined that a passive, *in situ* approach could match the requirements and that installing a subsurface colloidal activated carbon permeable reactive barrier should be explored to prevent further advection of the contamination.

A pilot test has been performed, completed using a 10m long barrier, with geological, hydrogeological and engineering/injection testing conducted to provide accurate information on contaminant flux zones. Direct push injection was used to emplace the colloidal activated carbon, followed by six months of monitoring.

The treatment was shown to be effective, reducing the contamination below performance criteria. Consent was given to install a 277m long full-scale barrier. Work on this started in February 2022, resulting in 7 months of installation and commissioning activities. The barrier has been warrantied for ten years to ensure ongoing efficacy and guarantee that the airport's off-site liability costs are defined and fixed.

Keywords

PFAS, In Situ, Remediation, Colloidal Activated Carbon, PRB, Injection

Background

A regional airport in Europe is divesting a large area at the edge of their site for residential housing development. The historic airport fire training area is located in the tranche of land to be divested. At this location, aqueous film forming foams (AFFF) containing per- and polyfluoroalklyl substances (PFAS) had been used for many years. During site investigation, PFAS contamination was identified in the groundwater at levels exceeding current guidelines (PFOS observed at 320 ng/L and PFOA up to 6,320 ng/L - both above the current drinking water inspectorate standard of 100 ng/L), which presented an environmental risk to the aquifer. A remedial options appraisal concluded the residential development of the site precluded the use of active extraction of contamination to the surface, and the long-term costs were considered prohibitive. It was determined that a passive, in situ approach could match the site requirements and that installing a subsurface colloidal activated carbon permeable reactive barrier (PRB) should be explored to prevent further advection of the contamination.

An area of the site was identified to complete a pilot test of the technology. Geological, hydrogeological and engineering/injection testing was conducted at this location to provide accurate and detailed information on contaminant flux zones. This was then used to design the appropriate

installation approach, including dose, spacing, depths (to intersect flux zones) and pressure.

The pilot study was completed using a 10 m long barrier comprising 14 injection locations. Direct push injection was used to emplace the colloidal activated carbon between 3-11 m BGL in the clay/ silt aquifer, targeting the identified permeable sandy lenses. Emplacement testing was completed to ensure the PRB installation had been completed as desired. This was followed by six months of validation monitoring using multi-level wells.

The treatment was shown to be effective, reducing the contamination PFOS and PFOA below performance criteria. Regulatory engagement had been maintained throughout, and planning consent was given to install a 277 m long full-scale barrier at the site. Work on this started in February 2022, resulting in 7 months of installation and commissioning activities. The barrier has been warrantied for ten years to ensure ongoing efficacy and guarantee that the airport's off-site liability costs are defined and fixed.

Aim

A description of the activities and resulting measurements of the design verification testing will be shown, as well as how these informed the pilot test approach. Validation results from the pilot will be shared and discussed. A description of the onsite practicalities of installation and commissioning of the PRB will be provided, including any issues encountered. Any full-scale installation verification or treatment validation monitoring data that is available will be presented.

Conclusion

This presentation will be of interest to environmental consultants, remediation contractors,

problem-holders and regulators. The presentation will explain the processes involved in treating PFAS contamination by which the aquifer surface is coated with a 1-2 μ m layer of activated carbon, which adsorbs PFAS from the groundwater. This will be demonstrated using the data from an active and ongoing site covering the design, investigation, application and monitoring results.

DESIGN, OPERATIONAL AND PROCEDURES FOR THE APPLICATION OF IN SITU CHEMICAL OXIDATION TREATMENTS IN FRACTURED BEDROCK AQUIFER IMPACTED BY AN OLD DNAPL

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Summary

In Situ Chemical Oxidation (ISCO) is one of the most applied in situ technologies for the remediation of soils and groundwater. It is based on applying strong oxidants under the surface able to degrade a wide variety of organic pollutants. Implementation of successful ISCO treatment depends on multiple factors such as, for example, choosing the right oxidant, distributing and achieving effective contact between the oxidant and the contaminants, understanding site specific conditions or optimizing delivery of the amendment at the right dose.

This work describes the evolution and performance over several years of the implementation of ISCO treatments as an effective remedy for the groundwater treatment in a fractured aquifer impacted by an old DNAPL (Dense Non Aqueous Phase Liquid). The DNAPL was generated in the production of lindane and other liquid wastes from distillation processes and was dumped directly upon the ground. This DNAPL is continuously feeding a dissolved plume of 1.5 km length composed by chemicals of different nature (mainly benzene, chlorobenzene and hexachlorocyclohexane, HCH). The specific hydrogeology and chemical nature of contaminants of concern (i.e. chlorinated pesticides) have been a major challenge to study the effectiveness of ISCO treatments at the site.

The study covers an initial screening for the potential application of the technique including different treatability studies to address key factors as oxidant selection, activation modes and dosages. Based on the previous studies, persulfate-based injections seemed to be the most promising option for treating target contaminants at field conditions. Over the following years it has been possible to implement this technology in pilot and large-scale field tests with high yields of contaminant removal. Here information is provided on the main results obtained, operating procedures, limitations and lessons learned in applying ISCO technologies as remediation strategy in fractured bedrock.

Keywords

In situ chemical oxidation; groundwater remediation; HCH

Introduction

Bailin's landfill is a former unlined landfill where industrial and distillation wastes generated during the manufacture of the pesticide lindane were disposed for several years. The DNAPL is composed by a wide variety of compounds [benzene, chlorobenzenes, chlorophenols, hexachlorocyclohexane (HCH), etc.], and has infiltrated into the rock impacting the aquifer underneath and creating a located source and a 1.5 km plume in a complex fractured bedrock environment that finally flows into a downstream river (Gállego river).

The bedrock formation consists of a series of interbedded vertical sandstone and mudstone layers (Figure 1) through which a complex network of fractures extends, although both lithologies have rather different hydrogeochemical characteristics. For example, sandstone layers have a greater continuity and fracture density that favor contaminant distribution downstream. Those characteristics imply that impacted groundwater mainly flows through a relatively narrow sandstone layer of 4 meters wide (M layer) that has continuity from the source to the Gállego river.

In 2014 the former landfill was dismantled, and the waste was removed and transferred to a new location. This action comprises the greatest contaminant mass reduction measure to date, however, the complete rehabilitation of the site requires the implementation of active remedial actions to remove the remaining DNAPL and control and reduce the contamination in groundwater.

In that sense, In Situ Chemical Oxidation (ISCO) has proven to be a viable alternative for the treatment of the dissolved phase plume present in the Bailín's aquifer [1]. In previous years, several laboratory and field tests have been carried out at the site using different oxidant products. Its application has allowed to study key aspects as contaminant mass removal yield, product adequacy and dosage or to identify patterns of behavior occurring in the fractured medium.



FIGURE 1. GEOLOGICAL CHARACTERISTICS OF BAILÍN SITE

This study describes the main results of the application of ISCO technology in a full-scale test carried out at the site.

Materials, methods and study area

Different commercial oxidant products have been proven mainly based on Fenton-like reactions (e.g. sodium percarbonate reagent) or persulfate chemistry [2, 3]. All the products tested were used in conjunction with an activator in order to allow contaminant degradation through direct oxidation, as well as, through free-radical mechanisms. Alkaline activated sodium persulfate has proven to be the most effective option for the destruction of the mixture of contaminants present in the aquifer. In this case, different species such as persulfate, superoxide and hydroxyl radicals are generated and responsible of carrying out contaminant oxidation through different degradation pathways [4]:

$$\begin{array}{ccc} \operatorname{Na}_2 \operatorname{S}_2 \operatorname{O}_8 & \longrightarrow & 2\operatorname{Na}^{2+} + 2\operatorname{S}_2 \operatorname{O}_8^{2-} \\ 2\operatorname{S}_2 \operatorname{O}_8^{2-} + 2\operatorname{H}_2 \operatorname{O} & \xrightarrow{\operatorname{OH}^-} & 3\operatorname{SO}_4^{2-} + \operatorname{SO}_4^{-} + \operatorname{O}_2^{-} + 4\operatorname{H}^+ \\ \operatorname{SO}_4^{--} + \operatorname{OH}^- & \longrightarrow & \operatorname{SO}_4^{--} + \operatorname{OH}^- \end{array}$$

Alkaline conditions are also key for the degradation of the recalcitrant compound HCH which instantly degrades to trichlorobenzenes at higher pH than 12 [5] as shown in Figure 2.

FIGURE 2. HYDRODECHLORINATION REACTION OF HCH TO 1,2,4-TRICHLOROBENZENE AT ALKALINE CONDITIONS

Application of the oxidant (sodium persulfate; $Na_2S_2O_8$; CAS 7775-27-1; Mw 238.10 g/mol) was performed through existing boreholes at recommended dosages between 5-20% (w:w) using an injection portable system developed in-house. Higher dosages could lead to precipitation of the products at the bottom of the boreholes and to an ineffective distribution of the oxidant in the aquifer. The test area is 450 meters long, with a maximum elevation difference of 25 m between the highest

and lowest point. Along this area, 15 boreholes have been selected as injection points to ensure contact between the oxidant and the contaminants. Injection wells were selected based on their location along the M-layer, hydraulic fracture connection, lithology, and drilling depth. In addition, a series of boreholes have been selected for monitoring and control of the development of the test all the way to the river, increasing the total length of the area influenced by the test to 700 m (Figure 3).

The injections were carried out during one month in alternative boreholes to ensure the correct distribution of the oxidant and adapting the injection volumes to the demand of each area and borehole.

For field monitoring and assessment of the test performance groundwater samples were collected at different time intervals according to standardized procedures for groundwater sampling. Some parameters such as pH, conductivity, temperature, redox potential, dissolved oxygen and oxidant concentrations were determined onsite from groundwater immediately after sampling. Also, groundwater levels, conductivity and pH were continuously monitored during injection events to ensure oxidant distribution.

All collected samples were submitted to the laboratory of the Government of Aragon (Sabiñánigo, Huesca) for the characterization of the pollutant burden. In total, 33 common pollutants routinely monitored at the site were quantified in these analyses in conjunction with major anions and cations (bicarbonates, sodium, sulfate, chlorides). Among them, the main pollutants benzene, monochlorobenzene and total HCH (which account for more than 90% of the total pollutant mass) has been analyzed. Other organic and chlorinated compounds present in lower concentrations such as chlorobenzenes and chlorophenols, among others, are also included in the analysis.

Results and discussion

Oxidant dosage

One of the key aspects for ISCO treatment is to be able to establish contact between the sufficient mass of oxidant with the contaminants present in groundwater for enough time to ensure its degradation. This consideration becomes even more important due to the particular characteristics of the Bailín aquifer, where the complex fracturing network can constrain the flow and distribution of the oxidant through the fractures. Therefore, in addition to the mass of oxidant required for the whole test, it is also important to consider the most proper concentration of the oxidant solutions.

Table 1 summarizes the organic compounds concentration determined in groundwater in one representative borehole prior to the treatment. Besides, different oxygenated compounds such as alcohols or organic acids were quantified as they can also be responsible of an important oxidant demand (even up to a 50%). Oxidant dose was determined considering the stochiometric ratio of sodium persulfate with each individual compound. At the end it was determined that 4.500 kg of sodium persulfate would be necessary to reach remediation goals considering the total area and duration of the field test.

TABLE 1. GROUNDWATER CHARACTERIZATION OFCONTAMINANT BURDEN AND OXYGENATEDCOMPOUNDS IDENTIFIED IN GROUNDWATER SAMPLES

Aromatic and chlorinated compounds						
Compound	Molecular formula	Molecular weight (g/mol)	Concentration (µg/l)			
Benzene	C6H6	78.11	8,586			
Toluene	С7Н7	92.14	ND			
Cresol	C7H8O	108.14	ND			
m-/p-Xylene	C8H10	106.16	ND			
o-Xylene	C8H10	106.16	ND			
Ethylbenzene	C8H10	106.16	ND			
Monochlorobenzene	C6H5Cl	112.56	84,786			
1,2-Dichlorobenzene	C6H4Cl2	147.01	3,119			
1,2-Dichlorobenzene	C6H4Cl3	147.01	213			
1,4-Dichlorobenzene	C6H4Cl4	147.01	2,712			
1,2,3-Trichlorobenzene	C6H3Cl3	181.45	ND			
1,2,4-Trichlorobenzene	C6H3Cl3	181.45	53			
1,3,5-Trichlorobenzene	C6H3Cl3	181.45	ND			
1,2,3,5- Tetrachlorobenzene	C6H2Cl4	215.89	ND			
1,2,4,5- Tetrachlorobenzene	C6H2Cl4	215.89	ND			
Pentachlorobenzene	C6HCl5	250.32	ND			
Hexachlorobenzene	C6C16	284.8	ND			
Phenol	C6H6O	94.11	274			
2-Chlorophenol	C6H5OCl	128.55	229			
3-Chlorophenol	C6H5OCl	128.55	1,143			
4-Chlorophenol	C6H5OCl	128.55	610			
2,6-Dichlorophenol	C6H4OCl2	163.00	5			
2,4-Dichlorophenol	C6H4OCl2	163.00	132			
2,4,6-Trichlorophenol	C6H3OCl3	197.45	802			
2,3,5,6- Tetrachlorophenol	C6H2OCl4	231.88	ND			
2,3,4,6- Tetrachlorophenol	C6H2OCl4	231.88	ND			
2,3,4,5- Tetrachlorophenol	C6H2OCl4	231.88	ND			
Pentachlorophenol	C6HOC15	266.34	1			
α-НСН	C6H6Cl6	290.81	281			
β-НСН	C6H6Cl6	290.81	80			
ү-НСН	C6H6Cl6	290.81	47			

Aromatic and chlorinated compounds						
Compound	Molecular formula	Molecular weight (g/mol)	Concentration (µg/l)			
δ-НСН	C6H6Cl6	290.81	12,508			
ε-НСН	C6H6Cl6	290.81	1,149			
		•				
Oxy	ygenated com	oounds				
Compound	Molecular formula	Molecular weight (g/ mol)	Concentration (µg/l)			
Methanol	32.04	CH4O	45,000			
Ethanol	46.07	C2H6O	ND			
i-Propanol	60.09	СЗН8О	ND			
t-Butanol	74.12	C4H8O	ND			
Isobutanol	74.12	C4H8O	ND			
n-Butanol	74.12	C4H8O	ND			
Formic acid	46.03	CH3O2	ND			
Acetic acid	60.05	C2H4O2	8,600			
Propanoic acid	74.08	C3H6O2	ND			
Butanoic acid	88.11	C4H8O2	ND			
Formaldehyde	30.03	CH2O	ND			
Acetone	58.08	СЗН6О	ND			

Injection performance

For the injection of the oxidant the total area of the field test was divided in four different sub-areas to ensure the proper distribution of the product in the saturated zone of the aquifer. Each area had different boreholes from which injections were made at the preferred depth of groundwater flow. In total, during the field works, 47,750 l and 4,500 kg of sodium persulfate were injected into the aquifer according to the dosage established before. Overall, this volume was distributed by zones, injecting 9,750 l in zone A, 7,000 l in zone B, 23,000 l in zone C and 8,000 l in zone D (see Figure 3).



FIGURE 3. PERSULFATE MASS AND VOLUME INJECTED DURING THE WHOLE FIELD TEST

Results

To evaluate the mass removal from the aquifer the reduction of initial concentrations of contaminants



FIGURE 4. EVOLUTION OF CHLOROBENZENE, HCH AND PERSULFATE CONCENTRATIONS IN THE CONTROL BOREHOLES IN THE OXIDATION TEST

in groundwater samples were estimated for boreholes located at different locations. Since the aquifer is not a closed system and there is a constant input from the upstream source, contaminant concentrations tend to recover their initial values over time.

As an example, Figure 4 shows the evolution of the concentrations of chlorobenzene and total HCH during the ISCO treatment in three selected boreholes. The concentration of persulfate is included in the secondary axis. In these graphs it can be seen that after the oxidant injections there is a reduction in the concentrations of all the compounds, reaching the minimum value during the last week of the test. As expected, in general, the most significant reductions for all compounds match with the maximum concentration of persulfate detected in each of the boreholes, which corresponded to 20, 60 and 16 g/l in P98, O1 and P127, respectively.

In general, the observed reduction in concentrations allowed the estimation of percentage elimination yields for the different analyzed compounds. The assessment of these yields also took into account the possible dilution effect produced while injecting the volume of oxidant into the aquifer. In most of the cases, benzene and chlorobenzene showed the highest removal percentages, with a maximum reduction for benzene of 94% and 93% for chlorobenzene. This fact is consistent with the faster kinetics presented by these pollutants in their reaction with persulfate.

Finally, positive removal yields of HCH isomers have been also obtained with average value close to 60% for monitoring boreholes. The observed reduction of HCH concentrations confirms that the chosen product, at an appropriate dosage, is able to induce some HCH degradation by dehydrohalogenation mechanisms.

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REMEDIATION OF HCHS-POLLUTED SOILS BY SURFACTANT-ENHANCED WASHING AND ACTIVATED PERSULFATE OXIDATION

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Summary

The existence of soils contaminated with hexachlorocyclohexanes (HCHs) represents a serious environmental problem. Their origin lies in the inadequate management of solid and liquid wastes generated during the production of lindane (γ -HCH). Solid waste consists of a mixture of HCH isomers: α -, β -, ϵ -, and δ -HCH, whose disposal pollutes surface soils. The remediation of these soils is limited by the low aqueous solubility of the pollutants (HCHs), which hinders their transfer to the aqueous phase and, therefore, their degradation. The use of surfactants, amphiphilic compounds able to reduce the water surface tension, can overcome this limitation.

This work focused on the remediation of real soil polluted with α -HCH and β -HCH (Σ HCHs = 373 mg/kg) by a coupled process: surfactant soil washing (SW) followed by the oxidation of the resulting emulsion with persulfate (PS) activated by alkali and temperature.

Three surfactants, one anionic: sodium dodecyl sulfate (SDS), and two non-ionic: Emulse-3® (E3) and Tween-80[®] (T80), were evaluated for SW experiments in batch conditions (water/soil ratio = 2, room temperature, 24 h). To optimize this process, the effect of the most representative variables: solution pH, reagents addition order and reagents concentration, has been studied. SW experiments have been carried out at neutral (7) and alkaline (>12) pH, with simultaneous (surfactant and NaOH) and sequential reagents addition (NaOH at zero time and surfactant after 4 h). The concentrations of surfactants tested were 2, 5 and 10 g/L, and the concentrations of NaOH: 0, 2.5, 4 and 13.5 g/L. The surfactants capacity to solubilize the chlorinated organic compounds (COCs) of the soil was determined through the partition coefficient (Kd), which represents the ratio between COCs concentration in soil and aqueous phases. This parameter was used to select the surfactants: the lower the Kd value, the higher the surfactant solubility capacity. The use of surfactants in SW experiments increased the solubilization of COCs from the soil to the aqueous phase, decreasing Kds, especially at alkaline conditions. Neutral pH is not suitable for the SW of these soils due to the low solubility of the pollutants (HCHs). At pH>12, HCHs hydrolyze to trichlorobenzenes (TCBs), compounds with significantly higher solubility, highly decreasing Kds. However, the non-ionic surfactant T80 showed low stability at highly alkaline conditions (NaOH = 13.5 g/L), and its use was ruled out. The higher the surfactant concentration, the higher the COCs solubilization. Considering the second step of the process (to avoid excessive unproductive consumption of PS), a value of 5 g/L of E3 and SDS and an alkali concentration of 4 g/L were chosen for further experiments. At these conditions, above 70% of the initial COCs were transferred from the soil to the emulsion with both surfactants. The second step of the remediation process was the treatment of the SW emulsions by PS activated by alkali and intensified by temperature (PS = 40 g/L, NaOH:PS = 2, and T = 40 °C). COCs conversion of 30% and 96% were achieved in 72 h when treating E3 and SDS-emulsions, respectively, highlighting the suitability of SDS for the combined process.

Keywords

HCHs, surfactants, soil remediation, soil washing, activated persulfate

Introduction

Pesticide contamination of soils resulting from agricultural processes, manufacturing, improper storage, and waste disposal has become a major environmental issue. Specifically, soil contamination with organochlorine pesticides (OCPs) is widespread worldwide due to many OCP production factories being abandoned because of the Stockholm Convention [1]. This is the case of soils contaminated with lindane (γ -hexachlorocyclohexane, γ -HCH) wastes. Lindane was among the most extensively used OCPs, generating large deposits of HCH wastes

worldwide [2]. Consequently, HCH-contaminated sites pose a threat to the environment and face an urgent need for remediation. The main limitations when treating HCHs-polluted soils are the pollutants adsorption onto the soil particles and their low solubility, limiting their transfer into the aqueous phase, where the degradation process takes mainly place [3, 4]. In this context, the use of surfactants has received increasing attention in the last few years. The on-site washing of polluted soils with surfactant solutions (which dramatically increases the solubility of these organic compounds) highlights as an interesting alternative for HCH-contaminated sites [5].

However, pollutants are not destroyed, and further treatments are required. In this sense, the resulting soil washing emulsions (SWEs) should be further treated to destroy the organic pollutants [6]. The application of persulfate (PS) as a powerful oxidant significantly increased within the last two decades. Moreover, to increase its efficiency PS can be activated by different methods by the addition of metal cations, alkali (NaOH), heat, etc.

In the soil washing (SW) step, factors such as type of surfactant and its concentration, soil type, pollutants characteristics, pH conditions, and soilto-water ratio should be considered. Concerning the oxidation treatment, to facilitate the selective pollutants oxidation, the surfactant should be relatively stable in the presence of the oxidant. In this context, the global treatment efficiency will be determined by the ability of the surfactant to solubilize the COCs and the oxidant's ability to further degrade the contaminants in the emulsion.

Most of the papers found in the literature employed lindane-spiked soils [7, 8] instead of real polluted soils, and the treatment of the resulting solutions has been rarely studied. Thus, further studies are required. In this context, the present work evaluates for the first time the washing of a real HCHspolluted soil. Three commercial surfactants, sodium dodecyl sulfate (SDS), Tween®-80 (T80), and Emulse®-3 (E3) have been evaluated. A polluted soil was collected from the old Bailín landfill close to Sabiñánigo (Spain). Firstly, the main variables of the SW process (surfactant, pH, reagents addition order, reagents concentration, liquid/soil ratio, number of washing cycles, etc.) have been studied. Secondly, the resulting SWEs have been treated by the alkaline activation of PS intensified with temperature.

Materials and Methods

Chemicals

Three commercial surfactants were used; i) E-Mulse[®]-3 (E3, EthicalChem), ii) Tween[®]-80 (T80, Sigma-Aldrich), and iii) sodium dodecyl sulfate (SDS, Sigma-Aldrich). N-hexane (Honeywell) and methanol (Fisher) have been used for pollutants extraction from the aqueous and solid phases, respectively. Sodium chloride (Sigma-Aldrich) was used to break the SDS emulsion for the chromatographic analysis. Bicyclohexyl and tetrachloroethane (Sigma-Aldrich) were used as standard internal compounds (ISTD) for pollutant quantification. Sodium persulfate (PS, Sigma-Aldrich) was used as oxidant and sodium hydroxide (Riedel-de Haën), to achieve alkaline conditions in SW and oxidation experiments. Potassium iodide (Fisher-Chemical) and sodium hydrogen carbonate (Panreac) were employed for PS quantification. Glucose (Riedel-de Haën) was used for total organic carbon (TOC) calibration. All the reagents used were of analytical grade. Solutions were prepared with ultra-pure water produced by a deionizing system (Millipore Direct-Q).

Polluted soil

A real HCH-polluted soil from the Bailín landfill (Sabiñánigo, Huesca, Spain) was collected at a depth of 0-0.3 m. The soil sample was crushed and the fraction with a particle diameter between 0.02 and 0.25 mm was selected [4, 9].

Soil washing and oxidation experiments

SW experiments were performed in 40 mL-PTFE batch reactors filled with 15 g of polluted soil and 30 mL of the aqueous solution (surfactant and/or alkali). Reactors were shaken in a rotatory agitator (LBX RR80, 80 rpm, 20°C), until reach equilibrium conditions (24 h) [9]. Firstly, the effect of the main variables of the SW process have been studied: i) surfactant (SDS, E3, and T80), pH (neutral and alkaline), reagents addition order (sequential and simultaneous), reagents concentration (C_{surf}=0-10 g/ L, $C_{\text{NaOH}}=0-13.5$ g/L), number of washing cycles, etc.). Secondly, once the most suitable surfactant and SW operating conditions have been selected, the resulting emulsions have been treated by PS activated with alkali and intensified with temperature (C_{PS} = 40 g/L, molar ratio NaOH:PS=2, 40°C). Oxidation runs were carried out in thermostated closed cylindrical glass vials (10 mL), magnetically stirred (80 rpm) and heated (TechRADLEYS heating stirrer plate).

Analytical techniques

A solid-liquid extraction was accomplished for COCs extraction from soil by mixing 15 g of soil with 30 mL of methanol in 40 mL-PTFE vials and introduced in an ultrasound bath (Power sonic 505) at 45 °C for 180 min [9]. After extraction, the sample was cooled, the organic and soil phases were separated by centrifugation (10 min, 9000 rpm, MEDTRONIC-BL-S, JP SELECTA®) and decantation. Subsequently, the organic phase was analyzed by gas chromatography (GC, Agilent 6890, Santa Clara, CA, USA) coupled with both a flame ionization detector (FID) and an electron capture detector (ECD) [3, 10]. Sample preparation for COCs quantification in the aqueous phases depends on the presence and surfactant used. Aqueous phases without surfactants were extracted by liquid-liquid extraction with hexane (1/1 mass ratio). In the case of SDS-emulsions, the emulsion was broken adding NaCl before the extraction with hexane. In emulsions containing nonionic surfactants (E3 and T80), the aqueous phase was diluted with methanol (1/10 volume ratio). After sample preparation, the corresponding organic phases obtained were analyzed by GC-FID/ECD. The initial and remanent surfactant concentration in the SWEs was quantified by TOC (Shimadzu TOC- V CSH), after subtracting the TOC corresponding to COCs in the aqueous phase. The PS concentration in the aqueous phase was determined by a spectrophotometric method [11] by adding the sample into a prepared water/KI/NaHCO₃ solution, and the iodine yellow color formed was measured at 352 nm (BOECO S-20 UV-VIS spectrophotometer). The pH was measured with a Basic 20-CRISON pH electrode.

Results and Discussion

The moles of each compound (n_i , µmol) in soil and aqueous phases were obtained considering the molar concentration obtained from GC analysis in the soil (q_i , soil, µmol/kg) and aqueous ($C_{i,aq}$, µmol/L) phases, the soil phase mass (0.015 kg), and the aqueous phase volume (0.030 L) used, respectively. The partition coefficient ($K_{d,COCs}$, L/kg) represents the ratio between the COCs (sum of all compounds present) concentration in the soil and aqueous phases at equilibrium conditions (Eq. 1). A lower value of the partition coefficient indicates greater solubilization of pollutants in the aqueous phase and, therefore, a greater solubilization capacity of the surfactant.

$$K_{d,COCs} = \frac{q_{COCs,soil}}{C_{COCs,aq}} \tag{1}$$

Polluted soil characterization

The molar distribution of pollutants in soil and aqueous phases at equilibrium conditions (in the absence of surfactants) at neutral and alkaline pH, is summarised in Table 1. At neutral pH, HCHs are the only pollutants. As can be seen, the soil was mainly polluted by α -HCH (80%) and β -HCH (13%) isomers. Low percentages (7%) of the other HCH isomers (γ -, δ -, and ϵ -HCH) were also detected. At alkaline conditions (pH>12), HCHs hydrolyze to trichlorobenzenes (TCBs) [4, 10], compounds with higher solubility. Consequently, the moles of COCs solubilized in the aqueous phase highly increased at pH>12, decreasing the partition coefficient (K_{d,COCs}) from 69.2 to 5.8 L/kg.

TABLE 1. MOLAR COCS DISTRIBUTION (MMOL) IN SOIL

COCs	Muz	n _i (µmol) H=7	n _i (μmol) pH>12		
	IVIW	Soil phase	Aqueous phase	Soil phase	Aqueous phase	
ΣTCBs	181.5	0.00	0.00	12.20	4.74	
α-HCH		15.44	0.26	0.00	0.00	
β-НСН	291	2.54	0.08	1.62	0.05	
Σγ,δ,ε- ΗCΗ		1.15	0.22	0.00	0.02	
ΣCOCs	-	19.13	0.56	13.82	4.81	

Selection of SW conditions

The selection of SW conditions: i) surfactant, ii) pH, iii) reagents addition order, iv) reagents concentration, and v) number of washing cycles has been made attending the surfactant ability to solubilize COCs from the soil to the SW emulsion. The effect of surfactant (SDS, E3, and T80) on COCs solubilization were determined at neutral (Figure 1-a) and alkaline (Figure 1-b) conditions. As shown, the surfactant addition at neutral pH improved COCs solubilization, significantly decreasing K_{d,COCs} values. At alkaline conditions (pH>12, Figure 1-b), higher COCs solubilization was obtained with E3 and SDS (K_{d,COCs}=1.8 L/kg) in comparison with the values obtained at neutral pH (K_{d,COCs}=8.0 and 12.0 L/kg for SDS and E3, respectively). In contrast, with the nonionic surfactant T80 a lower K_{d,COCs} value was obtained at neutral pH (K_{d,COCs}=6.8 L/kg) than at alkaline conditions (K_{d,COCs}=19.8 L/kg), suggesting that T80 stability decreased with the pH increase. Therefore, the effect of contacting time at pH>12 (sequential and simultaneous reagent addition) and NaOH concentration has been further analyzed.



FIGURE 1. EFFECT OF SURFACTANTS ON COCS SOLUBILIZATION AND $K_{D,COCS}$ VALUES (EQ. (1)) AT A) PH=7 AND B) PH>12. C_{SURF} =10 G L-1.

Sequential addition of reagents with E3 and SDS produced only slightly higher COCs solubilization compared to the simultaneous one (data not shown). The negative effect of NaOH on T80 stability is confirmed with the lower K_{d,COCs} values obtained in the sequential treatment. The effect of alkali concentration (2.5-13.5 g/L) on COCs distribution between soil and the aqueous phases, and the corresponding K_{d,COCs} values have been plotted in Figure 2. The decrease of NaOH concentration increases the COCs solubilized (T80), with the consequent decrease in the $K_{d,COCs}$ value. However, K_{d,COCs} value using T80 at alkaline pH is higher than those obtained with SDS and E3, discarding the T80 use. In the case of SDS and E3, the lower K_{d,COCs} values have been obtained at a C_{NaOH} of 4 g/L. Thus, a NaOH concentration of 4 g/L and simultaneous addition of reagents (alkali and surfactant) has been selected for SW with E3 and SDS.



FIGURE 2. EFFECT OF ALKALI CONCENTRATION ON COCS SOLUBILIZATION AND K_{D,COCS} VALUES (EQ. (1)) WHEN USING A) SDS, B) E3, AND C) T80. INITIAL PH>12 IN ALL RUNS. CSURF=10 G/L

The effect of surfactant (SDS and E3) concentration (2-10 g/L) was studied. The higher the surfactant concentration, the higher the COCs concentration in the emulsion, decreasing the K_{d,COCs} values (data not shown). As an excessive surfactant concentration in the subsequent oxidation stage is undesirable as it reduces the COCs availability towards radicals oxidation [12, 13], and can compete with contaminants for the radicals formed [12], a surfactant concentration of 5 g/L has been selected. Three successive SW cycles (C_{surf}=5, 2.5, and 1.25 g/L, C_{NaOH}=4, 0, and 0 g/L, respectively) were performed with SDS and E3. After the first, second and third SW cycle with SDS, 58.4%, 21.1% and 3.0% of the initial COCs in soil were solubilized to the aqueous phase, achieving a total removal of 82.5%. In the case of E3, final COCs removal was slightly higher (about 88.8%).

Oxidation of SW emulsions

The SWEs have been further treated by the alkaline activation of PS intensified by temperature [4]. SWEs were obtained from SW experiments at the optimal conditions selected (SDS and E3, $C_{surf}=5$ g/L, $C_{NaOH}=4$ g/L, 1 washing cycle) named SWE-SDS-1 and SWE-E3-1, respectively. Moreover, the SWEs resulting from the three successive SW cycles with SDS and E3: SWE-SDS-1,2,3 and SWE-E3-1,2,3 have also been treated. The measured concentration of surfactant (calculated from TOC measurements) and the COCs concentration (mainly TCBs) are summarized in Table 2.

TABLE 2. SOIL WASHING EMULSIONS (SWES) EMPLOYEDIN OXIDATION

SWE name	Surfactant	C _{surf} (g/L)	C _{COCs} (as TCBs, mg/L)
SWE-SDS-1	SDS	4.1	70.1
SWE-SDS-1,2,3	SDS	2.7	34.2
SWE-E3-1	E3	3.1	52.7
SWE-E3-1,2,3	E3	2.3	36.9

Slightly higher COCs conversion were obtained when treating SWE-E3-1,2,3 than SWE-E3-1 (Figure 3), which can be associated with the lower surfactant concentration (Table 2), as previously reported in bibliography [14]. When treating the SDS emulsions, higher COCs conversions were achieved (X_{COCs} >0.95, 72h) (Figure 3).



FIGURE 3. COCS CONVERSION WITH REACTION TIME WHEN TREATING SWES (TABLE 2). C_{PS}=40 G/L, NAOH:PS=2, T=40°C

Conclusions

At neutral pH, anionic (SDS) and nonionic (E3, T80) surfactants increase the COCs solubilization in the aqueous phase, decreasing the partition coefficient. At pH>12, higher COCs solubilization was achieved since HCHs hydrolyze to TCBs (higher solubility than the parents' pollutants). However, at basic pH, T80 stability is low, decreasing the COCs solubilization. The sequential addition of reagents resulted in slightly higher COCs solubilization. NaOH and surfactant concentration affected significantly the soil washing efficiency. The optimal SW conditions were obtained at moderate NaOH and surfactant (SDS or E3) concentrations (4 g/L and 5 g/L, respectively), extracting more than 80% of COCs from soil.

The resulting SWE (Σ TCBs=34-70 mg/L) was subsequently treated (C_{PS} =40 g/L, NaOH: PS=2, and T=40°C). COCs conversions of 30% and 96% were achieved in 72 h when treating E3 and SDSemulsions, respectively, highlighting the suitability of SDS system. Thus, the integrated SW and emulsion treatment process is a promising alternative for the remediation of real HCHspolluted soils.

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AIR SPARGING AND SOIL-VAPOR EXTRACTION PILOT TESTS IN BAILIN LANDFILL, SABIÑANIGO (HUESCA)

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Summary

Three air sparging and vapor extraction (AS/SVE) pilot tests have been performed in two different sites located in the middle area and source area of the dissolved plume of volatile organic compounds (VOCs) present in the former lindane (HCH) landfill of Bailin in Sabiñanigo, Huesca (Spain). The prime objectives of the pilot tests were testing and adapting several configurations based on AS/SVE technique in different sections of the plume, quantifying vapor mass removal rates, and evaluating a potential full-scale implementation. Selected configurations were a) AS/SVE, b) in-well air stripping (IWAS), c) AS/SVE with temperature increase, and d) AS/SVE combined with in-situ chemical oxidation (ISCO).

Since these methodologies could not be recommendable for its application in a fractured bedrock media such as the one that defines the site, the estimates made based on the Conceptual Model of the site and the knowledge of the hydrogeologic behavior in the pilot test areas suggested a good approach of these techniques for the evaluation of volatile mass elimination.

In 2018, configurations a), b) and c) were tested in a single well in he middle area of the plume. In 2019, configuration a) test was extended to four wells located in the same area, plus a configuration d) test using two additional wells for oxidant injection. Finally, in 2021, configuration a) test was performed in three wells located in the source area.

The design and built of the remediation equipment was conducted by the AECOM team members of the project related to the hydrogeological control and monitoring of the aquifer and remediation works in Bailin, which have been working on site for the last 14 years. The system was adapted to the particular conditions present in the test areas.

The execution of the tests was successful, and the results obtained were satisfactory and demonstrated the feasibility of these remediation techniques to be applied on site. Total mass removal rates were significant in all cases, although the methodology that showed the best results was AS/SVE with temperature increase. Nevertheless, mass removal rates obtained with the simplest configuration (AS/SVE) were favorable enough to avoid difficulties in logistics, since in a potential full-scale application it is recommendable to minimize the elements involved in the remediation system, as well as other matters such as work costs or sustainability.

Keywords

AS/SVE; IWAS; ISCO; temperature; VOC; Henry's law; removal rate

Methodology

In AS/SVE process, clean air is injected into the groundwater column in the test well and contaminants that are dissolved in groundwater are released from the water as vapor, that is extracted and treated. As SVE progresses, VOCcontaminated groundwater produces contaminant mass because of the disequilibrium according to Henry's law (vapor concentration equals water concentration multiplied by Henry's constant). Extracted VOC vapors are separated from condensed water in an air/water separator and contaminated vapors are treated in an off-gas treatment system before they are released to the atmosphere [1]. Since the media is made up by a solid matrix bedrock where permeability is given only by conductive fractures, which have an average thickness of 1 mm or less, all process is conducted inside the same well and the volume of air extracted is the same as that injected. In the IWAS configuration, groundwater is pumped and circulated back into the well to facilitate stripping and further vapor removal [2]. The ability to volatilize the contaminants of concern (COC) can be increased by heating the groundwater though a resistance installed at the bottom of the well [3].

During the implementation of the tests, a monitoring plan was established to monitor several parameters: i) in the groundwater, as groundwater levels, VOC concentration, temperature, pH, conductivity, redox potential and dissolved oxygen; ii) in the extracted vapor, as VOC concentration; and iii) in the AS/SVE system, as explosiveness, oxygen, CO_2 , CH_4 and HS_2 concentration, air injection and extraction rates, and air injection pressure.



FIGURE 1. SCHEMATIC PILOT TEST CONFIGURATIONS. PICTURE A) REPRESENTS THE AS/SVE PROCESS; PICTURE B) REPRESENTS THE IWAS PROCESS; AND PICTURE C) REPRESENTS THE AS/SVE PROCESS WITH TEMPERATURE INCREASE

Some parameters, as groundwater levels, temperature and conductivity, were continuously monitored with data loggers in control wells. Likewise, explosiveness, oxygen, CO_2 , CH_4 and HS_2 concentration, air injection and extraction rates, and air injection pressure were also continuously monitored thanks to the gauges installed in the AS/SVE system. Measurements could be displayed on-site on a computer and remotely using a web application. In addition, a groundwater sampling plan was performed before, during and after tests in order to determine the time in which VOCs reached a balance between volatilization and contribution of contaminant mass in the dissolved phase, achieving a constant mass removal rate which would allow a reduction in mass discharge downgradient. VOCs concentration in the extracted vapor were sampled using activated carbon (AC) tubes. COC analyzed were, in order of a b u n d a n c e i n t h e g r o u n d w a t e r, monochlorobenzene, dichlorobenzenes, benzene and trichlorobenzenes.

Execution

Pilot tests were performed in 2018 and 2019 on the so-called Zona Barrera, situated in the middle area of the dissolved plume, and in 2021 on the former HCH landfill, in a source area of the plume where residual DNAPL is present (Figure 3). Each of the tests was carried out in different wells within the performance area (Table 1).



FIGURE 2. AS/SVE SYSTEM. a) shows the portable equipment of the AS/SVE system installed on a trailer; b) shows the area in the former landfill where the third pilot test was performed; and pictures c), d) and e) show different monitoring devices used in the tests



FIGURE 3. PILOT TEST LOCATIONS.

Tests performed in 2018 and 2019 were situated in the middle area of the plume (Zona Barrera) while test performed in 2021 was situated in a source area of the plume, on the former HCH landfill. Small image below on the right shows monochlorobenzene dissolved plume distribution

Year / Area	Test	Test well	Air injection duration	Total test duration
	AS/SVE	I1	30 hours	32 hours
2018 / Zona	IWAS	I1	30 hours	40 hours
Barrera	AS/SVE + Temperature increase	I1	49 hours	73 hours
		I1	25 hours	25 hours
	AS/SVE	01	24 hours	24 hours
2019 /		I2	24 hours	24 hours
Zona Barrera		02	24 hours	24 hours
		I1		
	AS/SVE + ISCO*	P129*	24 hours	24 hours
	1500	P130*	•	
2021 /		P162	24 hours	48 hours
Former HCH	AS/SVE	P166	24 hours	48 hours
landfill		P184	24 hours	48 hours

TABLE 1. PILOT TEST CONFIGURATIONS

The evolution of the VOC vapor concentration measured with the gauges in the AS/SVE system was represented after each test (Figure 4). All graphs showed an initial rise in the recovered VOC concentration when AS/SVE was started follows by a period of stabilization. It should be notice that in the AS/SVE + ISCO pilot test some foaming issues appeared in the I1 test well in the second oxidant injection event (Figure 4, graph d) due to the amount of non-reacted oxidants that arrived at I1, where an intense bubbling was taking place.

Results and discussion

In order to assess the mass of VOCs removed from the groundwater, the rate of vapor mass removal (V_r) was estimated from the concentration of each COC analyzed with the AC tubes and the air extraction rate: $V_r = C_v \cdot Q_e$, where $C_v =$ concentration of the COC in vapor phase, M/L³ (e.g., g/volume), and Q_e = air extraction rate, L³/t (e.g., volume/h).

The properties of COCs that relate to assessing the suitability of the SVE include vapor pressure, solubility, octanol-water partition coefficient, air and water diffusivities, aerobic biodegradation rates, and mostly, Henry's law constant [4]. Henry 's constant defines the partitioning between water and air, and it is more important than vapor pressure for evaluating SVE suitability. Of the COCs evaluated, benzene has the highest Henry's constant, followed by monochlorobenzene, dichlorobenzenes and trichlorobenzenes. However, vapor mass removal rates obtained were proportional to the abundance of each COCs in the groundwater, as it can be seen in Table 2.









FIGURE 4. EVOLUTION OF VOC VAPOR CONCENTRATION RECOVERED IN 11.

Graph a) represents the evolution of recovered VOC in the 2018 test with the AS/SVE configuration; graph b) represents the evolution of recovered VOC in the 2018 test with the IWAS configuration; graph c) represents the evolution of recovered VOC in the 2018 test with the AS/SVE configuration with temperature increase; and graph d) represents the evolution of recovered VOC in the 2019 test with the AS/SVE and ISCO configuration. The red dots in each graph represent the vapor sampling events. Other actions in the system are also represented

Year / Area	Pilot test	Test well	Benzene (g/d)	Monochloro- benzene (g/d)	Sum of dichloro- benzenes (g/d)	Sum of trichloro- benzenes (g/d)	Total mass removal rate (g/d)
	AS/SVE	I1	10	101	23	4	138
2018 / Zona Barrera	IWAS	I1	16	128	35	7	186
	AS/SVE with T	I1	23	227	42	5	297
2019 / Zona Barrera		I1	18	163	30	3	215
	AS/SVE	01	16	128	26	4	174
		I2	6	71	17	2	96
		O2	14	115	21	2	153
	AS/SVE + ISCO	I1	12	107	17	2	137
2021 / Former HCH landfill	AS/SVE	P162	4	26	2	0	32
		P166	1	8	1	0	10
		P184	10	43	4	0.2	57

TABLE 2. VAPOR MASS REMOVAL RATES (G/D)

Vapor mass removal rates were higher in Zona Barrera since test wells located in the former HCH landfill presented lower initial groundwater concentrations and a limited hydraulic connectivity. In addition, all tests showed that, once the aeration began, the concentrations of COCs in the groundwater decreased significantly. Once the tests were finished, the baseline concentrations were recovered rapidly, since the contaminant mass is constantly flowing downgradient through the fractures from the dissolved plume. However, results showed that it is possible to remove contaminant mass and reduce concentrations in the dissolved phase, indicative that volatilization rate has been slightly higher than groundwater flow renewal in the test wells.

In light of the mass removal rates obtained, the application of these techniques as an alternative to eliminate contaminant mass and reduce mass flow is viable for full-scale implementation. Likewise, although higher rates could be obtained with the more complex configurations, the simplest configuration it is recommended for a full-scale application, due to all operation and maintenance work is easier, and the associated costs are lower. Furthermore, it is also the most sustainable configuration.

Finally, thanks to these results, it has been possible

to implement this technique at the site as a complementary mitigation and control measure in Zona Barrera, integrating it into a remediation system specifically designed and installed in this area.

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Summary

Sardas Landfill at Sabiñánigo, Huesca, is polluted with Dense Non-Aqueous Liquid Phases (DNAPLs) produced as liquid waste from lindane production. DNAPL is composed of a complex mixture of more than 28 chlorinated organic compounds (COCs) from Chlorobenzene to Heptachlorocyclohexane of hydrophobic character. DNAPL dumped in the landfill migrated by gravity through the subsurface and accumulated in the contact between the alluvial and marls layers (about 16 m b.g.l.). This DNAPL is a continuous source of groundwater pollution because of the slow COCs solubilization in the aqueous phase, with the associated risk for the close Gallego river and Sabiñanigo reservoir.

SEAR (Surfactant Enhanced Aquifer Remediation) technology was applied in a test cell of the Sardas Landfill (wells PS14x) since 2018 to 2021. Removal rate of residual DNAPL (in the contact between the alluvium and marls and adsorbed in the alluvial) was remarkably increased by injecting an aqueous solution of non-ionic and biodegradable surfactant (E-Mulse 3 ®). Different injection strategies have been studied, analyzing the effect of variables such as surfactant concentration (5-50 g/L), injection volumes (0.2-7 m³), injection and extraction flow rates (0.08-0.85 m³/h and 0.3-4.5 m³/h, respectively), number of injection wells (1-3), time elapsed between injection and extraction (16 h to 70 h), simultaneous or consecutive injection and extraction stages and the ratio of extracted volume to injected volume (1-8) on DNAPL recovery by solubilization or mobilization as an organic phase.

Higher DNAPL mass was recovered as a mobilized organic phase by injecting low flow rates of the surfactant solution (less than 0.3 m³/h) and higher extraction flow rates of the injected fluid (> 3 m³/h), with mass ratios of DNPAL recovered to surfactant injected higher than the unity. The interfacial tension between aqueous and DNAPL phases decreases in the surfactant presence and promotes DNAPL extraction by mobilization. Surfactant adsorption in the alluvium and surfactant absorption in the residual organic DNAPL increase when the time between injection and extraction increases. The strong surfactant adsorption is due to the clay presence in the alluvial. It causes the drop in dissolved COCs concentration (from about 2000 mg/L to 70 mg/L) in the aqueous phase over time, controlling the dispersion of contamination. If washing actions of the alluvial soil are needed, the time between injection and extraction should be reduced, being carried out almost immediately after injection. The extracted fluids were managed on-site before they were sent to the landfill wastewater treatment plant. SEAR treatment is a better choice until the residual contamination drops to a sufficient value and other methods, such as ISCO or bioremediation, could be applied.

Keywords

Lindane, DNAPL, Surfactant; alluvium; groundwater remediation, SEAR

1. Introduction

The remediation of polluted soil and groundwater by complex mixtures of hydrophobic organic contaminants (HOCs) has become an environmental challenge[1]. The accidental release or intentional dumping of liquid mixtures of HOCs into the environment produces non-aqueous phase liquids (NAPLs) that persist in the environment. The liquid wastes generated in the lindane production ($\rho=1.5$ cm3 g-1) were uncontrolled dumped in Sardas landfill. This dense organic nonaqueous liquid phase (DNAPL) is composed of a mixture of more than 28 chlorinated organic compounds (COCs) from chlorobenzene to heptachlorocyclohexane [2]. The DNAPL migrated by gravity through the subsurface until it reached the marls layer with low permeability, contaminating the alluvial. The alluvial is composed of a mixture of gravel and sand with interbedded clay and high hydraulic conductivity. The DNAPL was accumulated in the contact between the alluvial and marls layer (about 15 m b.g.l.) trapped in the soil pores or generating residual pools. The low solubilization of COCs in the aqueous phase causes the groundwater pollution, with the associated risk for the close Gallego river and Sabiñanigo reservoir [3]. The low solubility of HOCs in water limits the application of treatments such as "pump and treat" or "In Situ Chemical Oxidation" (ISCO) since those require high times to remove the contamination [4]. An effective treatment to

remediate polluted sites with DNAPLs is the

application of Surfactant Enhancement Aquifer

Remediation (SEAR) [5]. This technique injects an aqueous solution of surfactant into the contaminated area. The presence of surfactant in aqueous, organic and soil phases decreases the interfacial tension among phases, promoting both COCs solubilization and DNAPL mobilization. Then a polluted stream composed of organic compounds and the injected surfactant is extracted [5].

The first actions in the Sardas landfill cell took place in July 2018 [6]. A volume of 5.8 m³ of tap water with 13 g L⁻¹ of E3 and 130 mg L⁻¹ of a conservative tracer (bromide) was injected in an alluvial well (PS14B) at 0.6 m³ h⁻¹. The injected fluid transport was monitored in three surrounding wells (PS14D, PS14C and PS14) at 3m from PS14B. A high radial dispersion of the injected fluid was found [6]. In addition, a significant decrease of the surfactant in the solution was noticed during the time elapsed between injection and extraction due to surfactant adsorption in soil and surfactant absorption in DNAPL. The second injection of surfactant in the Sardas alluvial was in November 2020 [7]. In this case, a total of 9 m³ of an aqueous solution containing 20 g L⁻¹ of surfactant and 250 mg L-1 of bromide (conservative tracer) were injected in three alluvial wells (PS14B, PS14D and PS14E located in a triangle about 3 m side). A volume of 3 m³ was injected at each well at a flow rate of 0.3 m³ h⁻¹ for 10 h. Extracted fluids in wells PS14B, PS14C, PS14D and PS14E had a high concentration of solubilized contaminants (about 2000 mg L⁻¹), much higher than the corresponding for water saturated in DNAPL (about 70 mg L). In the SEAR tests in 2018 [6] and 2020 [7], no relevant recovery of DNAPL as an immiscible organic phase was found. This fact is explained as DNAPL is mainly located in the contact between the alluvial and the marls (about 16 m b.g.l.), and the fluids were injected and extracted at the middle of the alluvial depth (about 14.5 m b.g.l.). DNAPL recovered in 2018, and 2020 was less than 10 kg, mainly as solubilized COCs. New strategies were planned in 2021 to improve the effiency of DNAPL mass recovery for an injected surfactant mass.

In this work, E-Mulse 3® (E3) was selected as a non-ionic and biodegradable commercial since previous studied at the laboratory scale reported good results in the remediation of polluted soil with DNAPL from the Sardas alluvial [8]. E3 presented a high mass solubility ratio (MSR) of COCs at a wide range of pHs. In addition, E3 was relatively stable in the simultaneous application of oxidants and surfactants (S-ISCO) [9]. Seven injections of an aqueous emulsion of E3 were carried out in a cell test of about 9x9 m located in the Sardas Landfill (alluvial depth 3m) between April and November 2021. The influence of surfactant concentration, injection volume, injection and extraction flow rates, number of injection wells and time elapsed between injection and extraction on DNAPL recovery, solubilized or as organic phase, has been analyzed.

2. Material and Methods

2.1.Site Description

The soil profile of the polluted area can be conceptualized as a pile of four layers: i) an anthropic fill (0 to 4.8 m b.g.l); ii) a homogeneous silt layer (4.40 to 12.50 m b.g.l.); iii) gravel-sand layer (12.50 to 15.50 m b.g.l) knows as alluvial; iv) and an altered marl layer below the alluvial (>16 m b.g.l). [3, 10]. SEAR technology was applied in the Sardas Landfill test cell (wells PS14x) from 2018 to 2021. The pilot test area was selected considering the high concentration of COCs in the groundwater in well PS14, suggesting the presence of DNAPL nearby. Wells PS14x were screened 1 m in the silt layer, in the whole alluvial (about 3 m) and about 1 m in the altered marls. The DNAPL presence in the contact between graves and marls was confirmed by measuring the height of accumulated DNAPL in each piezometer.

2.2.Surfactant injection strategies in 2021

Surfactant injections were carried out between April and October 2021. The different strategies were developed in various injections and extraction events. Each event started with injecting a surfactant solution (5-50 g/L) in one or multiple piezometers at the corresponding depth (0.5 m above the marls layer or in the contact between the alluvial and the marl layer). The introduced fluids remained in contact with soil at different times depending on the event (16- 70h). After this time, the extraction from one or multiple piezometers was accomplished from the bottom of the piezometers or 0.5 m above the marl layer. The surfactant solution was injected and extracted with a flexible 1-inch PVC hose (Tiger Flex) and an electric transfer pump. Different volumes were injected (0.2-7 m³) at different injection and extraction flow rates (0.08-0.85 m³/h and 0.3-4.5 m³/h, respectively). In two events, a conservative tracer (bromide) was added in the injected fluid to study the transport of injected fluids.

During Event A, a solution of E3 (20 g/L) and bromide (260 mg/L) was injected in three piezometers (PS14B, PS14E, PS14I) at 0.30 m³/h during 8 h at 0.5 m above the marls layer. Surfactant and tracer concentrations were monitored with time in different piezometers. 31 h after the surfactant injection began, 6.52 m³ of GW was extracted was collected in the sedimentation tanks. After two weeks, a second GW extraction (2.21 m³) was carried out. In Event F the surfactant was injected in PS14B, PS14J and PS14M and simultaneously extracted in PS14I. Before surfactant injection, GW was monitored in the wells and during 40 minutes after the injection stopped. During Events B, C, D, E and G, the injection of surfactant solutions and the emulsions extraction were carried out in the same piezometer (PS5D, PS14E, PS14E, PS14I and PS14D, depending on the event), maintaining the solution at different times after the injection.

2.3.Analytical methods

The Identification of COCs in DNAPL and GW was carried out using a gas chromatograph (Agilent 6890N) coupled to a mass spectrometry detector.COCs were quantified using an Agilent 6890 GC with a flame ionization detector (FID) and an electron capture detector (ECD) [2]. The sample preparation for COCs analysis in the aqueous phase in the surfactant absence was concentrated by extraction (1:4 in the volume of nhexane). In contrast, the COCs in the emulsion samples were dissolved in methanol (1:10 in volume). The concentration of the conservative tracer (bromide anion) was determined using ionic chromatography (Metrohm 761 Compact IC), and the conductivity and pH of the samples were measured in the field with a portable pH/ conductivity unit (Model 914 pH/Conductometer, Metrohm). The surfactant concentration in the GW sample was calculated by analyzing the limonene concentration, the co-solvent in the commercial surfactant E3.

3. Results and Discussion

3.1.DNAPL characterization

DNAPL found at the piezometer bottom PS14D in September 2021 was analyzed. This organic phase is composed of ChloroBenzene (CB), DiChloroBenzene isomers (DCBs), TriChloroBenzene isomers (TCBs), Tetra ChloroBenzene isomers (TetraCBs) and PentaChlorocycloHexene (PentaCXs), HexaChlorocycloHexene (HexaCX) and HeptaChlorocycloHexene (HexaCX) and HeptaChlorocycloHexane (HeptaCX) isomers. The latter compounds are Non-Aromatics Chlorinated cyclic compounds and were lumped as NACs.

3.2.Results of injection events in 2021

The obtained results during injection events in 2021 showed that the dimensionless surfactant concentration (calculated with Eq.(1)) was always lower than the bromide concentration. In the event F about 95% of the bromide injected was recovered. On the contrary, only 12% of injected surfactant was recovered after extraction of 16 m3 of fluid in PS14I (a volume of 2.8 m³ of aqueous surfactant solution was injected). This finding inferred that the surfactant was adsorbed in the alluvial clays or the DNAPL during its transport through the subsurface [6]. The time elapsed between surfactant injection and extraction is crucial in the surfactant losses by adsorption [6].

$$F = \frac{C_j}{C_{jo}} \qquad j = \{surf, COCs\} \qquad (1)$$

In the sedimentation tanks where the extracted fluid of event F was collected, about 150 litres (225 kg) of DNAPL was recovered as an organic phase in the total GW removed. The organic phase obtained during extraction was partially in the form of small emulsion droplets that settled with time. In events B-E, G, the DNAPL recovered was mainly found as droplets sedimented with time.

The amount of DNAPL (as an organic-free phase or dissolved in the emulsion) removed with each extraction are summarized in Figure 1a. About 375 kg of DNAPL was extracted in Events A to G as an organic phase. The events that contributed more to this recovery were A and F. The mobilization of the organic phase at the contact between the alluvial and marls was enhanced by lowering the interfacial tension of this phase when surfactant was present in aqueous or organic phases, facilitating its extraction. DNAPL recovered with the extraction of GW without previous surfactant injection was negligible (data not shown).

More than 6000 m³ of aqueous phase should be extracted in a typical pump and treat treatment to recover the same mass of DNAPL extracted in the sum of events A to F. This volume is calculated considering an aqueous phase saturation in COCs of about 60 mg/L, and it is underestimated while saturation is not reached in GW. In addition, the less soluble compounds (NAC, TetraCBs and TCBs) will remain longer in the alluvial due to the lower relative solubility in GW. Regarding the strategies followed, event F was the most productive, considering the mass of surfactant injected and DNAPL recovered. In this injection event, a low flow rate was injected (as in the case of event A) but with simultaneous extraction in the well located inside the ring formed with the injection wells. Furthermore, higher extraction flow rates were used than in event A, and GW extracted was about 10 times the fluid injected (in event A the GW volume extracted was only about the volume injected).

3.3. Groundwater monitoring in 2021

The concentration of COCs in GW was compared before (April 2018) and after surfactant injection in November 2018 and before the events carried out in 2021 (Event A and F) from wells PS14, PS14B, PC14C and PS14D. The concentration of COCs in the GW are shown in Figure 2. A small effect of injection events during 2021 was noticed in the COCs concentration monitored in GW at wells PS14x.



FIGURE 1. AMOUNT OF DNAPL (AS ORGANIC PHASE AND SOLUBILIZED COCS) AND B) SURFACTANT IN THE FLUIDS EXTRACTED IN SURFACTANT INJECTION EVENTS 1 TO 7.

This fact can be explained by considering the two previous soil flushing experiments: the first in July 2018 [6] and the second in November 2020 [7]. After the surfactant injection in 2020, a remarkable COCs decrease in GW was noticed in 2021. This drop can be explained by considering that soil flushing carried out in 2018 and 2020 achieved a high removal of COCs adsorbed in the alluvial. In soil flushing carried out in 2018 and 2020, the surfactant was injected at the middle height of the alluvial, with a better distribution in the alluvial depth.



FIGURE 2. COCS CONCENTRATION IN GW BEFORE THE SURFACTANT INJECTIONS IN THE ALLUVIAL

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ISCO AND S-ISCO EVALUATION IN THE REMEDIATION OF SARDAS ALLUVIUM

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Summary

Sardas Landfill at Sabiñánigo, Huesca, is polluted with Dense Non-Aqueous Liquid Phases (DNAPLs) produced as liquid waste from lindane production. DNAPL dumped in the landfill migrated by gravity through the subsurface, being adsorbed in the alluvial soil, which is the permeable layer, contaminating the groundwater (GW) flow, with the associated risk for the Gallego river and Sabiñanigo reservoir in the vicinity.

In Situ Chemical Oxidation (ISCO) and ISCO enhanced by Surfactant addition (S-ISCO) have been studied at the lab scale using real polluted soils from the Sardas Alluvium. Soils corresponding to the alluvial layer were dried, sieved and characterized, with contamination levels of up to 9622 mg COCs/kg soil. The oxidant selected was Persulfate (PS) activated by alkali. Alkaline pH transformed the most toxic and chlorinated compounds (Hexa- and HeptaCHs) into less toxic and biodegradable compounds (Tri- and TetraCBs, respectively). The surfactant selected was a non-ionic and biodegradable one, E-Mulse[®] 3 (E3), commercialized by EthicalChem.

Experiments were carried out at batch and column scales with different oxidant and surfactant concentrations. A moderate improvement was found when surfactants and oxidants were added simultaneously due to the higher solubilization of COCs to the aqueous phase in the surfactant presence. After 8 Pore Volumes (PS 210 mM and molar PS/NaOH ratio 1:1) were added, more than 95% of COCs in soil (3680 mg/kg) were removed with ISCO and S-ISCO to non-toxic compound, confirmed by results of Microtox[®] bioassay.

Keywords

Lindane, DNAPL, ISCO, S-ISCO, Sardas Alluvial, Microtox®

1. Introduction

Lindane, the γ isomer of hexachlorocyclohexane (HCH), was produced and commercialized worldwide as a pesticide during the second half of the 20th century. However, the production process of lindane is highly inefficient and results in a large amount of waste. Moreover, lindane and byproducts are dangerous to human health and the environment, banned by the Stockholm convention. The dumping of wastes from lindane production resulted in many contamination sites requiring urgent remedial actions. This is the case for Sardas landfill (Sabiñánigo, Spain), where the company INQUINOSA dumped more than 140000 tonnes of HCH-waste. Liquid wastes from lindane production were a DNAPL containing chlorobenzenes (mono, di, tri and tetra) and different isomers of nonaromatic compounds (Penta and hexachlorocyclohexenes and Hexa and Hepta chlorocyclohexanes) [1]. These COCs are hydrophobic and denser then water. DNAPL migrated through the subsoil below the water table until it encountered impermeable layers. On its migration, DNAPL was adsorbed and trapped in the pores of the soil.

ISCO has been demonstrated to be an efficient and effective technique for removing COCs from contaminated sites over the last decade [2]. However, because of the low solubilities in water of COCs composing DNAPL, the simultaneous injection of surfactant and oxidant (S-ISCO) could reduce the remediation times. The surfactant injection promotes the solubilization of COCs from the soil to the aqueous phase, increasing the oxidation rate of pollutants in the liquid phase. S-ISCO was successfully applied in different polluted sites [3]. A surfactant is an organic molecule that competes with the organic pollutant for the oxidant, and good surfactant stability is required to avoid unproductive surfactant and oxidant consumption. Moreover, adding oxidants and surfactants to the subsoil could introduce toxicity that should be considered in further bioremediation treatments. In this work, remediation by ISCO and S-ISCO of real and highly polluted soil samples obtained at the Sardas landfill subsoil has been studied. Surfactant selected is a commercial, non-ionic and biodegradable surfactant, E-Mulse® 3 (E3) and the oxidant was persulfate activated by alkali, both selected in previous works [4]. The acute toxicity of the initial and polluted soil after in situ treatments and non-polluted soil has been determined by the Microtox® bioassay [5], giving practical information for a full-scale application.

2. Materials and methods

2.1. Soil samples

EMGRISA supplied the soil samples. These samples were taken from a depth of 15 - 16 m b.g.l in Sardas landfill. This depth corresponds to the layer where the groundwater flows and contains mainly gravels with some clay. Two soils, B1 and B2, with different pollutant concentrations were used. Both soils contain a significant concentration of carbonates (>40 %). Soil samples were dried at room temperature and sieved (0.25-2 mm of particle size). Polluted soil (B2) has a concentration of 3680 mg/kg of a mixture of 28 Chlorinated Organic Compounds (COCs). Soil used as a reference (B1) had a low pollutant concentration (20.4 mg/kg).

2.2. Chemicals

The oxidant selected for ISCO and S-ISCO experiments was sodium persulfate (PS) activated by alkali (NaOH). The alkaline activation of PS produces hydroxyl radicals that allow the removal of the COCs in the contaminated soil samples. The surfactant used was E-Mulse® 3®, E3, from EthicalChem. E3 is a polyethoxylated non-ionic surfactant selected in previous works [6]. E3 has relatively high stability with the oxidant and high COCs desorption capacity. For the analysis of the acute toxicity, the Microtox® bioassay was selected with the bacterial reagent (Vibrio fischeri, strain NRRL B-11177) and the reconstituent solution, both provided by ModernWater Inc.

2.3. ISCO and S-ISCO experiments

A total of 6 glass columns were built (two for ISCO and four for S-ISCO). Each column (diameter 3 cm and length 4.7 cm) contains 50 g of contaminated soil with a total pore volume (PV) of approximately 10 ml. Once the columns were assembled, one PV of milli-Q water was injected (0.3 ml/min) to obtain pore water saturation. Then, a new PV of an alkaline solution with NaOH (210 mM) was injected. After 24 h, the injection was repeated with the alkaline solution.

After the alkaline pretreatment, the ISCO and S-ISCO treatments were applied. Four or eight Pore Volumes, PVs (about 10 mL each) with the reagents were injected (0.3 mL/min) at each column. The effluent flushed from the column with each PV injected was analysed and stored. Afterwards, the column was disassembled, dried, and the soil analyzed.

In ISCO treatment, each PV contains a solution with 210 mM of PS and NaOH. In S-ISCO-5, each PV contains the same PS and NaOH concentration and 5 g/L of E3. In S-ISCO-10, the Pv injected

contains the same PS and NaOH concentration and 10 g/L of E3.

Each PV remains about 80 -96 h in the column before the next Pv is injected. In those columns with 8 Pv of reagents injected, the soil column was washed with 8 PVs of milli-Q water, simulating groundwater flow, before the column disassembled in those columns. In those columns where only 4 PVs are injected, the column was not washed with water before disassembling and analysis.

2.4. Analysis

COCs in soil were analyzed by gas chromatography with flame ionization and electron capture detectors (GC-FID/ECD) after extraction with MeOH by ETHOS ONE microwave (Milestone) following the EPA method 3546. COCs in aqueous phases without surfactant were extracted with hexane 1:1. In the presence of E3, the aqueous sample was diluted with MeOH 1:10 before the analysis (GC-FID/ECD). PS was analyzed in the aqueous phase by potentiometric titration (Metrohm, Tiamo 2.3). A Basic 20-CRISON pH electrode analyzed pH.

The Microtox[®] Basic Test measured the toxicity of aqueous phases. Toxicity Units of the Aqueous phase (TUs) are obtained following Eq. (1) [7]

$$TUs = \frac{100}{IC_{50}(\%)} \tag{1}$$

where IC_{50} is the dilution ratio of the sample producing a 50% bioluminescence inhibition.

The effective nominal concentration of a compound $(EC_{50}, \text{ mg/L})$ is the concentration value in The aqueous phase yielded a 50% bioluminescence inhibition. The *TUs* of a mixture can be estimated following Eq. (2) [7]:

$$TUs = \sum \frac{C_j}{EC_{50_j}} \tag{2}$$

where C_j is the concentration of each compound in the aqueous phase (mg/L).

The soil toxicity was evaluated by two methods [8]: i) The modified Basic Solid-Phase Test (mBSPT) by analyzing the light inhibition of an aqueous soil suspension. The EC_{50} (g/L) indicates the soil concentration in the aqueous solution producing a 50% bioluminescence inhibition.

ii) The adapted Organic Solvent Sample Solubilization Test (aOSSST). When hydrophobic compounds contaminate soils, the low solubility in water limits their bioavailability for toxicity analysis. Therefore, the toxicity of an organic extract is analyzed. Further information about the aOSSST analysis can be found elsewhere [8].

3. Results

3.1. Removal of COCs in ISCO and S-ISCO treatments

After alkaline pretreatment, the contaminated soil mainly consists of trichlorobenzenes (TCBs) and Tetrachlorobenzenes (TetraCBs). Pentacyclohexenes (PentaCXs), and Hexachlorocyclohexanes (HCHs), are transformed into TCBs, and Hexachlorocyclohexenes (HexaCXs) and Heptachlorocyclohexanes (HeptaCHs) are converted to TetraCBs [9].

Figure 1 shows the COCs elimination from the soil in ISCO, S-ISCO-5 and S-ISCO-10 treatments after injection of 4 or 8 PVs. To calculate COCs removal, the analysis of soil phases and collected PVs was considered. The S-ISCO treatments showed a higher COCs remotion than ISCO after 4 PVs injections, and surfactant addition can explain these results. E3 improves the desorption of COCs to the aqueous phase. This is congruent with the higher COC removal of S-ISCO-10 treatment than S-ISCO-5 (higher E3 concentration in the injections of S-ISCO-10). However, despite the better results with S-ISCO, ISCO achieves significant conversions because the oxidation reaction also occurs on the soil surface [9].



FIGURE 1. REMOVAL OF COCS (%) FROM THE SOIL PHASE AFTER INJECTION OF 4 AND 8 PVS FOR ISCO, S-ISCO-5 AND S-ISCO-10 TREATMENTS

3.2. Toxicity evaluation

The toxicity of the soil samples has been analyzed before and after the treatments (ISCO and S-ISCOs after 8 PVs injected) by two methods (mBSPT and aOSSST) [8]. The toxicity of soil samples by the mBSPT method is shown in Figure 2 and by the aOSSST in Figure 3.

As shown, the higher the concentration of COCs, the higher the soil toxicity, and this difference is more marked when using the aOSSST method. As can be seen, the soil toxicity after the oxidation treatments, with and without surfactants, was considerably reduced. Furthermore, similar toxicity values are obtained after injections of 8 PVs due to the high COCs removal (> 93 %) in both ISCO and S-ISCO. Toxicity of soils after ISCO and S-ISCO treatment was very similar to the value of the unpolluted soil B1 (low concentration of COCs). The presence of surfactant E3 under the conditions studied did not increase the toxicity of treated soils.

The toxicity of the aqueous phase of PVs collected was very low at the final treatment time, and no undetected compounds contributed to toxicity.



FIGURE 2. SOIL TOXICITY (1/EC50, MICROTOX® MBSPT) OF THE UNPOLLUTED, POLLUTED AND TREATED SOILS



FIGURE 3. SOIL ORGANIC EXTRACT TOXICITY (TUS SOEDIL, MICROTOX® AOSSST) (A) AND COCS CONCENTRATION (MG/KG) (EXPERIMENTAL DATA: PLAIN, ESTIMATIONS: DASHED); (B) OF THE UNPOLLUTED, POLLUTED AND TREATED SOILS

4. Conclusions

S-ISCO technology showed higher COCs conversions than ISCO in batch and column experiments. Higher E3 concentration in the aqueous phase caused higher COCs desorption to the aqueous phase and faster oxidation rates. However, the loss of surfactant due to adsorption should be considered in the S-ISCO application. Moreover, the oxidant competition between COCs and E3 causes oxidant consumption and the loss of surfactant.

Oxidation by PS activated by alkali showed a considerable decrease in the toxicity of soil treated, with EC_{50} values equivalent to those observed for a non-polluted soil sample. Furthermore, surfactant E3 did not cause an increase in toxicity under the conditions studied. Therefore, any of the proposed in situ treatments (ISCO or S-ISCO, with alkaline activation of PS) is suitable for large-scale application, as they lead to a high reduction of

COCs (>90%) and restore the soil to its original toxicity value.

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DESIGN AND VALIDATION OF ELECTROKINETIC TECHNIQUES FOR THE REMEDIATION OF THE ALLUVIAL SILT OF THE SARDAS LANDFILL (SABIÑANIGO) CONTAMINATED WITH HCHS

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Summary

In this work, electrokinetic soil remediation techniques will be evaluated for the treatment of COCs polluted silts. Electrokinetic treatment is suitable for working at great depths and in poorly permeable media and it is based on the application of an electric field among electrodes sited in the soil to induce different transport mechanisms such as electroosmosis, electromigration, electrophoresis as well as volatilization to gas phase due to the heating of the soil. Additionally, the electrolysis of water can take place on the electrolyte wells, leading to the generation of acid and basic fronts which may cause side processes such as dehalogenation. The present study ranges from laboratory scale tests (1 kg of soil) through bench scale tests (5 kg of soil) to real on-site test at the Sardas landfill (full scale). Additionally, a conceptual 1-D model has been developed to validate the experimental results and to determine the extent of the pollutant transport mechanisms from the soil to the liquid and gas phases. Results point out that during the treatment, the resulting intensity decreases due to the silt undergoes the depletion of ions. Electro-osmotic fluxes are very low and do not depend importantly on temperature and other operation variables, and the amounts of pollutants collected in electrolyte wells is always negligible. Regarding the effect of the electric field applied, it influences on the final speciation of pollutants because of the higher extension of the basic and acidic fronts that promote the dehalogenation of HCHs. Iron electrodes and the use of SDS solutions (as flushing fluid) also allow to attend a more intense dehalogenation of COCs. There is an important volatilization of the COCs but effective dragging of pollutants by gas is not very efficient as the amount of pollutants collected in the GAC adsorption column is very limited. However, the grasshopper effect may explain the depletion of these pollutants from soil and their accumulation in the walls and pipes of the mock-ups.

Keywords

Electrokinetic soil remediation; HCHs dehalogenation; Pollutants volatilization and subsequently condensation

Introduction

Development of efficient technologies for the remediation of soils polluted with hazardous species is becoming a priority for which a great effort is being made in the recent years. A particular case of interest is the remediation of soils polluted with synthetic pesticides because of the great impact that this chemical may have on the environment. In this context, hexachlorocyclohexane (HCH) is one of the organochlorine pesticides that has been widely used in recent decades, where widespread pollution has been reported in all spheres of the environment, such as in subsurface water, soil and air. Factors such as volatility, solubility and the long-range atmospheric transport capacity of the HCH isomers further facilitate their entry into the most varied ecosystems. Thus, the correct management and remediation of areas contaminated by HCH represents an urgent demand.

In electrokinetic treatment, the application of electric fields between anodes and cathodes placed into the polluted soil produced the transport of pollutants by different mechanisms, including dragging by the electro-osmotic flux, electrophoresis (when flushing fluids containing surfactants are used) and electromigration (when the pollutants contain ionic groups)[1-4]. However, going to large scale applications is not an easy task because of the complexity of controlling mechanism. In fact, the EK transport is not the most important process and ohmic heating may become the primary removal mechanisms in full application, in which the organics are volatilized and then, they should be adequately managed [5, 6].

This work tries to get more information about the mobility of chlorinated organic compounds (COC) in real ageing polluted silts and to determine if electrochemically assisted remediation technologies can be suitable for the removal of highly polluted dump

Materials and methods

For this study, unaltered soil samples were taken from 2 boreholes at a dept of 9.5-12 m where the silt contaminated is placed. These samples were extracted from the soil directly into a PVC pipe to maintain the natural conditions and distribution of the contaminants in the soil. Two sets of experiments have been carried out following a TRL4 and TRL5 (Technology Readiness Levels). The first one consists of introducing a column of soil contaminated with HCHs into a matrix of clean silty soil in a completely airtight methacrylate box (1D mock-up, Figure 1a). The 1D mock-ups are divided into 3 compartments: two at the ends corresponding to the electrolytic wells, where the electrodes, anode and cathode, and the rinsing fluid are housed. Pieces of 3x3x10cm were cut from the unaltered samples and mounted on the model in different positions: in the centre and near the anode or cathode compartments. The possible gas phase generated in the process was led into an activated carbon column by introducing pulsed air from the opposite end at a given frequency. The second series of tests was carried out using directly the unaltered samples (TRL5) shown in Figure 1b and using standard PVC materials for the construction of the experimental setup consisting of two electrode compartments, anode and cathode, two reservoir tanks for adding and collecting water with respect to the electroosmotic flow going from the anode to the cathode. In addition, in order to work as close as possible to real conditions, the rinsing fluid was local mains water. The individual PVC columns were approximately 50 cm long and 9 cm in diameter.



FIGURE 1. EXPERIMENTAL SET-UPS; A) 1D-MOCK-UP B) UNALTERED SOIL MOCK-UP

Results and Conclusions

To evaluate the treatability of the silty soil contaminated with industrial water from lindane production by electrokinetic remediation, a constant voltage was applied (1V/cm) in each test and the evolution of the intensity, the electroosmotic flux and the concentration of inorganic and organic compounds was monitored. In all cases, the intensity increases at the beginning of the experimental time until it reaches a maximum value and then decreases and remains close to zero. This decrease is related with the rapid mobilization of ionic species in the first days, that leads to a low ionic conductivity. This fact also influences on the electroosmotic flow which seems to vary around 0.5-1 cm/d.

The transport of pollutants by electroosmotic flow is low, it does not depend on the level of contamination of the silt, but on the intensity of the current. In any case, the amount of pollutants collected in the wells is minimal. The addition of SDS to the flushing fluid does not seem to contribute to improve the pollutant mobilization. Conversely, significant dehalogenation is observed, and it can be caused by the basic front (and some by the acid front), which is enhanced by the current intensity and by the reversibility in the application of the electric field.

In addition, significant volatilisation of organic compounds was observed, especially of the less chlorinated species (tetra, tri and di). It is favoured by air entrainment and temperature. It does not reach the GAC bed, but largely condenses on the walls. This justifies the mismatch in the balances. In this point, it is important to remark that the distribution of the organic pollutants in the unaltered samples is very heterogeneous. For this reason, it is difficult to establish the initial point in terms of concentration. As an example, Figure 2 shows data obtained in the post-mortem analysis of the one of the experiments carried out. For comparison purpose, the initial values of its own extremes and the average value of all the initial samples taken are also plotted. As can be observed, the concentration of trichlorobenzeces increases in the nearness of the cathodic compartment while the concentration of gamma-hexachlorociclohexane (Figure 2 b) decreases. This fact is related with the process of dehalogenation previously described. This is also observed in the profile of the average number of chlorine per molecule plotted in Figure 2 d. In the case of the total concentration of organic compounds (Figure 2 c) there is no clear trend. Since no compounds were detected in the liquid or gas phase, it indicates that the compounds do not move from the soil, but are only transformed and the scattering of the data may be due to the initial heterogeneous mixture.

Based on the data obtained at the laboratory and bench scale, a full-scale electroremediation study has been designed using the boreholes of the sampling as electrolyte wells. 9 m long carbon steel cylinders are inserted and used as electrodes (one central anode and three surrounding cathodes). It is expected that this arrangement favours the dehalogenation of COCs. In addition, granular activated carbon (GAC) columns are installed to trap the gaseous streams.



FIGURE 2. POST-MORTEM ANALYSIS OF THE SILTY SOIL IN THE UNALTERED SOIL MOCK-UP. a) Trichlorobenzenes concentration along the position. b) gamma-hexachlorociclohexane concentration along the position. c) total organics concentration along the position. d) total organic concentration in terms of average n° Cl per molecule along the position. - Average value of initial samples; - Average value of mock-up initial samples; ▲ Analysis after treatment; - Average value of analysis after treatment



FIGURE 3. PICTURE OF THE EXPERIMENTAL SET-UP IN THE REAL SITE

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DISMANTLING STRATEGIES FOR HIGHLY HCH-POLLUTED LANDFILL LEACHATE DUMP USING ELECTROCHEMICALLY ASSISTED TECHNOLOGY

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Summary

In this work, the electrochemical-assisted soil remediation technology is evaluated for the restoration of highly HCH-polluted sludge accumulated in a landfill pond as previous step for its dismantling without causing any leakage in case of HDPE film rupture. This sludge contains a very heterogeneous concentration of HCH, ranging from a few mg/kg to less than a dozen g/kg, and electrochemical-assisted soil remediation technology is presented as a good option to dry the sludge by inducing water transport and to reduce the hazardousness of the sludge by inducing dehalogenation as well as evaporation processes. To do this, different strategies are evaluated at bench scale prior to its implementation at full scale in the landfill pond. In a first stage, several tests are carried out using mock-ups in which a portion of sludge is placed into a silt matrix to study the transport of pollutants through a clean silt to the liquid and gas phases. Results point out the relevance of the transport of water to the cathodic wells whereas the mobilization of species to the electrolyte wells is negligible as compared to the compound dragged with air, which is also promoted by the temperature. In a second stage, bench scale mock-ups are filled with polluted sludge and the effect of electric field, surfactant addition and type of electrode material in the dewatering process are evaluated. Results shown that the dewatering of the sludge varies around 15-20 % depending on the operation conditions. Iron electrodes, the use of SDS solutions as flushing fluid and high electric field allow to attend a more intense dewatering. Finally, a holistic sludge-liquid-gas in situ remediation treatment is carried out in a delimited zone $(8 \times 8 \text{ m})$ of the landfill pond.

Keywords

Electrokinetic restoration of polluted ponds, sludge dewatering

Introduction

The Sardas landfill (Sabiñánigo) was in operation from the sixties of the last century until 1982. During its operation all types of waste, urban, rubble and industrial waste were dump. Some of these industrial wastes came from the manufacture of lindane, which caused a serious contamination problem due to the existence of organic compounds hazardous to health and the environment [1].

In 1996, the surface of the landfill was sealing and the front of the landfill closure with a cementbentonite screen. At this moment, a pond of 50x25 m2 was built a few meters from the Sabiñánigo reservoir, and with the bottom less than 1 m from the alluvial. This pond has been used to continuously collects leachates of different nature that flow from the landfill. The accumulated sludge remains saturated, and the distribution of contamination associated with HCHs residues is very heterogeneous, from a few mg/kg to less than a dozen g/kg. These sludges have a black colour, with grey tones on the surface by oxidation. They are very plastic, adherent, and difficult to handle. The basin is now close to its limiting capacity and its dismantling is a critical operation due to the very high risk of affecting groundwater and ultimately the Sabiñánigo reservoir in case of HDPE film rupture. Then, it is essential to avoid actions that can damage the pond and increase leachate infiltration.

In this context, the general aim of this work is the restoration and safe dismantling of highly HCHpolluted leachate reservoir using electrochemically assisted technology. In a first stage, it is done the characterization of the mobility of pollutants in the sludge contained in the pond under the action of electric fields and the evaluation of the effect of the main manipulable variables (intensity of the electric field, type of surfactant used as flushing fluid, type of electrodes). Then, the effect of the change of scale in the electrochemical treatment process and the treatment of liquid and gas phases generated during the remediation are evaluated.

Materials and methods

Figure 1a shows a picture of the experimental setup used for the study of the transport of the pollutants from the sludge through a natural soil. To do this, a cubic of 10x10x10 cm of real polluted sludge were placed in the centre of a mock-up. Secondly, to determine the transport of contaminants from the sludge to the electrolyte wells and the degree of dewatering several tests were carried out in a mock-up of 55 L of capacity (Figure 1 b).



FIGURE 1. EXPERIMENTAL SET-UP. A) SLUDGE CUBIC IN A KAOLINITE MATRIX; B) SLUDGE MOCK-UP

Results

A first scanning of operation conditions was performed using the 1-D mock-up. Tests were carried out following two operating strategies, in the first one the electrodes were stuck directly into the system so no flushing fluid was added [2], and in the second one the electrodes were inside an electrolyte well where water was introduced as a flushing fluid [3]. The influence of these two strategies on both the transport of contaminant from the sludge to the clean kaolinite matrix and to the liquid or gas phases, was studied. Results point out that the effects of dragging by the electroosmotic flow or the diffusion of the species is very low, and the main mechanisms of mobilization of the organic compounds is the volatilization. The higher the electric field applied the higher the temperature achieved in the system is, and then the higher is the amount of volatilized pollutants. In all cases efficiencies up to 70% in terms of hexachlorocyclohexanes removal are achieved. Efficiencies of up to 90% are achieved when is applying 3V cm⁻¹ (the highest electric field studied) using flushing fluid.

Then, using experimental set-up shown in Figure 1b, the effect of the main operation parameters on the sludge dewatering have been studied: electric field applied (0.5, 1, 3 V cm⁻¹); type of flushing fluids (water or aqueous solutions with sodium dodecyl sulphate, SDS) and the nature of the electrode material (vitreous carbon or iron). Table 1 summarizes the experimental conditions and the main results obtained.

In terms of water mobilization, there was not observed a clear effect of the electric field. In all cases, most of the water was mobilized in the first ten days of operation and then percentage removal remained constant until the end of the experiment. It is important to point out that the experiment performed at the highest potential (3 V cm⁻¹) presents the lower volume of water mobilized to the electrolyte wells. This can be related to the higher volatilization attained under this operation conditions due to the heating of the system is promoted by the higher ohmic losses. No significant differences are observed between the experiments performed at the same voltage (1V cm⁻¹) even though the electrode material is varied or SDS solutions are used as flushing fluid.

	Test 1	Test 2	Test 3	Test 4	Test 5
Electric field / Vcm ⁻¹	3	1	0.5	1	1
Electrode material	vitreous carbon				iron
Improvement fluid				SDS	
Moisture initial mass water/mass dry soil	0.34	0.32	0.31	0.38	0.37
Moisture final mass water/mass dry soil	0.26	0.23	0.27	0.26	0.28
mmol organics in water collected	0.06	0.1	0.3	0.4	0.2

Additionally, the degradation of the liquid waste streams generated in the electrochemical treatment of the sludge has been evaluated using two wellknown electrochemical advanced oxidation process: electrochemical oxidation with diamond based electrodes and with metal mixed oxides electrodes, and electrofenton. Results show that both EAOP can be satisfactorily used for the treatment of HCH-polluted wastewater and that the efficiency of the treatment depends on the current density applied and on the electrodic material used as anode. On the other hand, volatile compounds dragged with the gas phase are retained in a GAC adsorption column. After that, the GAC is regenerated with methanol. Then, this polluted methanol solution polluted is purified by conductive diamond electrolysis.

Further work

Finally, a field scale tests have been design. This type of treatment poses a significant engineering challenge due to the lack of references and the huge size of the polluted site. As far as the research team knows, it will be one of the largest test ever conducted with electrochemical technologies and perhaps will become a world reference. In a first approach, the sludge pond will be divided in sections of 8×8 sqm.

In the Figure 2 it is shown a scheme of the experimental set-up that will be built for this purpose. A floating platform with a plastic barrier will be installed to enclose the area of treatment. Then, nine iron cylindric electrodes are inserted into the sludge. Finally, a cover will be installed to collect the pollutants in the gas phase.

The tests will be carried out in several stages:

1) Mobilisation of pollutants (the addition of surfactant could be required);

2) To dry the sludge, the fluid supply would be stopped and the water arriving by electro-osmosis would be removed from the cathode. The process shall be stopped below the field capacity;



FIGURE 2. SCHEME OF THE IN-SITU PILOT TEST

3) The gases collected during the first stages will be treated by the most suitable Advanced Oxidation Process (AOPs) studied previous;

4) The extracted fluids collected during the first stages will be pumped to storage tanks and treated by the most suitable technology studied previously for this purpose.

The work will be carried out in batches from the first stage to make the most of the recovered surfactant; the rest of the treated fluids will be sent to the treatment plant. Finally, the dewatered sludge extracted from the pond will be treated by biopiles. Then, in function of the quality of the final product it will be used for the restoration of the landfill or in the case of not achieved the enough quality and alternative management will be propose such as a thermal desorption or incineration.

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