Block 1

LIFE SURFING



LIFE SURFING: "SURFactant ENHANCED CHEMICAL OXIDATION FOR remediatING DNAPL"

Net J., Cano, E., Fernández, J., Velilla, S.M.

Department of Agriculture, Livestock and Environment, Government of Aragon, Spain

Summary

The Government of Aragon leads the LIFE SURFING project, a pilot test whose aim is to demonstrate the field feasibility of a soil decontamination technique in fractured aquifers containing residual Dense Non-Aquous Phase Liquid (DNAPL) of a high pollutant mixture of multicomponent organic contaminants and POPs.

The LIFE SURFING project, developed in the framewok of the European LIFE Programme, and with whole title "SURFactant enhanced chemical oxidation for remediatING DNAPL" (LIFE17 ENV/ES/000260), has a budget of 2.1 million euros and a duration of 60 months.

The project will develop a field test in the fractured aquifer of the old Bailín landfill.

This old landfill was used by Inquinosa factory for the disposal of the waste. The factory produced lindane, as well as solid HCH. Inquinosa dumped liquid residues in there.

DNAPL was found in 2004 during the site monitoring activities and, since then, it has been pumped in Bailin boreholes. Nowadays, it does not accumulate any more, thus, it can be considered in residual phase. Nevertheless, this dense residue remains attached to the walls of the rock fractures and keeps present in a residual way. The objective of LIFE SURFING is to eliminate this residual phase, and to establish a methodology that can be transferred to a full scale level and even other sites with different DNAPLs and different geological conditions.

The consortium is formed by five partners: Government of Aragon, coordinating the project; the Complutense University of Madrid, carrying out the preliminary analysis and the design and assessment of the field test; the University of Stuttgart, carrying out a large-scale laboratory test; the IHPA, in charge of the study of transferability to other locations, and SARGA, for the implementation of the infrastructures and fieldwork.

In short, this contribution from the EU, via LIFE funds, will make it possible to increase safety conditions in the old Bailín landfill by removing an important amount of pollutants.

Keywords

LIFE, Demonstration test, Remediation, DNAPL, Lindane, HCH, POP, Bailin landfill

Introduction and problem

The Bailin site was a landfill where liquid and solid waste from the INQUINOSA company, producer of the obsolete pesticide "lindane", was dumped between 1983 and 1992.

Lindane (gamma isomer of hexachlorocyclohexane or γ HCH) and several of its derived residues are included in the list of persistent organic pollutants of the Stockholm Convention. Lindane production was banned in Europe by Regulation no. 850/2004, on Persistent Organic Pollutants (POPs).

In the Bailín landfill, 65,000 tons of solid HCH waste and 342,000 tons of contaminated soil were dumped, in addition, INQUINOSA dumped liquid waste from the production of lindane. These formed a dense phase or DNAPL (Dense Non-Aqueous Phase Liquid) with a great polluting potential and very difficult to remove, due to its strong hydrophobic character.

Although this DNAPL can be considered immobile, its multicomponent nature [1] favours the incorporation of a large amount of contaminants into the dissolved phase, reaching HCH saturation conditions in groundwater in some areas due to the balance between the aqueous and organic phases.

For this reason, runoff water that comes into touch with the landfill surface infiltrates inside the aquifer and, in contact with DNAPL, causes a serious environmental problem in the area.

Regarding the geology of the aquifer, the old Bailín landfill is located on a terrain that is formed by an alternation of sandstone and lutite, with vertical stratification [2]. The sandstone layers thickness is about 5 m, and they are fractured up to 40-50m deep. Lutites can be considered relatively impermeable, due to their low fracturing at depth, reason why water circulates preferentially in favour of fracturing in sandstones.

The main problem is located in the sandstone layers with the highest permeability due to fracturing, and specifically in a layer that has been called "M layer" because it is the only one with continuity reaching the main environmental receptor of contamination, the Gállego river.

The following figure shows the position of the "layer M" with respect to the HCH landfill and the Gállego river



After several actions to try to isolate the contamination in the old Bailín landfill, in 2014 the solid waste from the old landfill body was moved to a new security cell, guaranteeing its isolation.

Actions have been carried out in the area from 2004 to 2019, such as the execution of boreholes and their subsequent equipment to configure a network of points that has allowed the identification of a contamination plume from the Bailín landfill to the Gállego river, its monitoring its movement in the groundwater and the pumping DNAPL for its extraction and control.

Based on the work carried out and according to the studies, it has been identified that the contamination has also advanced vertically, affecting differently the rock mass and according to the family of fractures, up to variable depths of around 45 -50 meters.

From the moment it was detected, the DNAPL has been pumped in boreholes, the volume extracted being lower and lower, currently reaching the point of having the DNAPL practically finished, so that the existing DNAPL is found residually, adhered to fractures and in "cul-de-sac", which can no longer be extracted by pumping.

Although, in 2017, a demonstration project for the application of chemical oxidation in situ (ISCO) called the LIFE DISCOVERED was carried out at the Bailín site, which has shown its effectiveness in the dissolved phase, its effectiveness on the dense phase (DNAPL) it is minimal due to the hydrophobic character of this phase and the low solubility of the contaminants in water. However, concentrations in the dissolved plume will stay high as long as the DNAPL focus remains.

LIFE SURFING project overview

The LIFE SURFING Project arose to tackle this problem. Co-financed by the EU and developed within the framework of the European LIFE Program, the project full name is "SURFactant enhanced chemical oxidation for remediating DNAPL".

The LIFE SURFING project is a demonstration project developed through a pilot soil remediation test that is carried out at the site contaminated by HCH the Bailín fractured aquifer (Sabiñánigo, Huesca).

The main objective of the LIFE SURFING project is to demonstrate the effectiveness and feasibility of the combination of surfactant-enhanced extraction techniques (SEAR) and on-site oxidation treatments in a first phase and the subsequent application of the S-ISCO (surfactant-enhanced in situ chemical oxidation technique) to attack the residual DNAPL, and thus contribute to the elimination of DNAPL in the aquifer, or at least to its minimization until the application of final decontamination techniques, such as the application of bioaugmentation techniques that allow a sustainable recovery of the area.

In addition to the main objective of the project to demonstrate the applicability of the test for the removal and decontamination of residual DNAPL, the project has other objectives such as reducing the risk to Health; guarantee the reduction of environmental risks and analyse the large-scale applicability of the technique from a technical, economic and environmental point of view.

The LIFE SURFING project will be carried out at the Bailín landfill, however, this problem also exists in two other sources of contamination in the same municipality (the Lindane factory and another landfill located nearby) and in other European countries. Therefore, the results obtained could be extrapolated to these sites. To that aim, the replicability and transferability for its application in other locations affected by the same problem has been evaluated.

The project execution period is from January 1, 2019 to June 30, 2022, which due to the Covid 19 pandemic has been extended until December 31, 2023, with a total duration, including the extension, of 60 months. Total costs of the project are 2,081,507 \in of which the European Union finances 1,182,452 \in (56.8%).

Project partners

In order to carry out the requirements of the LIFE Program, a consortium of five partners was created, each of which performs certain tasks within the implementation of the project.

The partners that make up the consortium are: The Government of Aragon (GA) which is the coordinating partner of the project, the public company Sociedad Aragonesa de Gestión Agroambiental (SARGA), the International HCH and Pesticides Association (IHPA), the Complutense University of Madrid (UCM) and the University of Stuttgart (USTUTT).

The Government of Aragon carries out the tasks of managing and coordinating the entire project and provides the location and experienced technical personnel for the design and execution of the pilot test.

The International HCH and pesticides association (IHPA) provides experienced staff and performs tasks related to public awareness and dissemination of results.

The public company SARGA is involved in most of the actions of the project, providing material and human resources for the design and execution of preparatory actions, field actions, and for carrying out laboratory tests. They also collaborate actively in the management of the project and in the dissemination work.

The Complutense University of Madrid (UCM), through the IMPROQUIMA group, participates as a scientific-technical expert in the design and application of chemical oxidation treatments and/or application of surfactants in the remediation of sites contaminated by organic compounds that form dense phases. In addition to this experience, it has the infrastructure to carry out experiments on a laboratory scale and analytical equipment to determine the concentration of oxidants, chlorinated organic pollutants, inorganic compounds, metals, surfactants, both in aqueous matrices and in soil.

The University of Stuttgart (STUTT) is responsible for the test transferability. Through the Research Center for Subsurface Remediation (VEGAS) of the University of Stuttgart, it provides experienced technical personnel and special infrastructure for the design and execution of the transferability test of the S-ISCO technology to other sites with different geological and hydrogeological conditions, and for different types of contaminants. For this purpose, several experiments have been carried out at different scales under well-controlled conditions. Transferability is an essential requirement of the LIFE Program.

Project actions

For the execution of the project and the achievement of its objectives, the LIFE SURFING project is implemented through different actions to be carried out by the different project partners, these actions have been structured into 5 main blocks.

- A Actions, are the preparatory actions, these tasks include the experimental design of the test cell, studies of the optimal location of the pilot test cell, topography, engineering study of the design of the different zones (injection area, test area and barrier area), application for administrative permits, communication and consultation with committees and stakeholders, among other preparatory tasks.
- B Actions, are the Test implementation actions, being the main block of project actions, which due to their importance require further detailed explanations.
- C Actions, are the monitoring actions of the project. These actions are carried out at the same time as B actions, since they are monitoring and control actions, such as initial toxicity and biodegradability tests that consist of a characterization of the current situation in the aquifer of the existing bacterial populations, sampling and laboratory analysis in the injection, pumping and tracer tests carried out prior to the pilot test, determine the starting conditions of the different phases of the pilot test (SEAR, SISCO,

ISCO), among other tasks such as the ecological monitoring of the river to assess the improvement of environment due to the project.

- D Actions, are public awareness and disseminate the results actions, including tasks such as preparation of informative material, brochures, publication of articles in specialized magazines, creation of a web page, participation in seminars, information to stakeholders and the realization of the present 14th InternationalHCH and Pesticides Forum.
- E Actions, are the project management actions, including generic and specific project management tasks, such as meetings, preparation of protocols, preparation of schedules, processing and monitoring of supplier contracts, audits, etc.

The actions of block B (test implementation) deserve special mention, since they are the most important body of the project, since they are the tasks directly related to the pilot test itself.

LIFE SURFING pilot test (B actions)

The LIFE SURFING test is planned in 3 phases of test implementation and a preliminary preparatory phase, structured as follows:

Phase 0 of preparatory test. Consisting of injection and pumping hydrogeological tests, tracer tests and a test in the barrier zone.

The objective of these preparatory tests is to acquire the greatest possible knowledge of the of the aquifer, in order to implement the test itself in optimal conditions and with greater security guarantees. In this way, the aim is to find out aspects such as the distribution of fracturing and its connectivity, permeability, injection flows, flows transferred downstream, contact time of the fluid with the contaminant, arrival times of the tracers to the river and barrier zone, flow speed, operation of the safety techniques in the barrier zone, etc., all of the essential aspects for the execution of the test in optimal conditions and in the most effective and efficient way possible.

Phase 1. SEAR test. This phase consists of injecting surfactant with a small percentage of hydrogen peroxide into the selected piezometers, in some cases with recirculation, and finally pumping to recover the injected material and its draggings. This phase is planned in several injections in different piezometers and at different depths. Main objectives of this phase are:

• Solubilize the residual DNAPL and proceed to pump it, recovering the largest possible volume, avoiding the release of surfactant fluid and its drag downstream of the injection zone.

In order to maximize this main objective and guarantee environmental safety, the following objectives are set out:

• Reach the highest level possible with the injected fluids, avoiding not exceeding the level of lateral transmission in the aquifer, avoiding surges.

- Keep the surfactant as much time as possible in the aquifer.
- Intercept and treat the pollution front generated downstream.

This phase also includes on-site treatment of the extracted fluid that consists of a treatment through activated carbon, alkaline hydrolysis and a Fenton treatment in facilities near the injection area prepared for it.

Phase 2. S-ISCO test (enhanced in situ chemical oxidation with surfactants). This phase consists of the injection of an oxidant, sodium persulfate, with alkaline activation aided by the addition of a non-ionic surfactant. The injection is carried out in the piezometers selected by the data from the previous phase, and the injected fluid (surfactant + oxidant) is recirculated and finally the generated front is treated in the barrier zone.

The main objective of this phase is to degrade the largest possible volume of residual dense phase (DNAPL).

For this, as in the previous phase, the main objectives to be achieved to optimize the results in safety conditions are:

- Minimize the volumes released downstream of the injection zone.
- Reach the highest level possible
- Maintain contact with the reagents in the injection area as long as possible.
- Prolong the activation of the persulfate downstream of the injection zone.
- Follow the evolution of contaminants and reagents throughout the test layer (Layer M).

Phase 3. ISCO test (chemical oxidation) and evaluation of the rebound effect

The objective of this phase is to evaluate the possible rebound effect, since after the different injections of SEAR and S-ISCO fluids in the previous phases, it is possible that there is a diffusion of the contaminants and the rebound effect occurs.

Depending on the results of the evaluation, a new oxidant injection may be carried out, in principle persulphate with alkaline activation.

In all phases of implementation test, including phase 3, in case of it is carried out, the baseline conditions of the aquifer are determined prior to the injections of the different phases, likewise during and after the injections an exhaustive monitoring is carry out to verify the evolution of the test, which includes the measurement of levels and conductivity, gas samples, leachate samples and sampling in the Gállego river.

Conclusions

The LIFE SURFING project is a very promising project in the field of remediation of residues generated in the production of Lindane and other pesticides.

Specifically, at the Bailín landfill, this project takes a giant step forward in remediation of the site, thus opening up many possibilities for the application of these combined remediation techniques on a larger scale, as a step prior to the application of other techniques such as bioremediation.

Likewise, the necessary knowledge is acquired to evaluate the applicability of these combined remediation techniques in other locations affected by the same problem.

References

1. Santos, A., Fernandez, J., Guadano, J., Lorenzo, D., Romero, A., 2018a. Chlorinated organic compounds in liquid wastes (DNAPL) from lindane production dumped in landfills in Sabinanigo (Spain). Environ. Pollut. 242, 1616–1624.

2. J. Fernandez, M.A. Arjol, C. Cacho, POPcontaminated sites from HCH production in Sabinanigo, Spain, Environmental Science and Pollution Research, 20 (2013) 1937-1950.

- European Commission. Unit B3 LIFE and CIP Eco-Innovation. 2018. Grant Agreement number LIFE 17 ENV/ES/000260 LIFE SURFING.

- Government of Aragon, Sociedad Aragonesa de Gestión Ambiental. 2019. LIFE SURFING. LIFE 17 ENV/ES/000260 Partnership agreement Government of Aragon – Sociedad Aragonesa de Gestión Ambiental.

- Government of Aragon, Complutense University of Madrid. 2019. LIFE SURFING. LIFE 17 ENV/ ES/000260 Partnership agreement Government of Aragon – Complutense University of Madrid.

- Government of Aragon, Stichting International HCH and Pesticides Association. 2019. LIFE SURFING. LIFE 17 ENV/ES/000260 Partnership agreement Government of Aragon – Stichting International HCH and Pesticides Association.

- Government of Aragon, University of Stuttgart. 2019. LIFE SURFING. LIFE 17 ENV/ES/000260 Partnership agreement Government of Aragon – University of Stuttgart.

- Government of Aragon, Complutense University of Madrid. 2022. Document 04 Phase 1. SEAR protocol.

- Government of Aragon, Complutense University of Madrid. 2022. Document 05 Phase 2. S-ISCO protocol.

LIFE SURFING: "FACILITIES, EQUIPMENT, CONSUMABLES, AND RESOURCES IN THE TEST EXECUTION"

Sánchez-Valverde A.¹, Romero P.¹, Peiro A.¹, Arjol M.A.¹, Herranz C.¹, Cano, E.², Fernández J.²

¹Aragonese Society for Agro-Environmental Management SARGA, Zaragoza, Spain ²Department of Agriculture, Livestock and Environment, Government of Aragon, Spain

Summary

The Government of Aragon has undertaken an innovative pilot test for the elimination of residual DNAPL in a fractured aquifer under the LIFE SURFING project (Life LIFE17 ENV/ES/000260), which has involved a complicated task of planning and quantifying both, costs and resources.

The organization has been integrated by an interdisciplinary work team with knowledge on the geomorphological and hydrological characteristics of the site. Based on it, they defined the scope of the test, the design of the installation, and the execution of the works. Preventive and corrective measures have been applied to control the test performance in case of deviations in the development of the works.

The pilot test has been developed in a vertical layer of fractured rock where the pumpable dense phase (DNAPL) was already exhausted. The LIFE SURFING test has consisted of several phases of in situ tests (SEAR injections and S-ISCO injection) and on-site treatments of the SEAR extraction, which involved and intense with laboratory and fieldwork. The works have been carried out on an area of 380 linear meters of the so-called "M layer". For this, three different facilities were implemented:

Injection Zone, close to the dismantled Bailin landfill, constructed for the purpose of the carrying out the injections in the test cell. Mixture, injection and recirculation tanks, as well as pumps, flow-meters, and a complex circuit of pipes were placed there.

Test Zone, where the equipment for developing the on-site treatments (Fenton oxidation, alkaline hydrolysis and adsorption on activated carbon of the volume extracted by the SEAR injections) was installed.

Barrier Zone, located downstream of the tested cell, where equipment for the treatment of the volumes going out the test cell was installed.

The test had 14 months duration in which it has been necessary to carefully manage the material (electromechanical equipment and chemical reagents) and human resources. Once the work has been completed, a global analysis of the pilot test has been carried focused on the improvements to be made for future application at a large scale.

Keywords

Life Surfing, equipment, facilities, chemical products, pilot, test, feasibility.

Introduction

The LIFE SURFING project is a pilot soil remediation test that has been carried out in the location contaminated by HCH in the Bailín ravine (Sabiñánigo, Huesca) and its objective has been to verify the feasibility and effectiveness in the field of the combination of SEAR techniques (surfactant-enhanced aquifer remediation) and S-ISCO (surfactant-enhanced in-situ chemical oxidation) to remove residual dense phase (DNAPL) from the aquifer, thereby enabling site remediation. Next, all the steps that have been carried out, the test will be developed, starting with the previous studies (for the location of the most optimal location that would allow the development and control of the works), engineering design, witnessing and supervision of the piezometers of the test cell, execution of the works of the platforms to locate the equipment and facilities, and concluding with the planning and implementation of all material resources (reagents, chemical products, consumables, equipment) and personnel

necessary (test periods, protocols, security, laboratory, sampling depths, etc.) for the correct execution of the work.

The test was planned in four stages and we will now make a detailed and analytical description of each one of them.

Stage 1 - Preliminary Studies & Test Design

First of all, within the Bailin site, a *study* had to be carried out to select the most suitable area that would allow a controlled development of the pilot test. To this end, an exhaustive review of the information available on geology, hydrogeology and hydrochemistry in the vicinity of the landfill, with the presence of DNAPL, was carried out.

According to this review, *layer M* was selected as the best location since it is located in the immediate vicinity of the old HCH landfill already dismantled, the DNAPL was residual, the layer was well connected at depth and had enough continuity to perform injection, monitoring and pumping events. In addition, the M layer had boreholes that could be used, as well as execute additional boreholes. Very detailed information was also available on preferential flow paths, impacted areas, lithologies, etc.



FIGURE 1. LAYER M SELECTED FOR THE LIFE SURFING TEST AREA

After selecting the test area and in order to limit the risks and guarantee environmental safety downstream where the Gállego River is located, the *experimental and technical design of the test had to be carried out* and thus reduce the uncertainty associated with the execution and application in the field of remediation techniques in a very complex and fractured hydrogeological environment.

To carry out the design, it was necessary to analyze the available hydrogeological studies, geochemical data from the selected test area and reagent dosage from a detailed experimental design, based on laboratory tests with surfactants, as well as review and analysis of SEAR, S-ISCO research, in particular with surfactants and chemical oxidation laboratory treatments. At the same time, the field work to be carried out was defined, such as the adaptation of accesses, the drilling of new boreholes, the execution of hydraulic tests (pumping, injection and tracer tests) and the design of the safety barrier.

Engineering design was carried out to satisfy the technical requirements of the injection test and internal recirculation layer M.

In parallel, the Government of Aragon together with the UCM, defined the *Protocols and procedures* to carry out the *preliminary tests*, consisting of hydrogeological tests and thus establish the conditions of the hydrogeological flow and the connectivity of the fractured aquifer, the admissible injection and pumping flows, the tracer tests to estimate recovery rates and adjust the injection flows and pumping and a test of the barrier zone to check its effectiveness.

Finally, *the test execution protocol was prepared*, consisting of two phases:

Phase 1: SEAR test, consisting of 2 injection events. Phase 2: S-ISCO test, executed in 1 injection event. In these protocols, the control and follow-up methodology of the test was defined, including data collection and analysis in situ and in the laboratory, before, during and after each stage of the test was carried out.

Stage 2 - Facilities

All the infrastructures for the execution of the pilot tests and the location of the control boreholes were located in the surroundings of the "Pilot Test Cell". For the execution of the test inside the cell, 3 zones were defined: Injection Zone, Test Zone and Barrier Zone. Each of the three zones had its own electrical panel for manual or automatic control (level control by radar probes and pH control) of the electromechanical equipment based on the data obtained from the meters and flowmeters implemented in the zone. Injection and Barrier.

For the execution of the test, it was necessary to carry out civil works and facilities such as :

- Accesses and platforms for the execution of surveys. The task was especially complex due to the complicated orography of the terrain. Everything was planned with security guarantees so that the transfer of workers and necessary auxiliary materials will be carried out correctly in the execution. The concreted platforms allowed both the location of the drilling machinery during the construction phase, as well as the installation of the tanks, equipment and reagents during the execution of the test.

- 7 *piezometers* (P190-P196) that were located on layer M, on the slope of the dismantled basin of the Bailín landfill. The length of the piezometers ranged between 30 and 45 m depth.

The injection and test platforms, as well as the drilling platforms, were interconnected by means of a series of pipes for the transfer of reagents and water, used in the injection/extraction of reagents and leachate and subsequent treatment.

Once the civil works were completed, equipment was installed for the execution of layout tests prior to the final installation of the equipment, acquired in the rental modality, for 14 months and whose installation and connection lasted for 6 weeks.

In the Injection Zone, At a distance of 200 meters and more than 30 m above the level of the treatment area (Figure 2), the injection equipment and the feed line for the mixture of reagents to the piezometers to be treated were located. The area was completed with a recirculation tank and a mixing tank, which were communicated to facilitate the injection and pumping maneuvers of the fluids and reagents to the two injection lines. Also, in this area there was a soda tank (25%) of 1 m³.



FIGURE 2. AERIAL PHOTO OF THE TEST CELL, LAYER M AND THREE ZONES: INJECTION TEST AND BARRIER



FIGURE 3. MAIN ELEMENTS OF THE INJECTION SITE INSTALLATION

The Test Zone, constituted a platform that collected the leachates from the injection zone, sent by pumping. Different equipment was arranged to carry out the leachate treatments, with different techniques: activated carbon, Fenton and Hydrolysis.



FIGURE 4. MAIN ELEMENTS OF THE INSTALLATION OF THE TEST AREA



FIGURE 5. MAIN ELEMENTS OF THE INSTALLATION OF THE BARRIER ZONE

The Barrier Zone, constituted an area of more than 100m concentrating boreholes for injection from a control point (with a safety bucket and injection manifolds) for *dosage of persulfate and soda*. In addition, existing gas extraction equipment was set up in the area's survey network.

Between all the zones, more than 200 elements were installed between tanks, GRG reactors, manifolds, pumps, flowmeters, etc. and more than 1,000 m of high-density polyethylene pipes of different sections.

To complement and facilitate the handling, analysis, and monitoring of all test samples, a gas chromatograph with an electron capture detector (ECD) and flame ionization detector (FID) was purchased.

Stage 3 Execution of the test Chemicals & Consumables

To carry out the test, a total of 10,200 kg and 7,600 L of chemicals and reagents have been needed.

Emulse surfactant was selected, which, due to its properties (non-ionic, biodegradable, low foam generation) and its behavior in the medium, was more suitable.

Regarding consumables for the handling of chemical products and reagents, a large number of auxiliary equipment and tools have been used (dosing and submersible pumps, packers, measurement probes, point samplers, interface and TLC measurement probes, containers of sampling, bladder pumps, electrodes, pressure gauges, and small hardware and laboratory consumables), requiring continuous replacement to avoid cross contamination and material wear.

Personnel, laboratory analysis, environmental monitoring and safety and health

The tests were carried out manually, for proper registration and monitoring of all processes. For this purpose, different entities (UCM, Government of Aragon, SARGA), companies (Eutop, AECOM, Sondeos Jarem, Adiego Hermanos, Hidroman, Envirotecnics, etc.) and personnel continuously worked in the field for the tasks on-site monitoring and control, requiring the establishment of periodic weekly and daily operating shifts in a punctual and continuous manner, both for injection, pumping, control and monitoring.

Each test period lasted 5 weeks, with an initial week for preparations only, another for testing tracers, a third for carrying out the test, and a further two (minimum) follow-up weeks. 4 teams of 3 people each were needed, during the injection and control days, due to the continuous measurements performed.

TABLE 1. CHEMICALS AND REAGENTS

Product	Quantity (Kg)
Activated carbon in pellets for gases	500.0
Activated carbon for water	500.0
thickener	5.6
Ferrolin / Kurita	92.0
Fluka	1.0
Iron(II) sulfate heptahydrate	75.0
Sodium persulfate	250.0
Potassium Iodide PA-ISO 99.5%	2.0
Salt	1,200.0
Sodium bromide	75.0
Sodium persulfate	6,500.0
Caustic soda	1,000.0
SPAM-80 quality synthesis	2.0
TRITON X-100 synthesis quality	2.0
TWEEN-80 synthesis quality	2.0
Total	10,206.6
Product	Quantity (L)
1-Heptanol	25
20% sulfuric acid	10
Silicone defoamer	50
Buffer	3
Hydrogen peroxide 50%	1,400
Polyelectrolyte / Flocculant A-30L	25
25% soda	4,000
Surfactant emulse	2,082
Total	7,595

The previous work began in 2020 and involved more than 500 samples, among which the test in the Barrier Zone (August-Sep. 2021) with 361 samples stands out. During the year 2022, all the tests scheduled for the Life Surfing project were carried out, with a number of samples indicated in the Table 2 below.

In addition, carrying out the tests implied an increase in the control of the river, which involved 40 additional monthly samples to the control that is usually carried out, which is usually 150-170 monthly samples.

The samples obtained in the field were analyzed in the Bailin laboratory and in the Pirenarium laboratory, comparing the results of all the samples with analyzes carried out at the UCM.

In parallel, environmental and health and safety monitoring was carried out in process control, work protocols, PPE used, coordination of business activities, etc.

More than 500 personal protective equipment was used, including overalls, masks, and protective gloves.

14th International HCH and Pesticides Forum, 2023

TABLE 2. TESTS NUMBER

Samples	Base line	Old Barrier/ River others discharge		TOTAL	Gases	
Tracers	89		89	-		
SEAR 1	36	51	112	25	224	-
SEAR 2	36	46	102	31	215	9
SISCO	33	74	97	25	229	79
					757	88

Stage 4 - Economic analysis and conclusions reached

The economic analysis of the Life Surfing trial grouped by category is summarized in Table 3. The total cost of the test in outside media was ϵ 621,862.55. These costs do not include the analyzes carried out both in the reference laboratory of the Government of Aragon and in the UCM, as well as all the personnel that has intervened both from SARGA, GA and UCM throughout the planning, development and execution of the test.

TABLE 3. ECONOMIC ANALYSIS OF THE LIFE SURFING TRIAL

Summary costs contracted test Life	Total
Facilities	€233,969.69
Chemical products	€64,715.81
Consumables	€65,873.20
Staff External assistance	€256,536.42
Others (messaging, etc.)	€767.43
Total	€621,862.55

Conclusion

The remediation of contaminated soils is a process that requires a high investment and technical and economic planning, with which the feasibility cannot be evaluated if it is not measured in terms of responsibility with the environment to avoid consequences on a larger scale. The implementation of this test would not have been possible without the union of efforts and public resources both at a regional and European level.

It is estimated that with each kg of DNAPL that reaches a body of surface water, a volume of 50 hm³ is disabled for mouth consumption.

During the test work, a total of 240 kg of DNAPL were eliminated, which could cause the contamination of 12,000 hm³, the volume of some 48,000 Olympic swimming pools.

Each kg of residual DNAPL extracted has cost $\in 2,591$, which makes it necessary to reconsider the measures that prevent contamination and the importance of carrying out pilot tests that allow evaluating the viability of how to minimize the impact of those already contaminated sites, reducing the cost and incorporating the economic variable in the final decision.

Acknowledgments

This work has been supported by the Life Programme, through Aragon Government, UCM, and SARGA and collaboration companies to join efforts to do their best in favor of remediation of contaminated sites.

References

1. Service for the identification of a new location within Bailín site that allows the controlled development of the LIFE SURFING pilot test. Aecom. July 2019 - Life Surfing;

2.Memory of the expert technical assistance service for the testing and supervision of the piezometers of the "Test Cell" necessary for the pilot test of the Life Surfing Anufra. 2019 project. Life Surfing;

3. SURFING TEST EXPERIMENTAL DESIGN. December 2019 - Life Surfing;

4. SURFING TEST ENGINEERING DESIGN December 2019 - Life Surfing.

LIFE SURFING PROJECT, PREPARATORY WORKS FOR THE INJECTION OF SURFACTANTS AND OXIDANTS

Fernández J.¹ Santos A.², Herranz C³. Cano E.¹ Lorenzo D.², Arjol M.A.³, Salvatierra A³

¹Department of Agriculture, Livestock and Environment, Government of Aragon, Spain ²Chemical Engineering and Materials Department, University Complutense of Madrid, Spain. ³Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain

Summary

The LIFE SURFING Project has tested the application of SEAR and SISCO techniques in a fractured aquifer affected by a dense phase from lindane manufacturing residues. After 16 years of pumping the dense phase (DNAPL) in the Bailín landfill aquifer (Sabiñánigo, Huesca), a situation has been reached in which physical extraction is already inefficient, which makes it necessary to address the application of chemical techniques that allow cleaning the residual DNAPL.

Detailed information on lithologies and fracturing has been obtained during the boreholes execution in the test area. In addition, samples have been taken from the fractures of the borehole cores to delimit the distribution of the DNAPL.

Seven hydrogeological tests (injection, pumping and combined) have been carried out to establish connectivity between boreholes, estimate response times to water level changes, establish conditions for flow and connectivity (lithological, structural, barriers, etc.), and the admissible injection and pumping flow.

Six tracer tests have been carried out, with sodium chloride and bromide as the tracers. Compared with the aquifer, a high conductivity was achieved with NaCl, allowing detailed monitoring of conductivity vertical evolution in control boreholes. Sodium bromide allows for estimating recovery rates and adjusting the necessary volumes and injection and pumping strategies.

Finally, downstream, a barrier zone has been equipped to minimize the mass and toxicity of POPs that could be mobilized in the application of surfactants. In this area, the application of caustic soda, sodium persulfate, temperature and aeration are combined. This treatment reached an effectivity greater than 99% in HCH elimination and greater than 90% in benzene and chlorobenzene removal, which are the most abundant chlorinated compounds.

This set of tests constitutes the fundamental methodology to carry out SEAR and SISCO treatments in a heterogeneous fractured aquifer with DNAPL. Its implementation has allowed the LIFE SURFING project to address these treatments successfully.

Keywords

Lindane, DNAPL, fractured aquifer, surfactants, persulfate, tracer test, hydrogeological test.

Introduction

During the eighties of the previous century, INQUINOSA disposed of lindane manufacturing residues directly on the ground at the Bailín landfill. These included a dense non-aqueous phase (DNAPL) [1]. This dense phase comprises more than 28 organochlorines, mainly from benzene to heptachlorobenzenes [2]. Due to their toxicity and environmental persistence, some have been included in the list of persistent organic pollutants by the Stockholm Convention [3]. This residue percolated in favor of fracturing, reaching the base of the water table. In its progress, it exceeded the western limit of the landfill and advanced for around 300 m towards the Gállego River, located 800 m from the landfill. The landfill was located on a vertical alternation of sandstone and siltstone, with different degrees of fracturing. Below 10 m, fracturing affects only the sandstone layers, generating a series of isolated aquifers that flow in the direction of the layers towards the Gállego River.

In 2004, this DNAPL was detected in a new borehole, its dispersion was delimited, and the pumping and external waste management began. After extracting more than 30,000 liters, the DNAPL remains in a residual phase. In 2017, the application of surfactants and the combination with oxidants was addressed through the Life SURFING project: "SURFactant enhanced chemical oxidation for remediatING DNAPL" (EU LIFE Program LIFE17 ENV/ES/000260). Lithologies and fracturing, together with the lithostratigraphic changes in the same layer, determine the advance of the contaminants rate. The porosity (0.4%) and general permeability of the aquifer are low (between 0.1 and 0.01 m/day), and advance rates higher than 300 m/day have been measured in favor of well-communicated fractures. The risk to the Gállego River when the dissolved contamination by surfactant use increases must be evaluated.

Experimental Setups and procedure

Surfactant Selection:

For this project, mixtures of Tween and Span, SDS and E-Mulse 3[®] were tested. In addition to the solubilization capacity and the viscosity modification, the behaviour in an alkaline medium was tested to analyze the compatibility with the persulfate activated with sodium hydroxide. Laboratory work is the subject of communication in this same Forum.

Selection and execution of the test cell:

The test cell has 8 boreholes, 6 newly executed, (fig 1). The cell length between the injection boreholes and the downstream borehole is 48.5 meters, with a longitudinal separation between boreholes variable between 5 and 10 meters.



FIGURE 1. DISTRIBUTION AND FUNCTIONS OF THE BOREHOLES IN THE TEST CELL. IN GREEN, NEWLY EXECUTED BOREHOLES DURING LIFE SURFING

The boreholes were carried out by rotation with continuous core recovery, a diameter of 130 mm, and continuous water injection. The soundings have not been equipped to facilitate the use of shutters. Extensive testing was carried out during drilling (lithology; fracturing: opening, inclination, fills, DNAPL indications; degree of weathering), 17 Lugeon tests were carried out, 87 samples were taken from the fracture faces on which extraction was carried out with methanol assisted by ultrasound. The COCs were analyzed on the extract with a gas chromatograph coupled with FID (flame ionization detector) and ECD (electron capture detector) detectors (AGILENT, model 7890B). Hydrogeological behavior of the test cell:

The connectivity between boreholes, speed of response to water level changes, critical factors (lithological, structural, barriers, etc.) for flow and connectivity, admissible injection and pumping flows, and volumes required in injection and pumping strategies must be evaluated.

The test area constitutes a heterogeneous fractured aquifer with a width of 1 meter; the depth oscillates between 25 and 50 meters; the sedimentological disposition of the materials (fluvial-deltaic environment with conglomerates, sandstones and siltstones) generates zones of variable permeability in the three directions. In the 1990s a partial bentonite cement screen built randomly modified the connectivity between boreholes. Lastly, the storage capacity is small, resulting in a rapid rise in the groundwater table and north-south communication with other layers. Based on these characteristics, the boundary conditions required for applying the classic hydrogeological test and calculation methodologies for porous or fractured media can not be used. It has been decided to carry out injections (with a drinking water network) and pumping tests (Table 1), reproducing possible actions during the injection of oxidants and surfactants in the SEAR and S-ISCO treatments. Monitoring has been extended to 35 boreholes, from upstream of the cell to the banks of the Gállego River.

TABLE 1. HYDROGEOLOGICAL TESTS CARRIED OUT IN THE LIFE SURFING PROJECT-1

Injection in P192: flow rate injected without exceeding level 810 m. Recovery time (level and conductivity). Pumping in P171: test at stepped flow rates, flowlevel drop correlation and maximum stable level drop. Injection in P192 and P195: flow rate injected without exceeding level 810 m in the injection wells, the influence of the siltstone lens in P192 and P194. Injection in P192-P195 (packer P198): reverse the water levels upstream of the new boreholes to treat the fractures with DNAPL that remain in the vadose zone Injection in P198 (packer: P198, P195 and P192): reverse gradients, minimize transfers downstream and force circulation in the lower part of the groundwater table. Injection in P198, pumping in P192 and P195 (packer: P195 and P198): reverse gradients, minimize downstream transfers and force circulation in the lower part of the groundwater table. Pumping in P171-P198: maximum extractable flow without drying the wells to recover the injected volumes.

6 tracer tests have been carried out to establish the real movement of the reagents (Table 2), which was intended to establish the injection conditions to reach the objective level and a residence time of several hours, the preferential routes, how it moves the tracer downstream, depths at which it moves, mass and transit time, flow rates by injection and pumping, areas with DNAPL presence, recovery rate and possible injection, pumping and isolation (packer) strategies.

The injected volume varied between 5 and 12 m³ per test using a solution with NaCl (10 g/l), NaBr (0.4 g/l) and 1-Heptanol (500 ppm). Common salt generates conductivities contrasted with the aquifer, which allows vertical conductivity profiles to be made, delimiting fractures or preferential circulation sections. Also, the placement of level and conductivity probes allows their continuous measurement, establishing the exact moment the injected fluid reaches a borehole. Bromide allows recovery and dilution rates to be established, while 1-Heptanol was tested to establish areas with DNAP that should preferably be retained.

TABLE 2. TRACER TESTS-1

Injection test in P192: check that the injected flow is distributed to saturate the vadose zone and the upper part of the water table. Time of arrival and passage in the barrier zone.
Injection test in P198 on packer, pumping in P171-P195 and P196: Injectable flow to reach the maximum level possible in P198 and P196 without exceeding level 810 in P192. Balance the losses of fluids downstream with the injection to maintain the maximum level as long as possible.
Injection test in P198 bis, with double packer, pumping in P171 and P172 and recirculation to P198, Pumping for recovery in P171, P172, P192, P195 and P196. Balance the losses of fluids downstream with the injection to maintain the maximum height as long as possible. Optimize tracer recovery.
Injection-pumping test in P172 and P171: Feasibility of injection and pumping in short times in the same borehole and recovery yields.
Injection-pumping test at the bottom of the cell: Establish whether there is a connection in the deepest section of boreholes P195 to P198.
Injection test in P129 to verify that the tracer reaches the closest boreholes to the river.

Barrier zone operation:

To prevent the surfactant and solubilized COCs from reaching the Gállego River, a barrier is provided consisting of:

- Dosage of NaOH (25%) to base the aquifer at a target pH of 12. It is arranged in three boreholes P81 (117 m from the test cell), P55 (146 m) and P79 (309 m)
- Aeration and vapor extraction in boreholes I1 (at 312 m) and O1 (at 322 m)
- Dosing of Na2S2O8 with alkaline activation (soda 25%) in O2 (at 344 m from the cell) and P98 (at 441 m).

With this arrangement, the tracer was injected into wells P198 and P195. A double packer was placed in P198 under the injection point. Fluid was recirculated from P171 and P172 to P198 and P195. During the second, third and fourth day after the tracer injection, a surfactant solution of 3, 2.5 and 1 g/l was injected at the beginning of the barrier zone, to simulate the arrival and passage of the surfactant plume. It avoided the surfactant passing through areas with a dense phase. During the execution of the test, control was established through conductivity profiles and sampling and control lasted for three weeks after the injection of tracers.

Results and discussion

E-Mulse 3[®] surfactant has been selected over Tween-Span mixtures due to its good cosolvent capacity, good behavior in alkaline conditions, good biodegradability and easier handling in the preparation of surfactant solutions.

The execution of the boreholes of the test cell and its testification showed that the heterogeneity of the environment is very high. During the last Lugeon test, there was a 10-meter drop in the water table, connecting the lower part of the P198 borehole with P172 and P171. The selected zone divides the M layer into two hydro geologically independent sublayers in low water separated by siltstones. The fractures with the possible presence of DNAPL are located from the P194 well downstream. Several methanol extractions in the fractures show COCs sum values between 0.5 and 50 g/m², concentrations that are indicative of the presence of DNAPL. After the drop of the water table, several of these fractures remain in the vadose zone, conditioning the injection strategies.

The hydrogeological tests show that the injection of fluids in low water is resolved with the vertical filling of the vadose zone. To saturate the area of interest without generating transversal flow to other layers, a flow rate close to 16 l/min is necessary, which must be maintained during the reaction time by equalizing inputs and outputs downstream. With packers in P198, the downstream flow released can be reduced to 10 l/min. Below level 796, the boreholes upstream of P198 are disconnected, interrupting downstream communication. Depending on the recovery of the initial conductivity conditions, the fluid velocity in the cell is between 5 and 10 m/h. A response has been observed in the evolution of water levels downstream in all the wells equipped with divers. At the beginning of the barrier zone (350 m from P198) the water level rise would indicate velocities between 1,100 and 1,500 m/d, considered excessively fast and explained by pressure adjustment.

During the tracer tests the response of the water levels is similar to that observed in the hydrogeological tests. At the beginning of the barrier zone, the water level response has an average delay of 5 hours, while the arrival of the injected fluids (increase in conductivity) occurs after 24 hours until reaching the maximum value at 52 hours, from the start of the injection. If the tracer is not extracted in the cell, this maximum value represents a mixing percentage of 30-70 (tracer-leachate), indicative that the dispersive component increases notably throughout the plume (Figure 2). In the case of pumping to recover tracer, the maximum percentage that reaches the barrier zone is 12.5%.

The use of bromide does not provide more information than conductivity. However, its use is justified to carry out mass balances in tracer recovery. Heptanol has not shown differences in most of the tests, it has not been possible in the area of the cell to identify specific areas with DNAPL, foreseeably, the contact time is short, and equilibrium is not reached.



FIGURE 2: REPRESENTATION OF THE DIMENSIONLESS VARIABLE F IN THE VERTICAL OF EACH BOREHOLE OVER TIME IN THE TRACER INJECTION TEST AT P192. $F_t = \frac{(k_t - k_o)_{cota}}{k_{inyección}}$, WHERE K_T IS THE CONDUCTIVITY AT TIME T AT LEVEL X, K₀ IS THE CONDUCTIVITY AT TIME ZERO AT THAT LEVEL, AND K_{INJECTION} IS THE CONDUCTIVITY OF THE INJECTED FLUID

The test to check the barrier zone function simulates the selected surfactant injection strategy. The mass recovery of tracers by pumping is between 63-72% of the injected mass.

The injection of caustic soda allows the pH to be maintained in suitable conditions throughout the tracer step, which is reflected in the practical elimination of HCHs and the high generation of trichlorobenzenes (Table 3). In addition, a high generation of dichlorobenzenes (not verified in the laboratory) is produced. However, downstream of the persulfate injection, the pH tends to neutralize due to the carbonated nature of the aquifer.

A high degree of dispersion of the fluid injected was noticed. Considering the volume of fluid transmitted downstream of the cell remains constant (in most of the boreholes, the initial level is recovered), the concentration of bromide injected in P198 would be reduced to 3.2% when it reached the Gallego river. Table 3 shows the dilution of bromide downstream and the corresponding COCs concentrations.

In the barrier zone, applying aeration and persulfate with alkaline activation has eliminated the surfactant in just 20 m of travel, in addition to significantly reducing the concentration of the lighter chlorinated substances that reach this area, maintaining the concentration of the heavier chlorinated substances practically at zero.

Conclusions

During the execution of the test cell boreholes, it was revealed that the thickness of the sandstone layer is limited to 1 m, which allows for filling the layer width by injecting the volume at a single point. Many of the fractures in which evidence of DNAPL is detected have remained in the vadose zone, so the injections must reach the maximum level without connecting with parallel layers.

The injected flow is distributed mainly in the vertical, saturating the vadose zone and with less distribution in the highest part of the water table. The injection of reagents must be carried out in low water conditions.

The effective permeability in the cell area above the water table in low waters (summer, autumn) and up to the approximate level 809 is 0.4%. The volume stored upstream of the P198 well is approximately 2.4 m³. In the first test, the release of flows downstream of the cell was approximately 16 *V*min. However, cleaning fractures during the tests has improved the connection between boreholes. In the last test, the equilibrium flow has gone to 32 l/min.

	TABLE 3. EVOLUTION	OF THE TRACER AND	COCS CONCENTRATION	ALONG THE BARRIER ZONE-1
--	--------------------	-------------------	--------------------	--------------------------

				Ir	iitial	Final			
Well	Distance to P198 (m)	Passage time (h)	Br-Peak (mg/l)	∑COC (mg/l)	\sum SCOV ¹ (mg/l)	∑COC (mg/l)	\sum SCOV ¹ (mg/l)		
P81	135	69,1	260	83,7	30,4	65,9	0,21		
P79	327	86,3	148	344	316	18	0,03		
P127	367	200	87	30,8	13	27,6	0,01		
I1	388	220	93	25,8	25,6	15	0		
O2	420	337	55	33	21,1	4,2	0,03		

¹The SCOV is the sum of chlorinated compounds heavier than pentachlorobenzene

With the injection-extraction strategy applied, the recovery of reagents by pumping after ceasing the injection is between 60 and 70% of the injected mass. This percentage means that, in the case of injecting surfactants, 30-40% of the injected mass must be treated in the barrier zone to prevent it from reaching the Gállego river. From the start of the injection, the response time to adopt measures in the barrier zone is approximately 27 hours, reaching the peak at 52 hours. The dispersion of the injected fluids causes the release flow from the cell to last up to 5 days after the injection.

In a heterogeneous fractured medium, previous studies (detailed testing of boreholes, hydrogeological and tracer tests) are essential for a safe design in the application of surfactants.

Acknowledgements

This work has been supported by EU LIFE

Program (LIFE17 ENV/ES/000260) and the Aragon Government.

References

1. J. Fernandez, M.A. Arjol, C. Cacho, POPcontaminated sites from HCH production in Sabinanigo, Spain, Environmental Science and Pollution Research, 20 (2013) 1937-1950.

2. Santos, A., Fernandez, J., Guadano, J., Lorenzo, D., Romero, A., 2018a. Chlorinated organic compounds in liquid wastes (DNAPL) from lindane production dumped in landfills in Sabinanigo (Spain). Environ. Pollut. 242, 1616–1624.

3. J. Vijgen, B. de Borst, R. Weber, T. Stobiecki, M. Forter, HCH and Lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue,

Environmental Pollution, 248 (2019) 696-705

LIFE SURFING PROJECT, ENHANCED SURFACTANTS EXTRACTION (SEAR) IN A FRACTURED AQUIFER

Fernández, J.¹ Santos, A.², Herranz, C³. Net, J.¹ Lorenzo, D.², Arjol, M.A.³

¹Department of Agriculture, Livestock and Environment, Government of Aragon, Spain ²Chemical Engineering and Materials Department, University Complutense of Madrid, Spain. ³Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain

Summary

The LIFE SURFING project has tested the application of SEAR and SISCO techniques in the fractured aquifer of the Bailín landfill (Sabiñánigo, Huesca). After 16 years of pumping and treatment, the dense phase (DNAPL) from lindane manufacturing residues is in the residual phase, with very low pumping performance. After several hydrogeological and tracer tests, two tests have been designed and carried out in which a solution of a non-ionic surfactant (E-Mulse 3[®]), sodium chloride and sodium bromide as tracers to facilitate monitoring and mass balances, and hydrogen peroxide to favor the dispersion of the reagents.

The injections have made it possible to reach the vadose zone, where the presence of DNAPL was detected in some fractures, as well as sufficient dispersion and contact time (minimum 6 hours). In the first test, 9.3 m³ were injected, and 7.1 m³ were extracted. The maximum concentration of POPs in the recovered volumes was 5 g/l, with an average concentration of 0.4 g/l. In the second test, 6 m³ were injected, and 5.9 m³ were recovered, with a maximum concentration of POPs of 5 g/l and a mean value of 2.5 g/l.

A NaOH solution was injected into the downstream flow to prevent the polluted volumes released from reaching the Gállego River. NaOH addition favors the dehydrochlorination of the heavier chlorinated substances and the breaking of the surfactant emulsion. In the barrier zone, located between the injection zone and the river, the application of caustic soda, sodium persulfate, temperature and aeration has been combined. The surfactant released downstream disappeared by hydrolysis, dilution and absorption and did not reach the barrier zone. The POPs downstream of the barrier zone have not exceeded 40 ppm of the total sum, representing the heaviest chlorinated compounds between 1 and 5% of the total POP mass.

Once the tests were finished, the boreholes were cleaned. In this operation, more than 100 kg of DNAPL have been recovered. The area where the injections were made was left with minimal concentrations of DNAPL in conditions to execute the assay of joint application of oxidants and surfactants (SISCO).

Keywords

Lindane, DNAPL, fractured aquifer, surfactants, SEAR, persulfate.

Introduction

During the eighties of the previous century, INQUINOSA dumped residues from lindane manufacturing directly on the ground at the Bailín landfill. These residues included a dense nonaqueous phase (DNAPL) [1]. This dense phase comprises more than 28 organochlorines, mainly from benzene to heptachlorobenzenes [2]. Due to their toxicity and environmental persistence, some have been included in the list of persistent organic pollutants by the Stockholm Convention [3]. This residue percolated in favor of fracturing, reaching depths up to 40 meters. In its progress, it exceeded the western landfill limit and reached around 300 m towards the Gállego River. In 2004, this DNAPL was detected in a new borehole, its progress was delimited, and pumping and external management of the dense phase began. After extracting more than 30,000 liters the DNAPL is in a residual phase.

Laboratory work began in 2011 to address surfactant-enhanced extraction. When the current situation was reached in 2017, the application of surfactants and the combination with oxidants was addressed through the Life SURFING project: "SURFactant enhanced chemical oxidation for remediatING DNAPL" (EU LIFE Program LIFE17 ENV/ES/000260). The E-Mulse 3[®] surfactant was selected on a laboratory scale due to its good cosolvent capacity, good behavior in alkaline media, ease of handling and good biodegradability. Subsequently, the necessary installations were executed, and the test cell boreholes were drilled. The heterogeneous fractured nature of the aquifer required an extensive campaign of hydrogeological and tracer tests to know in detail the communication between boreholes, the injection flows required to saturate the areas with DNAPL and the strategies to maximize the contact time and the recovery of injected fluids. Finally, the operation of a barrier zone that combines alkaline hydrolysis, aeration and vapor capture, and oxidation with persulfate was tested. These previous works have facilitated the design of two tests for extracting dense phase improved with surfactants.

SEAR 1:

This first test aims to solubilize the dense residual phase between boreholes P192 and P198 and recover the maximum volume of surfactant and contaminants. Before the test execution, sampling and vertical profiles of conductivity were measured.

A double packer was placed at P198 to reduce the flow leakages downstream of the cell. Surfactant solution was injected in boreholes P198 and P195 with a flow rate of 1 m3/h, until the desired groundwater level was reached. Pneumatic pumps were placed at P171 and P172 boreholes to minimize downstream losses. During the surfactant injection, the flows extracted in P171 are recirculated to the P195 borehole. After the injection, fluids extracted at P171 were sent to the decanter. Operation in borehole P172 is similar, but the fluid extracted is recirculated to well P198. Wells P196 and P195 are equipped with electric pumps to recover the injected fluids once the injection is finished. These polluted emulsions are pumped and discharged to a decanter. To degrade the surfactant and the COCs leakages downstream, NaOH dispensers are installed in the P81, P55 and P129 wells. In boreholes I1 and O1, oxidizer, antifoam and air were injected, and generated vapors were captured. Downstream oxidant and NaOH were also added to the P99 borehole.

Previously to the surfactant injection, pumping was carried out in the cell to reach a water level low enough. 12 m³ with 19.8 g/l of Emulse[®], 2.5 g/l of NaCl (final conductivity 6500 µS/cm), 190 mg/l of NaBr and 1% H₂O₂ prepared for injection into the test cell. 10 m³ of an aqueous solution containing 80 g/l of sodium persulfate and NaOH at pH 12 was prepared for the oxidant injection in the barrier zone. Next to the aeration boreholes, a 10% solution of defoamersilicone based is available. In addition to continuous measurements with divers, manual vertical conductivity profiles and sampling at discrete depths were carried out in 31 boreholes. pH, conductivity, bromide, surfactant and COCs were determined in groundwater samples. The monitoring was maintained in each borehole until recovering initial groundwater levels.

SEAR 2:

The second test aims to solubilize the dense residual phase in boreholes P171 and P172 and recover the maximum volume of surfactant and contaminants. The distance between boreholes is 9 m, so a push-and-pull type test was considered. The aqueous surfactant solution is injected in boreholes P171 and P172 at an approximate flow rate of 1 m³/h, to reach the highest groundwater level possible. In total, 6 m³ were injected for 5.5 hours. To reduce the downstream leakage flow, an electric pump was installed at P174, 57 m downstream of P171. The extracted flows at P174,

were recirculated to P98. For the recovery of injected fluids after the injection has finished, well P171 is equipped with an electric pump, well P172 is equipped with a pneumatic pump, and well P174 is equipped with an electric pump. The pumping is maintained during the injection and until the end of the pumping in P171. The equipment of the barrier zone is maintained to degrade the surfactant and COCs leakage downstream. To monitor the test, 29 fixed probes (divers) are available, 18 with level, conductivity and temperature measurement and 11 with level and temperature.

6 m³ of surfactant solution with an average concentration of 17 g/l of E-Mulse $3^{\text{(B)}}$, 3.8 g/l of NaCl, 186 ppm of NaBr and 1% of H₂O₂ were prepared for injection. 9 m³ of an aqueous solution containing 80 g/l of sodium persulfate and NaOH at pH 12 was prepared for the oxidant injection in the barrier zone. The oxidant injection began 2 hours after the surfactant injection started and was maintained for 55 hours in I1 and O1; a total of 8 m³ were injected.

At the same time that persulfate was injected, aeration was carried out from the bottom of the same boreholes and maintained for 10 days. In addition to continuous measurements with divers, manual vertical conductivity profiles and sampling at discrete depths were carried out in 28 boreholes. These samples determine pH, conductivity, bromide, surfactant and COCs. The monitoring was maintained in each borehole until recovering initial groundwater levels.

Results and discussion

In the first test, 9.3 m³ of the surfactant solution was injected (for 8 hours). The contribution of peroxide favors the generation of bubbles and foam, allowing it to reach all the areas with the possible presence of DNAPL. In addition, it promotes the cleaning of the fractures by mobilizing clays that accumulate in the boreholes and the decanter. 7.13 m³ of polluted emulsion have been collected by pumping, recovering 55% of the injected tracer and 30% of the injected surfactant, which shows that surfactant behavior is not conservative. The response of groundwater levels in the test cell is fast (Figure 1). After pumping, the groundwater table drop was 2 meters below the previous level of the groundwater table, indicating that the extraction of fines and clays with the emulsion increased the communication between boreholes.

Before the barrier zone, the behavior of the groundwater levels is complex. There is a fast rise with the injection, then the groundwater level drops, but it rises again; the peak of groundwater level is noticed at 5 days, and the decline lasts up to 10 days. Considering the conductivity increases and the bromide arrival, the injected fluid escaping downstream reaches the barrier zone on the same day of injection, faster and deeper than noticed in

previous tracer tests. The subsequent rise in groundwater levels and possibly the greater depth in the circulation of reagents can be attributed to the improvement in communication at low levels observed in the test cell, which allows the flow to be maintained downstream for longer, but with fluids without reagents.

In the barrier zone, NaOH dosing begins when the surfactant is injected. The injection of sodium persulfate activated with NaOH began 2 hours after the surfactant injection and was maintained for 50 hours in I1 and O1. A total of 10 m^3 were injected. In the cell, concentrations of solubilized COCs (Figure 2) of more than 5 g/l are reached, which decay rapidly downstream. The surfactant leakage from the cell (fig. 2) does not reach the well located

75 meters downstream from the injection point (P198). Surfactant that escaped from the cell is absorbed in the DNAPL or adsorbed in the clayey fraction that fills some fractures downstream. On the contrary, leaked bromide shows conservative behavior during its transport downstream until it reaches the zone with persulfate.

The COCs composition downstream is modified by the effect of NaOH, and alkaline hydrolysis transforms the heavier chlorinated COCs into tetra-, tri- and dichlorobenzene. After aeration and oxidation in the barrier zone, the COCs concentration drops to values below 10 ppm, and HCHs concentrations are below the detection limit.



FIGURE 1. EVOLUTION OF GROUNDWATER LEVELS IN THE SEAR 1 TEST



FIGURE 2. EVOLUTION OF COCS, SURFACTANT AND TRACER DOWNSTREAM IN THE SEAR 1 TEST

In the second SEAR test, the injection of reagents was maintained for 5 hours with a total injected volume of 5.96 m^3 . As in the first test, the generation of foams almost saturated the vadose zone. 5.9 m³ of extracted polluted emulsion were pumped, recovering 60% and 40% of the injected tracer and surfactant, respectively.

The test zone boreholes immediately recover the initial level after pumping (Figure 3), but the groundwater level continues to drop for a week until stabilizing 4 meters below the initial groundwater level. Again, an improvement in

communication between boreholes is noticed with depth.

Up to the barrier zone, fast response of groundwater levels due to the injection is noted. However, the response in the barrier zone and up to the river was lower than noticed in previous tests. After reaching the groundwater level peak, there was no descent in all cases, indicating that the entered flow was filling a section with poor communication.

Considering the arrival of the bromide, the leakage of the injected fluids reaches the barrier zone at 24 hours, with a longer delay than noticed in other tests, which is justified by the lower volume that

circulates downstream and the seasonal low groundwater levels.



FIGURE 3. EVOLUTION OF GROUNDWATER LEVELS IN THE SEAR 2 TEST

Circulation downstream only occurs when wellcommunicated levels between boreholes are reached

In the barrier area, the dosing of NaOH began at the time the injection began, it was maintained for 60 hours, and 170 liters of 25% NaOH were added. The pH values in P55 well have been maintained above 11.5 while the fluid escaped from the test cell crossed this well.

The injection of sodium persulfate activated with NaOH began 2 hours after the start of the surfactant injection and was maintained for 60 hours in I1 and O1. A total of 7 m³ were injected. As in the previous test, aeration was carried out in these boreholes. The dosing of activated persulfate was reinforced by injecting 300 L of PS solution downstream (in P98) for 48 hours after finishing the injection in I1 and O1. NaOH dosage downstream of the barrier zone maintained the pH over 11.5 until the plume of leakage fluids crossed this well and persulfate was exhausted.

In the wells with surfactant injection, concentrations of solubilized COCs (fig. 4) higher than 2.5 g/l are reached. Surfactant concentration was detected up to 120 meters (P81) downstream of the injection point, with COCs concentration up to

5 g/l. The surfactant no longer reaches 150 m, although high concentrations of COCs are maintained, which are already rebalanced at 300 meters with maximum values of 0.3 g/l. As in the previous test, the bromide shows the conservative condition and does not decay until it crosses the persulfate dosing zone. Also, as in the previous test, the concentration of COCs drops to values below 10 ppm after aeration and oxidation in the barrier zone, with HCHs falling below the detection limit. Two weeks after the injection, with the groundwater table stabilized, the depth of the boreholes was manually measured, observing an accumulation of fines of up to 10 m in those located in the test cell and downstream to P55. The boreholes were carried out using a self-priming tanker truck, 12 m³ of leachate and fines were extracted with approximately 10 kg of DNAPL in solution and 90 kg as DNAPL mixed with the fines. Three months after the end of the test, the COCs concentrations in the test cell wells remain below those before the surfactant tests, having increased the concentration of VOCs compared to SCOVs. The lower concentration of HCH and other heavier chlorinated substances shows that the presence of DNAPL has been significantly reduced.



FIGURE 4. EVOLUTION OF COCS, SURFACTANT AND TRACER THROUGHOUT THE LAYER IN THE SEAR 2 TEST.

Conclusions

Surfactant-enhanced dense phase extraction is a viable technique in heterogeneous fractured media. However, it requires exhaustive knowledge of the aquifer to design the injection strategy and recovery of surfactant and mobilized contaminants. Adding hydrogen peroxide favors the generation of foams that have filled the vadose area, reaching levels with the surfactant that cannot be reached in the surfactant's absence. In addition, the generation of foams has slowed down the flow downstream and has improved the polluted emulsion recovery by pumping.

There has been a significant mobilization of fines and clays clogging the bottoms of the wells test cell and DNAPL with these particles.

The accumulation of dense phases has not been directly observed due to the significant accumulation of fines. However, the COCs concentrations in the sludge removed from the boreholes using a self-priming tanker truck reached 100 g/l in the wet sample. The surfactant does not have a conservative behavior, being adsorbed in the clays that fill fractures and absorbed in the DNAPL. Surfactant destabilizes at high pHs, preventing its arrival at the barrier zone. The dosing of NaOH downstream favors the alkaline hydrolysis of the heavier chlorinated compounds. The injected fluids escaping downwards that reached the barrier zone have very low HCH and heptachlorocyclohexanes, and moderate concentrations of trichlorobenzenes and lighter chlorinated substances, which facilitates degradation by oxidation with alkali-activated persulfate and aeration. However, to maintain the activation of the persulfate downstream, it is necessary to add NaOH due to the tendency to neutralize the pH in a carbonated medium.

Acknowledgements

This work has been supported by EU LIFE Program (LIFE17 ENV/ES/000260) and the Aragon Government.

References

1. J. Fernandez, M.A. Arjol, C. Cacho, POPcontaminated sites from HCH production in Sabinanigo, Spain, Environmental Science and Pollution Research, 20 (2013) 1937-1950.

2. Santos, A., Fernandez, J., Guadano, J., Lorenzo, D., Romero, A., 2018a. Chlorinated organic compounds in liquid wastes (DNAPL) from lindane production dumped in landfills in Sabinanigo (Spain). Environ. Pollut. 242, 1616–1624.

3. J. Vijgen, B. de Borst, R. Weber, T. Stobiecki, M. Forter, HCH and Lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue, Environmental Pollution, 248 (2019) 696-705.

LIFE SURFING PROJECT, IN SITU CHEMICAL OXIDATION ENHANCED WITH SURFACTANTS (SISCO) IN A FRACTURED AQUIFER

Fernández, J.¹ Santos, A.², Herranz, C.³ Net, J.¹, Saez P.², Arjol, M.A.³, Lorenzo, D.²

¹Department of Agriculture, Livestock and Environment, Government of Aragon, Spain ²Chemical Engineering and Materials Department, University Complutense of Madrid, Spain. ³Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain

Summary

The LIFE SURFING project has tested the application of SEAR and SISCO techniques in the fractured aquifer of the Bailín landfill (Sabiñánigo, Huesca). To minimise the presence of a dense organic phase (DNAPL) composed of more than 28 Chlorinated Organic Compounds (COCs), a test combining surfactants and oxidants (SISCO) was carried out after surfactant application. A solution of persulfate (40 g/l), surfactant (E-Mulse 3[®], 4 g/l) and NaOH (10 g/l) as an activator was injected into two wells. The pH of the injected fluid was strongly alkaline (pH>12). 21.6 m³ of this solution was injected in a 1 m³ pulse over two days. This procedure increases the contact time between the injected fluids and the subsoil to reach the target groundwater levels and increase the injected fluid dispersion. Downstream of the test cell, the groundwater is pumped and recirculated back to the cell. In addition, the foam has been generated to minimise the flow of injected fluids escaping downstream. A solution of xanthan gum (2 g/l) and E-Mulse 3[®] (5 g/l), with an airflow, have been injected downstream of the recirculation well for this purpose.

To maintain the aquifer strong alkaline pH and prolong the persulfate activation time, a NaOH aqueous solution has been injected into various wells downstream, compensating for the buffer effect of the carbonated medium.

In the test cell, the contact time of the reagents in the vadose zone was limited. In contrast, in the saturated zone, the oxidation reaction has been maintained until the exhaustion of persulfate.

COPs solubilisation and oxidation continued downstream until the surfactant and oxidants were exhausted, maintaining the oxidation reaction in the saturated zone. The injected fluid that escaped from the test cell reached the barrier zone without a dense organic phase and with low solubilised COCs.

It is estimated that around 20 kg of DNAPL has been degraded without noticing a significant rebound in concentrations after two months. Actions to increase the contact time, particularly the recirculation rates and the foam barrier, are necessary to extend this treatment to the whole site.

Keywords

Lindane, DNAPL, fractured aquifer, surfactants, SISCO, persulfate.

Introduction

During the eighties of the previous century, INQUINOSA dumped wastes of lindane manufacturing directly on the ground at the Bailín landfill. This waste included a dense non-aqueous phase (DNAPL) [1]. This dense phase comprises more than 28 organochlorines, mostly from chlorobenzene to heptachlorobenzenes [2]. Due to their toxicity and environmental persistence, some have been included in the list of persistent organic pollutants by the Stockholm Convention [3].

In 2004, this DNAPL was detected in a newly constructed well. Its advance was described, pumping and external management of the dense phase began, and more than 30,000 liters of DNAPL as liquid phase was extracted. In 2011, the DNAPL extraction yield dropped, and laboratory work was initiated to investigate the DNAPL extraction enhanced by surfactants. In 2017, applying surfactants and the combination with oxidants was addressed through the Life SURFING project: 'SURFactant enhanced chemical oxidation for remediating DNAPL' (EU LIFE Program LIFE17 ENV/ES/000260) to eliminate the residual DNAPL in the subsoil of the old landfill.

In the project first phase, E-Mulse 3[®] was selected as a surfactant at the laboratory scale due to its good cosolvent capacity, good behavior in alkaline media, ease of handling and good biodegradability. Oxidant (persulfate) and activator (NaOH) were selected in the previous LIFE Discovered project "Lab to field, soil remediation demonstrative project: new ISCO application to DNAPL multicomponent environmental problem".

The necessary facilities were installed in LIFE SURFING, and new cell wells were drilled. The heterogeneous fractured nature of the aquifer demanded an extensive hydrogeological and tracer testing campaign [4] to design two surfactant-enhanced dense phase extraction (SEAR) tests [5]. After removing most of the dense phase in the cell, the aquifer was ready to apply surfactant enhanced in situ oxidation (SISCO) technologies, which is the subject of the present communication.

Experimental Setups and procedure

24 m³ of the surfactant-oxidant solution with 21.8 g/l of $Na_2S_2O_8$, a molar ratio NaOH: PS 1:1 and 3 g/l of E-Mulse 3[®] was prepared (the pH in the mixing tank is higher than 12).

The injection was carried out in wells P195 and P198 in 16 pulses during 30 hours, injecting 1 m³ each hour, with a last pulse at 44 hours in which 2 m³ were injected.

To minimise the groundwater entry, diluting the reagents, 1 m³ of the prepared oxidant-surfactant solution was dosed at a rate of 100 l/hour upstream of the test cell (P179N) after the last injection of each day. An electric pump was installed in well P172 (9.3 m downstream of P198) to recirculate the flows escaping downstream to the test cell. In addition, a double packer was placed in P198 to isolate the area with better downstream of P198, a solution of 5 g/l of E-Mulse 3[®] and 2% Xanthan Gum was dosed at an average flow rate of 20 l/h during the entire SISCO injection time, with simultaneous injection of airflow to generate foams.

A solution of 25% in NaOH was dosed in wells P174, P55, P79 and P98 from the injection beginning to 48 hours after the injection ended to maintain the groundwater pH around 12. In the barrier zone, aeration (5 m³/h per well) and vapor extraction (6 m³/h per well) were maintained in wells I1 and O1 for 14 days from the start of injection. Foam generation in these wells was controlled by adding a siliconised defoamer.

The test monitoring was carried out using 23 fixedlevel probes. Vertical conductivity profiles and groundwater sampling with a discrete sampler were carried out in 33 wells to cover the passage of the escaped fluids plume. On these samples, pH, conductivity, surfactant, persulfate, free chlorine and COCs were determined.

Results and discussion

The injection of reagents by pulses allowed them to reach the target groundwater levels in the test cell (Figure 1) and favored the COCs solubilisation in the vadose zone. After each injection, the initial groundwater levels recovered rapidly (with oscillations between 4 and 6 meters). It is unknown if the contact time was sufficient to establish an equilibrium with the contaminants absorbed in the rock matrix. It is necessary to wait for the season with high water groundwater levels to observe a possible rebound in the COCs concentrations. However, the adsorbed DNAPL will be further removed by an oxidation treatment without surfactant or bioremediation.

The generation of a foam barrier at P171 (18 m downstream of the injection at P198) has been partially efficient. Foam generation occurred in the vadose zone, and the layer foam width was

unknown. Increasing the efficiency of the foam injection requires investigation yet. The direct injection of foam under packers will favor its diffusion below the water table and in the layer width. It is also necessary to improve the durability of the foam.



FIGURE 1. EVOLUTION OF WATER TABLE LEVELS. THE GRAPH ON THE TOP SHOWS THE WELLS IN THE INJECTION ZONE. THE GRAPH ON THE BOTTOM SHOWS THE WELLS DOWNSTREAM OF THE INJECTION ZONE, KEEPING THE EVOLUTION IN ONE OF THE INJECTION WELLS AS A CONTRAST

Downstream, the escaped fluids from the test cells generate a plume in the groundwater with a high dispersion component (Figure 1). Three days after injection, this plume has wholly passed well P81 (at 117 meters from P171). Up to this well, the recovery of the previous groundwater levels occurred 4 days after the injection started. Downstream from well P79 (at 250 m from P171) and the end of the barrier zone (well P223 at 440 m from P171), it was delayed between 6 and 14 hours in starting the rise in groundwater levels. The maximum groundwater level rise in these wells (around 10 m) was reached between 40 and 70 hours, and this maximum was maintained for at least 20 days. A filling effect until reaching a water level with better communication downstream explains this observation. A slow recovery of the groundwater level was noticed during the next 3 months. The groundwater level rise is smoothed downstream, reaching 3 meters at P222 (at 601 m from P171) and 40 cm at P142 (at 845 m from P171), with a tendency in both cases to recover the previous level after 5 days.

The conductivity changes can not establish the pass of the escaped fluids plume while this parameter was modified by adding NaOH downstream of the injection point. Persulfate may be a good indicator as it has reached the wells closest to the river, although this is a reagent and not a conservative tracer. Persulfate (PS) (Figure 2) reached concentrations above 10 g/l up to 450 m from the injection point.

Downstream, up to well P222 (601m from P171), PS arrival was delayed up to 48 hours, and in the wells closest to the river, PS was lower than 1 g/l.





FIGURE 2. EVOLUTION ALONG THE M-LAYER AND WITH TIME SINCE INJECTION OF PERSULFATE CONCENTRATION, SURFACTANT AND PH In well P198 and those wells located upstream, the consumption of persulfate is prolonged until 500 hours in the saturated zone, associated with the pH changes.

The saturated zone acted as a batch reactor. The PS depletion in groundwater was also affected by the density of PS solutions, producing a PS gradient with accumulation in the bottom of the well with time. In the barrier zone and downstream, PS drops below 5 g/l at around 150 hours due to reaction, dispersion and accumulation in wells that did not recover the initial groundwater level. The pH dropped downwards due to the buffering effect of the carbonate aquifer, and an alkali dosage was necessary over time and across the layer to keep the PS activation.

As shown on Figure 2, the surfactant reaches the beginning of the barrier zone with maximum concentrations below 0.5 g/l and disappears along this zone. The surfactant showed a progressive depletion (Figure 3), faster in the zone with DNAPL, disappearing in wells I1 and O1 (340 m from the end of the injection cell), associated with a greater consumption of persulfate, favored by the mixing produced by the aeration and the increase in temperature generated in both wells.



FIGURE 3. EVOLUTION OF PEAKS OF REAGENTS AND COCS CONCENTRATION ALONG LAYER M.

400 Distance to P171 (m) 600

800

-200

0

200

Maximum COCs concentration in groundwater downstream of the test cell (Figure 3) was 0.7 g/l (P55 at 145 m from P171, due to the DNAPL presence in this well). As long as the surfactant capacity is maintained and DNAPL is present, the

0

1000

COCs concentrations are high. A significant concentration of SCOV was noticed due to the dehydrochlorination of heavier non-cyclic COCs at alkaline pH, increasing TCB and TetraCB concentrations. In some wells, the alkaline hydrolysis seems to progress, generating high concentrations of dichlorobenzene, a process already observed in other field tests that we have not reproduced in the laboratory.

The reaction of dissolved COCs with the oxidant (Figure 3 and Figure 4) continued downstream of well P55 (200 m from the injection point) until the depletion of persulfate.



FIGURE 4. EVOLUTION OF COCS PARTITIONING IN TWO WELLS LOCATED BEFORE THE BARRIER ZONE.

Most chlorinated compounds (PCX+HCX+HCH+ +HeCH) disappear, and COCs are reduced to 75 and 97% of the peak value with time. The zone works as a discontinuous reactor if the initial groundwater level has not been recovered. The COCs concentration throughout the M layer depends on DNAPL and surfactant presence, pH (dehydrochlorination reactions) and COCs oxidation by persulfate. The trend is always towards the total disappearance of the heaviest COCs. An initial increase in DCB, TCB, and TetraCB was noticed with the depletion of these compounds with time and distance.

The effectiveness of the S-ISCO was evaluated considering that the base groundwater level was recovered in the injection zone (upstream of P171). The injected volume, except approximately 2 m³ of storage capacity in the saturated zone of the cell, has circulated downstream. In wells recovering the groundwater level, the instant flow rate and mass of COCs and reagents passing at the corresponding distance from P198 were estimated, at least up to well P79 (Table 1).

Downstream, the groundwater base level was not recovered: with the difference in groundwater levels and average permeability, it has been estimated that 6 m^3 have been retained.

The drop of COCs concentrations to values below 10 ppm and the integration of COCs profiles with time

in the M layer allows estimating that about 20 kg of COCs have been oxidised to non-harmful compounds.

Two months after the end of the test, the concentrations in the test cell remain very low, and no rebound has been noticed in the saturated zone. However, are the groundwater levels are low, the rebounds in the vadose zone will be analysed in the next season.

TABLE 1. MASS OF COCS PASSING THROUGH WELLS DOWNSTREAM OF THE TEST CELL IN THE S-ISCO TEST

Compound	P174	P81	P55	P79	P222
PS (kg)	355	347	568	213	35
Emulse (kg)	21.0	6.6	10.3	1.6	0.0
CBs (g)	911	402	1017	516	53
DCBs (g)	1362	651	2016	753	66
TCBs (g)	2636	1217	3205	1026	42
TetraCBs (g)	2884	1325	3387	748	10
PentaCX (g)	918	268	1531	177	1
HexaCX (g)	9.1	1.1	20.5	0.8	0.1
HCH (g)	662	163	1054	74	1
HeptaCH (g)	7.7	2.0	26.8	0.8	0.2
$\sum \text{COCs}(g)$	9475	4075	12365	3322	173

Conclusions

The simultaneous injection of oxidant (persulfate activated with alkali) and surfactant allows the effective degradation of organochlorines in a fractured medium that has been affected by DNAPL infiltration. A proper injection strategy was designed to increase the contact time between residual DNAPL and oxidants in the target area.

Techniques (such as recirculation and application of foam barriers) that slow down the flow escaping downstream of the target zone were also applied. However, the foam barrier showed limited efficiency under the conditions tested. It is crucial to ensure that oxidant activation is maintained downstream to complete the COCs oxidation before the scaped fluid reaches the Gallego river. For that purpose, alkali inputs along the generated plume in the M layer are required. In the S-ISCO carried out al LIFE SURFING project, the residence time injected fluid in the M layer was high enough to reach the depletion of oxidant, COCs and surfactant to values that not suppose a risk for the receptors.

The alkaline pH in the M layer yielded a rapid dehydrochlorination of the heavier COCs. The formed COCs are more easily oxidable in the presence of PS and alkaline pH. The selected surfactant E-Mulse 3[®] solubilises DNAPL and is stable in alkaline conditions. Surfactant was partially retained in the soil matrix and degraded by the oxidant during its transport through the M layer, achieving negligible concentration at the groundwater discharge to the Gallego river.

In the LIFE SURFING Project, 240 kg of DNAPL have been removed, 20 kg of which were removed in situ during the S-ISCO test. The treatment developed and applied in Bailín to eliminate the residual DNAPL in a fractured medium using surfactants and oxidants is not a fixed protocol but a methodology that must be adapted to each case. A detailed characterisation of the aquifer behaviour is critical for the success of SEAR and S-ISCO trials. Moreover, the injection strategy design should allow for reaching the target zones and achieving a sufficient contact time. Implementation of downstream measures to control the advance of the plume with dissolved COCs and reagents must also be carefully considered.

Acknowledgements

This work has been supported by EU LIFE Program (LIFE17 ENV/ES/000260) and the Aragon Government.

References

1. J. Fernandez, M.A. Arjol, C. Cacho, POPcontaminated sites from HCH production in Sabinanigo, Spain, Environmental Science and Pollution Research, 20 (2013) 1937-1950.

2. Santos, A., Fernandez, J., Guadano, J., Lorenzo, D., Romero, A., 2018a. Chlorinated

organic compounds in liquid wastes (DNAPL) from lindane production dumped in

landfills in Sabinanigo (Spain). Environ. Pollut. 242, 1616–1624.

3. J. Vijgen, B. de Borst, R. Weber, T. Stobiecki, M. Forter, HCH and Lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue, Environmental Pollution, 248 (2019) 696-7054. Fernández J. Santos A., Herranz C., Cano E., Lorenzo D., Arjol M.A., Salvatierra A., Life SURFING project, preparatory works for the injection of surfactants and oxidants. In this same Forum.

5. Fernández J. Santos A., Herranz C., Net J., Lorenzo D., Arjol M.A., Life SURFING project, enhanced surfactants extraction (SEAR) in a fractured aquifer. In this same Forum.

LIFE SURFING PROJECT: CONTAMINATED EMULSION TREATMENT BY ADSORPTION IN GAC AND ADSORBENT REGENERATION

Sanchez-Yepes, A.¹, Santos, A.¹, Fernández, J.² Herranz, C.³ Cano, E.², Lorenzo, D.¹

¹Chemical Engineering and Materials Department, University Complutense of Madrid, Spain ²Department of Agriculture, Livestock and Environment, Government of Aragon, Spain ³Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain

Summary

The LIFE SURFING Project has tested the application of Surfactant Enhanced Aquifer Remediation (SEAR) and In Situ Chemical Oxidation enhanced by Surfactant addition (SISCO) in the Bailin Landfill (Sabiñanigo, Spain). The fractured aquifer was contaminated by discharges of a dense organic phase produced as residuum in the lindane manufacture nearby. This DNAPL comprises a complex mixture of more than 28 Chlorinated Organic Compounds, COCs. Physical extraction of DNAPL is already inefficient, and more advanced techniques were required for either DNAPL extraction or in situ degradation. SEAR has been successfully applied in the LIFE SURFING project to extract the residual DNAPL from the most polluted area of the landfill. The injected fluids are extracted in the SEAR treatment, and contamination is transferred from the subsoil to the extracted emulsion. This polluted emulsion containing dissolved COCs and surfactant needs to be treated to eliminate the COCs and, if possible, recover the surfactant. In this context, adsorption on Granular Activated Carbon (GAC) has been proposed as an on-site treatment of the polluted fluids extracted in SEAR application in the landfill. In the circular economy scenario and to avoid transporting contaminated residues out of the landfill, on-site regeneration of spent GAC has been studied using Thermal Activated Persulfate (TAP). A column filled 20 g of GAC used in the wastewater treatment plant of Bailin Landfill has been built and operated at a lab scale. A volume of 280 ml of a polluted emulsion obtained in the SEAR event of the LIFE SURFING project carried out in May 2022 was adsorbed on GAG (COCs and surfactant, E-Mulse 3[®], concentrations being 9100 and 12000 mg/l, respectively). The saturated GAG was regenerated with TAP at 60°C (PS concentration 40 g/l) and a new adsorption cycle was carried out. This procedure was repeated three times to determine the recovery of the adsorption capacity and the selective oxidation of COCs in the GAG surface. It was found that GAG adsorbed about 115 mg $COCs/g_{GAC}$, being this value stable in successive adsorption-regeneration cycles. The unproductive PS consumption decreases in the presence of adsorbed organic compounds, and the surfactant adsorption decreases with the regeneration cycles (from 144 to 47 mg $E3/g_{GAC}$). Therefore, the adsorption-regeneration cycles tested allow selective removal of COCs from the emulsion, partially recovering the surfactant used and reusing the GAC without generating a secondary residuum.

Keywords

Granular Activated Carbon, LIFE SURFING, Thermal Activated Persulfate, DNAPL, Bailin, Regeneration

Introduction

The LIFE SURFING Project has tested the application of Surfactant Enhanced Aquifer Remediation (SEAR) and In Situ Chemical Oxidation enhanced by Surfactant addition (SISCO) in a fractured aquifer affected by a dense phase from lindane manufacturing residues. After 16 years of pumping the Dense Non-Aqueous Phase Liquid (DNAPL) in the Bailín landfill aquifer (Sabiñánigo, Huesca), the physical extraction of DNAPL is already inefficient, which makes it necessary for the application of chemical techniques that allow cleaning of the residual DNAPL. This DNAPL comprises a complex mixture of more than 28 Chlorinated Organic Compounds, COCs [1].

In the SEAR technology, an aqueous solution containing the surfactant (cosolvents and salts are optional) is injected into the subsurface and then extracted and treated on-site. When a surfactant is added to the aqueous phase, interfacial tension decreases, enhancing the solubilization and mobilization of DNAPL[2, 3]. In the LIFE SURFING project, a nonionic and biodegradable surfactant, E-Mulse 3[®], previously selected at lab scale [4], has been used and injected in the cell test of the Bailin Landfill. Extraction of the injected fluid is required to avoid contamination dispersion out of the cell test. The extracted fluid is a polluted emulsion containing the surfactant, the solubilized DNAPL and mobilized DNAPL as the organic phase. The extracted fluid from the SEAR application in the LIFE SURFING project was sent to a decanter, where the organic phase (mainly as droplets) settled with time. The supernatant containing the solubilized DNAPL and the surfactant must be treated. Several technologies have been tested in the literature for this scope. Some papers studied the selective oxidation of organic compounds in the mixture with the recovery of the surfactant capacity [5-7]. However, the COCs are not mineralized, and there is a loss of surfactant stability associated with the unproductive consumption of the oxidant by the surfactant [8]. Few papers deal with the selective adsorption of the organic pollutants in the emulsion on activated carbon [9]. These works used an aqueous emulsion of the surfactant spiked with a single organic compound, and experiments were carried out batchwise.

Moreover, the regeneration of the spent adsorbent has been scarcely studied. In a previous work[10], the regeneration of Granular Activated Carbon (GAC) saturated with 350 mg/kg of 124 Trichlorobenzene was studied by an aqueous solution (166 mM) of Thermal Activated Persulfate at a temperature range from 20 to 80°C. The temperature selected was 60°C, and the regeneration time was 3 h. About 40% of the adsorption capacity was recovered after each cycle of regeneration-adsorption at these conditions. Washing with water was required between cycles to eliminate the sulfates from the GAC surfaces. In this previous work GAC saturation was done with milliQ water spiked with 124 TCB and batch studies were carried out using a low ratio of mass GAC to Volume of aqueous phase $\left(\frac{W_{GAC}}{V_{aq}} = 5\frac{g}{L}\right)$.

Therefore, the effectivity of this process must be checked at conditions closer to the real application. In the present work, a column filled with the GAC used in the wastewater treatment plant of Bailin Landfill will be employed. Firstly, the polluted emulsion recovered in the SEAR event of the LIFE SURFING project carried out in May 2022 will be adsorbed on GAG. Secondly, the saturated GAG will be regenerated with TAP. Finally, a new polluted emulsion will be adsorbed in the GAG to determine the adsorption capacity recovery. Several cycles of adsorption-regeneration are carried out at the column scale. The selective adsorption of surfactant and organic pollutants and the corresponding persulfate consumption are determined at each cycle.

Materials and Methods

DNAPL sample from Bailin landfill (Sabiñánigo, Huesca) solubilized in an aqueous emulsion of nonionic commercial surfactant (E-Mulse 3[®], E3) has been treated. The surfactant E3 is non-toxic and biodegradable, and DNAPL is a complex mixture of more than 28 Chlorinated Organic Compounds (COCs) selected elsewhere [4, 8].

The Granular Activated Carbon (GAC) used as an adsorbent has a BET surface area of 905 m²·g⁻¹, total pore volume of 0.42 cm²·g⁻¹. More details about physicochemical properties and pre-treatment can be found elsewhere [10].

The oxidant used to regenerate the spent GAC was Sodium persulfate (P.S.), supplied by Sigma-Aldrich. Other reagents used to quantify P.S., like potassium iodide (K.I.), sodium carbonate (NaHCO₃) and sodium thiosulfate (Na₂S₂O₃), were also supplied by Sigma-Aldrich.

The characterization and quantification of the COCs in the emulsion were performed by G.C. (Agilent 6890, Santa Clara, CA, USA) with both a flame ionization detector (FID) and an electron capture detector (ECD). The concentration of E3 in the emulsion was quantified by TOC, after subtracting the TOC corresponding to the solubilized DNAPL. The PS concentration in the aqueous phase was determined by titration. The concentration of chloride, sulfates and short-chain organic acids in this aqueous phase was determined by ion chromatography.

The experiments were carried out in a glass column 118 mm in length and 28 mm in internal diameter. A packed bed of 50 mm in length and 20 g of GAC was placed inside the column and between two glass wool packings. Once the column was loaded, the bed density was 537 kg·m⁻³ and the porosity was 0.43. The column was fed by a peristaltic pump with a fixed flow rate of 2 ml·min⁻¹. The column flow yielded a residence time of 15 min and a volume of water in the column of about 50 ml.

Three adsorption-regeneration cycles were performed. Firstly, the adsorption of the emulsion on the GAC was carried out by feeding 280 ml of the polluted emulsion from a bottle without headspace (to minimize the loss of COCs by volatilization). The solution was pumped through the column at a flow rate of 2 ml·min⁻¹ and a 25°C for 144 h, recirculating the column effluent to the bottle. The emulsion composition was analyzed every 24 h by taking 1 ml from inside the bottle. The recirculation stopped at 144 h, and the liquid in the bottle was analyzed. Finally, a volume of 50 ml of milli-Q water is fed to the column, and the effluent of this washing is collected and analyzed for mass balance.

Regeneration of spent GAC was carried out by feeding 250 ml of a PS solution (63 g·l-1) to the column, at 60°C and a flow rate of 2 ml·min-1. The column effluent was not recirculated but collected and analyzed. The bottle containing the oxidant solution was immersed in a water bath heated to 60°C. The column temperature was kept at 60°C using an electric resistance that embraces the column. After regeneration, the GAC was washed with three volumes of 50 ml of milli-Q water at 60°C to remove the sulfates formed by the decomposition of PS, which remain adsorbed on the surface of the GAC. More details about this washing step can be found elsewhere [10]. During the process, the concentration of PS, COCs and TOC was measured at the exit of the column. A blank regeneration run was carried out at the same operating conditions but using fresh GAG in the column (without adsorption of COCs and E3).

Resaturation of the regenerated GAC with a new polluted emulsion was performed under the same operating conditions described for the first adsorption cycle. This procedure was repeated for a total of three adsorption and regeneration cycles.

Results and Discussion

Emulsion Characterization

The aqueous emulsion extracted contains the surfactant, E3, and solubilized COCs. COCs identified and quantified are chlorobenzene (CB), dichlorobenzenes (DCB), trichlorobenzenes (TCB), tetrachlorobenzenes (TTCB), pentacyclohexenes (PCX), hexaclorocyclohexanes (HCH), hexachlorocyclohexane (HCX) and heptachlorocyclohexanes (HeCH) isomers. The mass concentration (mg·L-1), molar concentration (mmol·L-1) and molar mass of each compound in the emulsion is summarised in Table 1. The mass percentage of each chlorinated organic compound in the sum of COCs is also given in Table 1.

 TABLE 1. COMPOSITION OF THE POLLUTED EMULSION

 FED TO THE GAC COLUMN

COCs	Mw	C _j (mg·L ⁻¹)	C _j (mmol·L-1)	mass% COCs
СВ	112.5	678.06	6.03	7.45
DCB	147	557.77	3.79	6.13
ТСВ	181.45	736.40	4.06	8.09
TTCB	216	582.95	2.70	6.41
PCX	254	35.25	0.14	0.39
РСВ	250	1804.05	7.22	19.82
НСХ	289	500.53	1.73	5.50
НСН	291	2381.19	8.18	26.17
HeCH	325	1823.79	5.61	20.04
Sum COCs		9100	39.46	100
Surfactant E3		11700		

The measured TOC of the emulsion was 9627 mg·L⁻¹. The COCs contribution to the TOC value is 2841 mg·L⁻¹. Therefore, the TOC corresponding to the surfactant is calculated as 6786 mg·L⁻¹. Taking into account that the ratio of carbon per gram of E3 is 0.58 $g_C \cdot g_{E3}^{-1}$ [4] a concentration of E3 of about 11.7 g·L⁻¹

Adsorption capacity and PS consumption in adsorption-regeneration cycles

The amount of COCs and E3 adsorbed on GAC in the successive adsorption cycles was quantified and the values obtained are shown in Table 2. Cycle 0 (C0) considers the adsorption in the fresh pretreated GAC, and Cycle 1 (C1) and Cycle 2 (C2) correspond to the adsorption of the polluted emulsion on the GAC column after the first and second regeneration cycle, respectively. The percentage of removed COCs and E3 from the bottle containing the SEAR emulsion (280 ml, composition in Table 1) has been calculated at each cycle and results are shown in Figure 1. As shown in Figure 1 and the amount of adsorbed COCs slightly decreases after the first regeneration cycle, but a constant value is obtained in C1 and C2. More than 99% of COCs in the emulsion were adsorbed in C0, and more than 90% were adsorbed in C1 and C2.

On the contrary, the amount of E3 removed from the emulsion by adsorption on GAC decreases at each cycle, indicating selective adsorption of COCs after GAC regeneration with TAP. The COCs evolution with time in the bottle is shown in Figure 2a. As shown, high adsorption of COCs on GAC was observed in C0, C1 and C2 between the first 24 and 48 h. At 120 h, the adsorption equilibrium was reached in C1 and C2. The PS concentration was measured at the column exit during the regeneration process, and results at each cycle are shown in Figure 2b. For the scope of comparison, the PS concentration at the column effluent when TAP is fed to a column with fresh GAC is also shown in Figure 2b. It is found that the adsorption of organic compounds on the GAC seems to protect the GAC surface against both GAC oxidation and unproductive oxidant consumption. When TAP is fed to the column filled with fresh GAC, the PS at the exit column is negligible, which means that PS is completely consumed in oxidizing the adsorbent surface, as reported previously [10]. The mass of PS consumed per gram of GAC at each regeneration cycle has been calculated and compared with that obtained with fresh GAC (neither COCs nor E3 adsorbed) at the same operating conditions. Results are shown in Table 3.

TABLE 2. COCS AND EMULSE ADSORBED IN THE GACIN THE ADSORPTION-REGENERATION CYCLES

	$mg_{COC} \cdot g_{GAC}^{-1}$	$m g_{E3} \cdot g_{GAC}^{-1}$
C0	127.13	144.02
C1	118.18	95.55
C2	114.90	47.56

TABLE 3. RATIO OF PS CONSUMED TO THE MASS OF FRESH AND REGENERATED GAC

Cycle	Fresh GAC	Cycle 0	Cycle 1	Cycle 2
gPS·wGA C-1	>0.78	0.64	0.55	0.49

FIGURE 1. PERCENTAGE OF COCS AND E3 ADSORBED IN GAG (20 G) FROM EMULSION (0.28 L,TABLE 1)

Conclusions

The polluted emulsions obtained in the application of SEAR treatment in the LIFE SURFING project were successfully managed by cycles of adsorption in Granular Activated Carbon and GAG regeneration with Thermally Activated Persulfate (TAP). The observed selective adsorption of COCs from the emulsion in the successive adsorptionregeneration cycles results in a selective recovery of the surfactant that could be reused for a new extraction of COCs with the SEAR technology. This way, a circular economy scenario is promoted for GAG and surfactant use.

The organic compounds adsorbed in the GAG surface inhibit the oxidation of the GAG internal surface and reduce the unproductive oxidant consumption. The decrease of PS consumption at each regeneration cycle maintaining the COCs adsorption capacity indicates a better efficiency of the oxidant in the COCs degradation with each cycle.

Acknowledgements

This work was supported by the EU LIFE Program (LIFE17 ENV/ES/000260), the Regional Government of Madrid through the CARESOIL project (S2018/EMT-4317), and the Spanish Ministry of Economy, Industry, and Competitiveness, through project PID2019-105934RB-I00. Andrés Sánchez-Yepes thanks the Ministry of Science and Innovation for supporting pre-doctoral contracts with FPI grant PRE2020-093195.

References

1. Santos, A., et al., Chlorinated organic compounds in liquid wastes (DNAPL) from lindane production dumped in landfills in Sabinanigo (Spain). Environ Pollut, 2018. 242(Pt B): p. 1616-1624.

2. Kang, S., et al., Évaluation of ethoxylated nonionic surfactants for solubilization of chlorinated organic phases: Effects of partitioning loss and macroemulsion formation. Journal of Contaminant Hydrology, 2019. 223.

3. Pennell, K.D., N.L. Capiro, and D.I. Walker, *SURFACTANT AND COSOLVENT FLUSHING*, in *Chlorinated Solvent Source Zone Remediation*, B.H. Kueper, et al., Editors. 2014. p. 353-394.

4. Garcia-Cervilla, R., et al., Surfactant-Enhanced Solubilization of Chlorinated Organic Compounds Contained in DNAPL from Lindane Waste: Effect of Surfactant Type and pH. Int J Environ Res Public Health, 2020. 17(12).

5. Hanafiah, S.A., et al., Treatment of heavy petroleum hydrocarbons polluted soil leachates by ultrafiltration and oxidation for surfactant recovery. Journal of Environmental Chemical Engineering, 2018. 6(2): p. 2568-2576.

6. Huang, K., et al., Effects of ferric ion on the photo-treatment of nonionic surfactant Brij35 washing waste containing 2,2',4,4'-terabromodiphenyl ether. J Hazard Mater, 2021. 415: p. 125572.

7. Li, Y., et al., Electrochemically reversible foam enhanced flushing for PAHs-contaminated soil: Stability of surfactant foam, effects of soil factors, and surfactant reversible recovery. Chemosphere, 2020. 260: p. 127645.

8. García-Cervilla, R., et al., Compatibility of nonionic and anionic surfactants with persulfate activated by alkali in the abatement of chlorinated organic compounds in aqueous phase. Science of The Total Environment, 2021. 751: p. 141782.

9. Rosas, J.M., A. Santos, and A. Romero, Soil-Washing Effluent Treatment by Selective Adsorption of Toxic Organic Contaminants on Activated Carbon. Water, Air, & Soil Pollution, 2013. 224(5).

10. Sanchez-Yepes, A., et al., Regeneration of Granulated Spent Activated Carbon with 1,2,4-Trichlorobenzene Using Thermally Activated Persulfate. Ind Eng Chem Res, 2022. 61(27): p. 9611-9620.

ON SITE REMEDIATION OF FLUIDS EXTRACTED IN SEAR TREATMENT IN THE LIFE SURFING PROJECT AT BAILIN – SABIÑÁNIGO (HUESCA): SELECTIVE POLLUTANTS OXIDATION AND ADSORPTION

Herranz, C.¹, Fernández, J.², Santos, A.³, Salvatierra, A.¹, Cano, E.², Lorenzo, D.³, Arjol, M.A.¹

¹Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain ²Department of Agriculture, Livestock and Environment, Government of Aragon, Spain ³Chemical Engineering and Materials Department, University Complutense of Madrid, Spain

Summary

A soil remediation pilot test was carried out at the Bailin landfill within the LIFE SURFING project. Various techniques for on-site decontamination of aqueous phases generated in the cited project, highly polluted with chlorinated organic compounds (COCs) and also containing surfactants, are evaluated. These on-site treatments aim to reduce the contaminant load of the aqueous phase to pollutant concentrations values that allow the discharge in the wastewater treatment plant located at the Bailín landfill or to recover the fluids with surfactant capacity for their reuse. The techniques applied to achieve these objectives in the on-site pilot plant were treatment by activated carbon and its regeneration by persulfate, advanced oxidation processes (Fenton Reagent) and thermal alkaline hydrolysis with aeration with retention of volatiles on granular activated carbon. In this work, an emulsion containing 5.166 g/l of solubilized COCs and 10 g/l of non-ionic surfactant E-Mulse $3^{\text{@}}$ has been treated at room conditions and pH=3 with stoichiometric H₂O₂ concentration and ratios H₂O₂/Fe²⁺ of 45/1 (Fenton Reagent) More than 95% of COCs were selectively eliminated at 48 h. Besides, an emulsion containing 16 g/l of surfactant and 8 g/l of COCs has been successfully adsorbed on GAG, and GAG has been regenerated with thermally activated persulfate at 45°C. However, an unproductive consumption of PS was found with GAG. The treated fluid can be discharged in the Bailin WWTP or be reinjected in the subsoil.

Keywords

Lindane, COCs, HCH, Fenton oxidation, surfactant, GAC adsorption and regeneration

Introduction

The production of the pesticide Lindane (γ hexachlorocyclohexane, γ -HCH) has generated large amounts of residues in the world, including its isomers (α -, β -, δ -, ϵ -HCH) and other organochlorine compounds. Due to their toxicity and environmental persistence, some have been included in the list of persistent organic pollutants by the Stockholm Convention [1]. The INQUINOSA factory, located in Sabiñánigo (Huesca), operated from 1975 to 1992. During this period, solid and liquid wastes from Lindane production were deposited in an uncontrolled manner in the near landfills of Bailin and Sardas. The Lindane purification generated solid and liquid wastes. The liquid waste was a dense non-aqueous phase liquid (DNAPL) composed of more than 28 chlorinated organic compounds that migrated vertically through the soil, contaminating the groundwater in both landfills[2]. To remediate the environmental problem of Lindane and other chlorinated organic compounds in the aquifer of the Bailin landfill, the LIFE SURFING Project was carried out by applying various techniques for the decontamination of subsoil with DNAPL. The first remediation technology applied in the LIFE SURFING project was the injection of an aqueous surfactant solution with simultaneous extraction of a contaminated fluid containing the liquid organic phase and an aqueous emulsion with surfactant and solubilized COCs (SEAR, Surfactant Enhanced Aquifer Remediation).

The emulsion resulting from the SEAR tests of the LIFE SURFING project was treated using three techniques: 1) selective COCs oxidation in the emulsion by adding hydrogen peroxide as the oxidant and ferrous iron as the catalyst (Fenton 2) adsorption of the polluted Reagent) [3] emulsion obtained in the SEAR treatment on an activated carbon (AC) filter and regeneration of saturated AC filter by oxidation of the adsorbed organics by persulfate activated by temperature [4] and 3) air stripping enhanced by temperature and alkali addition to volatilize chlorinated organic contaminants (COCs) in the aqueous emulsion. This work summarized the results obtained at the pilot scale for selective COCs oxidation with the Fenton Reagent and COCs adsorption on granular activated carbon (GAG) and GAC regeneration with thermally activated persulfate (PS).

The first technique tested was the selective COCs oxidation in the emulsion by adding hydrogen peroxide as the oxidant and ferrous iron as the catalyst (Fenton Reagent). Fe²⁺ reacts with hydrogen peroxide generating the hydroxyl radical ('OH), Eq.1, with great oxidizing power:

 $H_2O_2 + Fe^{2+} \rightarrow OH^- + Fe^{3+} + OH^-$

The catalyst, Fe^{2+} , is regenerated by Eq. (2) reaction, producing the HO2⁻ radical with lower oxidizing power:

(1)

 $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^+ + H^+$ (2)

The second technique used in this study was the adsorption of the polluted emulsion obtained in the SEAR treatment on a granular activated carbon (GAC) filter. The saturated GAC filter was regenerated by oxidation of the adsorbed organics by persulfate activated by temperature [4]

$$S_2O_{8^2}$$
 Temperature $\rightarrow 2SO_4$ (3)

Experimental Setups and procedure

A non-ionic commercial and biodegradable surfactant was used in SEAR treatment, E-Mulse 3[®]. The following setups were built to conduct the two on-site treatments studied.

Selective Oxidation of COCs with Fenton Reagent

The Aragon Government also conducted a pilot test at the Bailin landfill to study the selective abatement of COCs in the emulsion using the Fenton Reagent. A 300-litre tank was conditioned for the test. An agitator, a recirculation system, a pH electrode and an activated carbon filter for the gas outlet were arranged in the experimental setup. A gas compressor produced an air stream fed to the top of the tank at a very low airflow to facilitate the gas exit.

The tank was filled with 200 litres of groundwater from the Bailin landfill, adding 2 kg of surfactant (10 g/l) and kept under stirring and recirculation for 1 hour. An amount of 1.03 kg of DNAPL (5.166 g/l DNAPL, about 24 mM) from the Bailin landfill was added, and the emulsion was kept under stirring and recirculation for 2 hours. The reagents H₂O₂ and FeSO₄.7H₂O were added (5 mM in Fe²⁺ and 220 mM in H_2O_2) to start the Fenton reaction, keeping the tank under agitation and recirculation. The H_2O_2 concentration is about 90% of the theoretical stoichiometric dosage for COCs A minimum air intake was mineralization. maintained in the tank upper part to facilitate the exit of produced gases (mainly oxygen) to the activated carbon filter. After reagent addition, the pH of the solution was 5.7, adjusted to 3.3 with H₂SO₄.

The tank was kept under stirring at room temperature, and reaction samples were taken at 2, 5, 10, 24, 48, and 72 hours when the test was stopped. The samples were neutralized with NaOH and centrifuged. After that, the COCs composition of the samples was determined with a Gas Chromatograph coupled with FID (flame ionization detector) and ECD (electron capture detector) detectors (AGILENT, model 7890B).

Adsorption of COCs and surfactant on AC and AC regeneration with Thermal activated Persulfate

The Granular Activated Carbon (GAC) used as the adsorbent has a BET surface area of 905 $m^2 \cdot g^{-1}$ and a total pore volume of 0.42 cm³ g⁻¹. This GAC was also used in the WWTP of the Bailin landfill. More details about physicochemical properties and pre-treatment can be found elsewhere [4]. The oxidant used to regenerate the spent GAC was Sodium persulfate (PS) activated by temperature.

Some runs have been carried out at laboratory scale feeding 280 ml of a solution containing 9.1 g/l of DNAPL from Bailin landfill and 11.7 g/l of surfactant E-Mulse $3^{\text{(B)}}$ to a glass column with 20 g of GAC. Three adsorption (room temperature)-regeneration (T=60°C) cycles were performed. More details can be found in another communication sent to this congress.

An adsorption-regeneration experiment was carried out at a pilot scale at Bailin landfill. A sealed fibreglass bed was filled with 250 kg of the GAC. The activated carbon bed was filled with water, and bed porosity was estimated at 275 litres. 4 kg of Emulse-3 (16 g/l) and 2 kg DNAPL (8 g/l) were added to 250 liters of water from the Bailin landfill. The suspension was homogenized in a single tank and fed to the activated carbon bed using a peristaltic pump with a flow rate of 400 l/h, which means a residence time of 40 minutes. The exit of the GAG filter was recirculated to the feeding tank. Aqueous samples were taken at the inlet and outlet of the carbon filter at 1, 2, 3, 4, 5, 7 and 20 h, and COCs concentration was measured. After the adsorption tests (the same GAC filter bed was used in both), the AC bed was drained, and two quartz resistors were placed inside at 1/3 and 2/3 of the height of the tank. The control thermostat at 45 °C was placed in the upper part of the tank. 500 l of sodium persulfate (40 g/l) was prepared. The PS mass was calculated as 75% of the stoichiometric for mineralization of added COCs. The injection of the oxidant solution to the GAC bed with the adsorbed COCs and surfactant started at a flow rate of 1 m3/hour. It took 45 minutes to reach a temperature of 42°C in the upper part of the AC bed. Aqueous samples were taken at the entrance and exit of the tank at 1, 5, and 20 hours after the oxidant injection began. COCs, surface tension and PS were measured in the aqueous samples. The COCs remained in the activated carbon (after GAG bed, draining, washing, disassembling and drying) were extracted with methanol in an ultrasonic bath, and GAG regeneration by the oxidant was evaluated. The GAC mass of the filter was divided into four sub-lots, from the top (C4) to the bottom (C1). After homogenization, a sample of each lot was taken, and adsorbed COCs were extracted. The extract was analyzed by mass gas chromatography with FID and ECD detectors.

Results and Discussion

Fenton Reagent

Conversions of COCs above 80% were obtained at the laboratory scale using 100% and 200% of the stoichiometric amounts of hydrogen peroxide at 144 h and 48 h, respectively [3]. Non-aromatic compounds were more recalcitrant to oxidation by hydroxyl radicals than chlorobenzenes. The surfactant oxidation was significantly lower than the pollutant abatement, with selective oxidation of COCs in the emulsion. Surfactant capacity reduction depended on the initial concentration of H₂O₂. Values of 50%, 40% and 20% of surfactant capacity reduction were noticed at 144 h with H₂O₂ of 200%, 100% and 50% of the stoichiometric amount, respectively. Therefore, a remarkable surfactant capacity was maintained after the oxidation treatment, and the solution could be reused in further SEAR steps, improving the circular economy of the process.

Results from the experiments at the pilot scale are summarized in Figure 1. As shown, a conversion of COCs higher than 95% was obtained at 48 h, which did not increase with time due to the total oxidant consumption at 48 h. In the case of reinjecting the final solution after the Fenton treatment, the precipitation of iron hydroxides in the aquifer could occur, modifying the soil porosity. Therefore, 5 days after carrying out the Fenton test, the aqueous phase was neutralized with NaOH 25% to precipitate the iron. The initial pH was 3, and the final pH was 11.4. At pH 11, the formation of small flocs began, whereas larger flocs did not occur until a pH of 11.4 was reached. Two aqueous samples were taken from the aqueous phase in the tank, and the average composition of both samples is shown in Figure 1. As can be seen, the alkaline pH produced the dehydrochlorination of HCHs and HeptaCHs, with conversions close to the unity.

The solubilization capacity of the aqueous emulsion after the Fenton treatment (removal of COCs) and further basification (to remove by precipitation of the iron hydroxide) was evaluated by adding 5 ml of DNAPL to 100 ml of this remaining aqueous phase (75 g/l of DNAPL). The mixture was kept under stirring for 24 hours in an ultrasonic bath. The aqueous phase was analyzed, and solubilized COCs measured was about 9 g/l, indicating that a surfactant concentration of about 10 g/l remains in solution after the COCs abatement by Fenton treatment. Therefore, the COCs have been selectively oxidized, and the remaining solution keeps a high surfactant capacity after the Fenton treatment, in agreement with the results obtained in the lab test [3]. Moreover, basifying the aqueous phase after the Fenton treatment led to the dehydrochlorination reactions. Consequently, the main COCs in the solution were TCB and TetraCB, while HCHs and HeptaCHs were only detected at low concentrations. The lab and bench-scale test results indicate that the Fenton process is a possible post-treatment of the COCs in the emulsion, even if the total surfactant concentration is not recovered. However, attention should be paid to avoiding gas accumulation in the oxidation tank.

FIGURE 1. COCS CONVERSION IN THE EMULSION BY FENTON REAGENT (PILOT TEST)

COCs adsorption on GAG and GAG regeneration by Thermally Activated Persulfate (TAP)

On the laboratory scale, it has been demonstrated that GAG saturated with COCs (114 mg/g) and surfactant (144 mg/g) recovered 80% of this COCs adsorption capacity in the successive adsorptionregeneration cycles. On the contrary, lower surfactant adsorption was found with each cycle, showing a selective COCs adsorption after regeneration of the adsorbent.

From the experiment carried out at the pilot scale, it was found that COCs and surfactant fed to the column were almost totally adsorbed (> 99%), and negligible amounts of COCs were found at the exit of the GAG filter. The surface Tension of the fluid at the GAG filter exit was higher than 50 mN/m (surfactant concentration lower than 150 mg/l). Therefore, 40 min of contact time ensured organic adsorption. These results can be explained since the COCs amount fed to the GAG filter is much lower than the saturation capacity of the GAC. The ratio of COCs and surfactant mass in the emulsion volume to the mass of GAG used in the pilot plant test (8 and 16 mg/g, respectively) are much lower than those corresponding to the saturation values (120 and 160 mg/g, respectively). Therefore, the aqueous stream leaving the GAG filter is adequate for its treatment at the Bailín WWTP. After GAG regeneration, a significant concentration of COCs, around 30%, remained in the GAG filter. This can be explained as the mass of PS used was lower than the stoichiometric required for adsorbed COCs.

Moreover, PS is also decomposed by the GAG surface [4], and consumption of PS by adsorbed surfactant is also expected. An estimated value of 0.5 g PS per g GAG has been estimated from lab experiments. The exhaustion of PS through the GAG filter explains the COCs profile remaining in the GAC filter from the bottom (C1) to the top (C4), shown in Figure 2.

The column bottom (C1) is expected to have the highest COCs concentration before TAP regeneration. Therefore, the effectiveness of TAP is proven by the lower COCs concentration at the bottom column after TAP regeneration of GAG. The texture of the active carbon has remained unchanged after the treatment.

FIGURE 2. EFFICIENCY OF TAP IN COCS OXIDATION IN GAG FILTER

Conclusions

The treatment of fluid extracted in the SEAR treatment used in the LIFE SURFING project requires on-site treatment before it can be sent to the WWTP or reinjected in the subsoil. Selective COCs oxidation was achieved with the Fenton Reagents using stochiometric dosages of hydrogen peroxide in less than 48 h at room conditions and pH=3. A proper tank reactor design, reagents dosage and management of produced gases are required to scale up this process. The adsorption of

polluted emulsions in GAG ensures high retention of both COCs and surfactants. However, GAG regeneration is required in the circular economy scenario to avoid waste dispersion out of the site. From lab and pilot-plant experiments, promising results are obtained in the adsorption of emulsion on GAG and regeneration with TAP. However, the unproductive consumption of the oxidant with GAG must be considered in the economy of the process. The cost of the treatment needs to be optimized by adjusting reagent dosages and operation conditions.

Acknowledgements

This work has been supported by EU LIFE Program (LIFE17 ENV/ES/000260) and the Aragon Government

References

1. J. Vijgen, B. de Borst, R. Weber, T. Stobiecki, M. Forter, HCH and Lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue, Environmental Pollution, 248 (2019) 696-705.

2. J. Fernandez, M.A. Arjol, C. Cacho, POPcontaminated sites from HCH production in Sabinanigo, Spain, Environmental Science and Pollution Research, 20 (2013) 1937-1950.

3. C.M. Dominguez, A. Romero, A. Santos, Selective removal of chlorinated organic compounds from lindane wastes by combination of nonionic surfactant soil flushing and Fenton oxidation, Chemical Engineering Journal, 376 (2019).

4. A. Sanchez-Yepes, A. Santos, J.M. Rosas, J. Rodriguez-Mirasol, T. Cordero, D. Lorenzo, Regeneration of Granulated Spent Activated Carbon with 1,2,4-Trichlorobenzene Using Thermally Activated Persulfate, Ind Eng Chem Res, 61 (2022) 9611-9620.

ON SITE ALKALINE HYDROLYSIS OF FLUIDS EXTRACTED IN SEAR TREATMENT IN THE LIFE SURFING PROJECT AT BAILIN – SABIÑÁNIGO (HUESCA)

Herranz, C.¹, Fernández, J.², Santos, A.³, Salvatierra, A.¹, Cano, E.², Lorenzo, D.³, Arjol, M.A.¹

¹Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain; ²Department of Agriculture, Livestock and Environment, Government of Aragon, Spain; ³Chemical Engineering and Materials Department, University Complutense of Madrid, Spain

Summary

A soil remediation pilot test was carried out at the Bailin landfill within the LIFE SURFING project. Various techniques for on-site decontamination of aqueous phases generated in the cited project, highly polluted with chlorinated organic compounds (COCs) and also containing surfactants, are evaluated. These on-site treatments aim to reduce the contaminant load of the aqueous phase to pollutant concentrations values that allow the discharge in the wastewater treatment plant located at the Bailín landfill or to recover the fluids with surfactant capacity for their reuse. The techniques applied to achieve these objectives in the on-site pilot plant were treatment by activated carbon and its regeneration by persulfate, advanced oxidation processes (Fenton Reagent) and thermal alkaline hydrolysis with aeration with retention of volatiles on activated carbon.

The results obtained at a pilot scale using alkaline hydrolysis tests enhanced by temperature and aeration are discussed in this work. After SEAR treatment in the LIFE SURFING Project, polluted aqueous phases were remediated. Three experiments with alkali addition and air stripping were carried out at a temperature from 45 to 50°C. Initial HCHs concentration ranged from 119 to 389 mg/l, and more than 99% of HCHs were eliminated at 6 h. However, times up to 71 h were required to achieve a total COCs reduction of 94-98%. This time also ensured a total elimination of the surfactant. The treated fluid can be discharged in the WWTP or be reinjected in the subsoil. The cost of the treatment mainly depends on the correct thermal isolation.

Keywords

Lindane, COCs, HCH, Fenton oxidation, alkaline hydrolysis, surfactant, dehydrochlorination

Introduction

The production of the pesticide Lindane (γ hexachlorocyclohexane, y-HCH) has generated large amounts of residues in the world, including its isomers (α -, β -, δ -, ϵ -HCH) and other organochlorine compounds. Due to their toxicity and environmental persistence, some have been included in the list of persistent organic pollutants by the Stockholm Convention [1]. The INQUINOSA factory, located in Sabiñánigo (Huesca), operated from 1975 to 1992. During this period, solid and liquid wastes from Lindane production were deposited in an uncontrolled manner in the near landfills of Bailin and Sardas. The Lindane purification generated solid and liquid wastes. The liquid waste was a dense non-aqueous phase liquid (DNAPL) composed of more than 28 chlorinated organic compounds that migrated vertically through the soil, contaminating the groundwater in both landfills[2]. To remediate the environmental problem of Lindane and other chlorinated organic compounds in the aquifer of the Bailin landfill, the LIFE SURFING Project was carried out by applying various techniques for the decontamination of subsoil with DNAPL. The first remediation technology applied in the LIFE SURFING project was the injection of an aqueous surfactant solution with simultaneous extraction of a contaminated fluid containing the liquid organic phase and an aqueous emulsion with surfactant and solubilized COCs (SEAR, Surfactant Enhanced Aquifer Remediation). The emulsion resulting from the SEAR tests of the LIFE SURFING project was treated using three techniques: 1) selective COCs oxidation in the emulsion by adding hydrogen peroxide as the oxidant and ferrous iron as the catalyst (Fenton Reagent) [3], 2) adsorption of the polluted emulsion obtained in the SEAR treatment on an activated carbon (AC) filter and regeneration of saturated AC filter by oxidation of the adsorbed organics by persulfate activated by temperature [4] and 3) alkalization with NaOH and temperatureenhanced air stripping to volatilize chlorinated organic contaminants (COCs) in the aqueous emulsion.

Alkali addition promotes dehydrochlorination of the more chlorinated compounds to more volatile compounds, as shown in Figure 1[5], enhancing their volatility. Alkaline hydrolysis of HCH and PentaCX generates trichlorobenzenes, while H e p t a C H a n d H e x a C X g e n e r a t e tetrachlorobenzenes. The heavier compounds lose hydrogens and chlorines and are transformed into lighter compounds in several steps, according to the literature [6]. The lighter compounds volatilize with heat and aeration. Still, maintaining alkaline conditions suggests that hydroxide action may also favour their conversion to dichlorobenzenes and benzenes until they mineralize to CO₂, H₂O and Cl-. However, the promotion by alkali of this last reaction has not been proven yet in the laboratory The air stream with volatilized COCs is sent to an activated carbon filter that retains these compounds. Alkali addition and temperature can also affect the volatility of the chlorinated organic compounds and surfactant stability in the emulsion [7].

FIGURE 1. DEHYDROCHLORINATION REACTIONS AT ALKALINE PH [5]

Experimental Set-ups and procedure

The aqueous phase generated in the SEAR tests is evacuated to two intermediate tanks, through which it is distributed in batches to the three on-site treatments. A non-ionic commercial and biodegradable surfactant was used in SEAR treatment, E-mulse 3[®].

The alkaline hydrolysis treatment was carried out in a double-chamber reactor, the first with aeration and the second with expansion, to minimize the generation of foams. Alkali (NaOH, 25% aqueous solution) was added to the reactor using a pulse pump. The aqueous phase was recirculated from the second chamber to the reactor and heated externally with two 24 kW heaters. Antifoam is injected into the recirculated fluid using a dosing pump. The recirculated water is fed into the reactor as a spray, promoting foam breaking and the volatilization of the lighter organics. Volatilized COCs leave the second chamber with the air stream, retained in two active carbon filters in series.

Results and discusión

The pollutant load concentration in the polluted SEAR emulsions ranged from 100-380 ppm of HCHs and 450-1200 ppm of COCs.

Three pilot tests were performed (Hid-1, Hid-2, Hid-3) with alkaline hydrolysis and air stripping enhanced by temperature. In the three runs, a temperature of 45°C was fixed. Table 1 summarizes the most relevant data at each test, indicating the initial and final COCs concentration and the time required for enough COCs to decrease in the aqueous phase that allows the discharge of the aqueous phase to be treated in the Bailin wastewater treatment plant.

1.- In the Hid-1 test, 1835 1 of the emulsion were treated with an initial HCH sum concentration of 118.78 ppm, COCs sum of 448.75 ppm and 0.58 g/l of E-Mulse 3[®]. At 6.75 hours and with 19.73 l of an aqueous solution of 25% NaOH, a reduction of 99.5% of the initial HCHs and surfactant concentrations in the emulsion was achieved. pH was kept at a value higher than 12, adding alkali if necessary. The test was maintained for about 69 hours to reach COCs concentrations that allow the discharge of the aqueous phase to the Bailin WWTP or the reinjection of the alkaline-treated aqueous phase. The pH was kept manually at a value higher than 12 (between 11.2 and 13.1, the average value being 12.56) by adding alkali if necessary and the total NaOH consumption at 25% was 32.04 l.

2.- In the Hid-2 test, 1907 l were treated with a contaminant load of 388.83 ppm of HCHs and 1209.84 ppm of COCs. Due to the higher contaminant load of the aqueous phase, it took 21 hours of treatment to achieve 99.5% degradation of the HCH isomers and 48 hours to degrade the surfactant. The test was maintained for 71.75 hours in which 114.89 L of NaOH (25% in weight) were consumed, obtaining a 99.8% reduction in HCH and 93.8% of COCs reduction. In this experiment, alkali was added automatically with the pulse pump, and the set point for pH was 11.7. However, due to a malfunction of the dosing system, alkali was added uncontrolled, and an average pH of 12.74 was obtained.

3.- In the Hid-3 test, 2122 l of the aqueous emulsion was treated with a pollutant load of 118.76 ppm of sum de HCH, 454,05 sum of COCs and 1.49 g/l of E-Mulse 3[®]. At 2.5 hours, a 97.2% reduction of HCHs had been obtained; at 21 hours, 99.6% of HCH and surfactant had been degraded.

The test was maintained for 74.5 hours, obtaining a final value of 17.04 ppm sum COCs.

Table 1 shows the evolution of HCH isomers with time in the three pilot tests. The isomer β -HCH is the most recalcitrant, whose degradation is slower and more gradual (due to the position of its chlorines). The calculation of organic matter removed from the aqueous phase in each test is also shown. Organic profiles with time are also shown in Figure 2.

Because the reactor has not been adequately insulated, a fraction of volatiles was lost and not retained in the active carbon, so it was impossible to estimate the volatilized fraction of the organic matter eliminated in the polluted fluid from the SEAR treatment.

Conclusions

The following conclusions can be drawn from the three tests HD1, HD2 and HD3:

a) The hydrolysis treatment achieves total HCH isomers and E-Mulse $3^{\textcircled{R}}$ degradation in a short time (less than 6 h) at 45° C and pH 12.

b) HCHs are degraded in the first hours, but longer times, 71.75 h, are required to achieve COCs reduction higher than 94%

c) The first intermediates generated in the first step are 1,2,4-TCB and TetraCBs, but dehydrochlorination seems to continue generating dichlorobenzenes and chlorobenzenes, a degradative pathway not found at the laboratory scale.

d) Heat favours dehydrochlorination reaction, and aeration promotes the evacuation of volatiles and chlorophenols from the aqueous matrix.

e) Total sealing of the reactor and piping avoids loss of volatiles in the atmosphere.

f) To avoid an excess of alkali addition, an automatic pH control system is required.

g) After treatment to the required level, the alkaline aqueous phase can be reinjected into the aquifer favouring heavier organochlorine dehydrochlorination.

h) 63-73% of the total cost of each test was due to the electrical consumption for heating the aqueous phase. This cost can be dramatically decreased with better isolation.

FIGURE 2. EVOLUTION OF HCHS, COCS AND SURFACTANT CONCENTRATIONS WITH TIME IN EXPERIMENTS HD-1, HD-2 AND HD-3.

TABLE 1. COMPOSITION OF THE EMULSION OBTAINED FROM SEAR STEP, EFFICIENCIES OF COCS REMOVAL BY AIR STRIPPING AND ALKALI ADDITION ENHANCED BY TEMPERATURE AND COST ANALYSIS

	HID -1 (28th June 2022)			HID -2 (18th July 2022)				HID -3 (25th October 2022)						
	V treated = 1835 1				V treated = 1907 l				V treated = 2122 1					
	NaOH Antifoa	= 32.04 1 m = 6.6 1			NaOH = Antifoam	NaOH = 114.89 1 Antifoam = 3.8 1			NaOH - Antifoa	NaOH = 350 l Antifoam = 6.3 l				
	Begin			End	Begin			End	Extra	Begin			End	Extra
Time (h)	0 h	6.75	45	69	0	21	48	71.75	186.5	0	2.5	21	74.5	217.5
α-HCH ppm	22.32	0.09	0.11	0.08	74.51	0.94	0.39	0.26	0.24	28.36	0.15	0.14	0.15	0.12
β-НСН ррт	0.61	0.49	0.12	0.02	1.57	0.56	0.26	0.09	0.35	0.415	0.51	0.29	0.04	< 0.01
γ-HCH ppm	72.88	< 0.01	0.02	<0.01	127.03	0.17	0.03	0.24	0.06	57.26	2.11	<0.01	< 0.01	< 0.01
δ-НСН ррт	14.25	0.04	0.09	0.11	162.18	0.32	0.09	0.24	0.31	24.71	0.02	<0.01	< 0.01	< 0.01
ε-HCH ppm	8.72	<0.01	<0.01	< 0.01	23.54	0.07	0.02	0.09	0.05	8.02	0.56	<0.01	<0.01	< 0.01
Suma HCH ppm	118.78	0.62	0.34	0.21	388.83	2.06	0.79	0.92	1.01	118.76	3.35	0.43	0.19	0.12
Suma COCs ppm	448.75	217.11	15.85	5.57	1209.84	522.07	305.86	74.77	82.72	454.05	280.2	85.71	17.04	18.14
E-Mulse 3, g/l	0.58	<0.01	<0.01	< 0.01	0.65	0.19	<0.01	<0.01	<0.01	1.49	0.87	< 0.01	<0.01	<0.01
ΣHCH removed from aq phase, g	217.58	1	1	1	739.57					251.75				
ΣCOCs removed from aq phase, g	813.24				2149.42				925.00					
	DECO	NTAMIN.	ATION Y	IELDS, 9	%									
Time (h)	0	6.75	45	69	0	21	48	71.75	186.5	0	2.5	21	74.5	217.5
α-HCH ppm	-	99.6	99.5	99.6	-	98.7	99.5	99.7	99.7	-	99.5	99.5	99.5	99.6
β-НСН ррт	-	19.7	80.3	96.7	-	64.3	83.4	94.3	77.7	-	-22.9	30.1	90.4	100.0
ү-НСН ррт	-	100.0	100.0	100.0	-	99.9	100.0	99.8	100.0	-	96.3	100.0	100.0	100.0
δ-НСН ррт	-	99.7	99.4	99.2	-	99.8	99.9	99.9	99.8	-	99.9	100.0	100.0	100.0
ε-HCH ppm	-	100.0	100.0	100.0	-	99.7	99.9	99.6	99.8	-	93.0	100.0	100.0	100.0
Suma HCH ppm	-	99.5	99.7	99.8	-	99.5	99.8	99.8	99.7	-	97.2	99.6	99.8	99.9
Suma COCs ppm	-	51.6	96.5	98.8	-	56.8	74.7	93.8	93.2	-	38.3	81.1	96.2	96.0
E-Mulse 3, g/l	-	100.0	100.0	100.0	-	70.8	100.0	100.0	100.0	-	41.6	100.0	100.0	100.0

Acknowledgements

This work has been supported by EU LIFE Program (LIFE SURFING, ref LIFE17 ENV/ES/ 000260) and the Aragon Government.

References

1. J. Vijgen, B. de Borst, R. Weber, T. Stobiecki, M. Forter, HCH and Lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue, Environmental Pollution, 248 (2019) 696-705.

2. J. Fernandez, M.A. Arjol, C. Cacho, POPcontaminated sites from HCH production in Sabinanigo, Spain, Environmental Science and Pollution Research, 20 (2013) 1937-1950.

3. C.M. Dominguez, A. Romero, A. Santos, Selective removal of chlorinated organic compounds from lindane wastes by combination of nonionic surfactant soil flushing and Fenton oxidation, Chemical Engineering Journal, 376 (2019).

4. A. Sanchez-Yepes, A. Santos, J.M. Rosas, J. Rodriguez-Mirasol, T. Cordero, D. Lorenzo, Regeneration of Granulated Spent Activated Carbon with 1,2,4-Trichlorobenzene Using Thermally Activated Persulfate, Ind Eng Chem Res, 61 (2022) 9611-9620.

5. D. Lorenzo, R. Garcia-Cervilla, A. Romero, A. Santos, Partitioning of chlorinated organic compounds from dense non-aqueous phase liquids and contaminated soils from lindane production wastes to the aqueous phase, Chemosphere, 239 (2020) 124798.

6. Bescós Viñuales, A., Salvatella Ibáñez, L., 2019. Modelización de reacciones de deshidrocloración de residuos de fabricación de lindano. Facultad de Ciencias – UNIZAR 2019.

7. P. Saez, A. Santos, R. Garcia-Cervilla, A. Romero, D. Lorenzo, Non-Ionic Surfactant Recovery in Surfactant Enhancement Aquifer Remediation Effluent with Chlorobenzenes by Semivolatile Chlorinated Organic Compounds Volatilization, Int J Environ Res Public Health, 19 (2022).