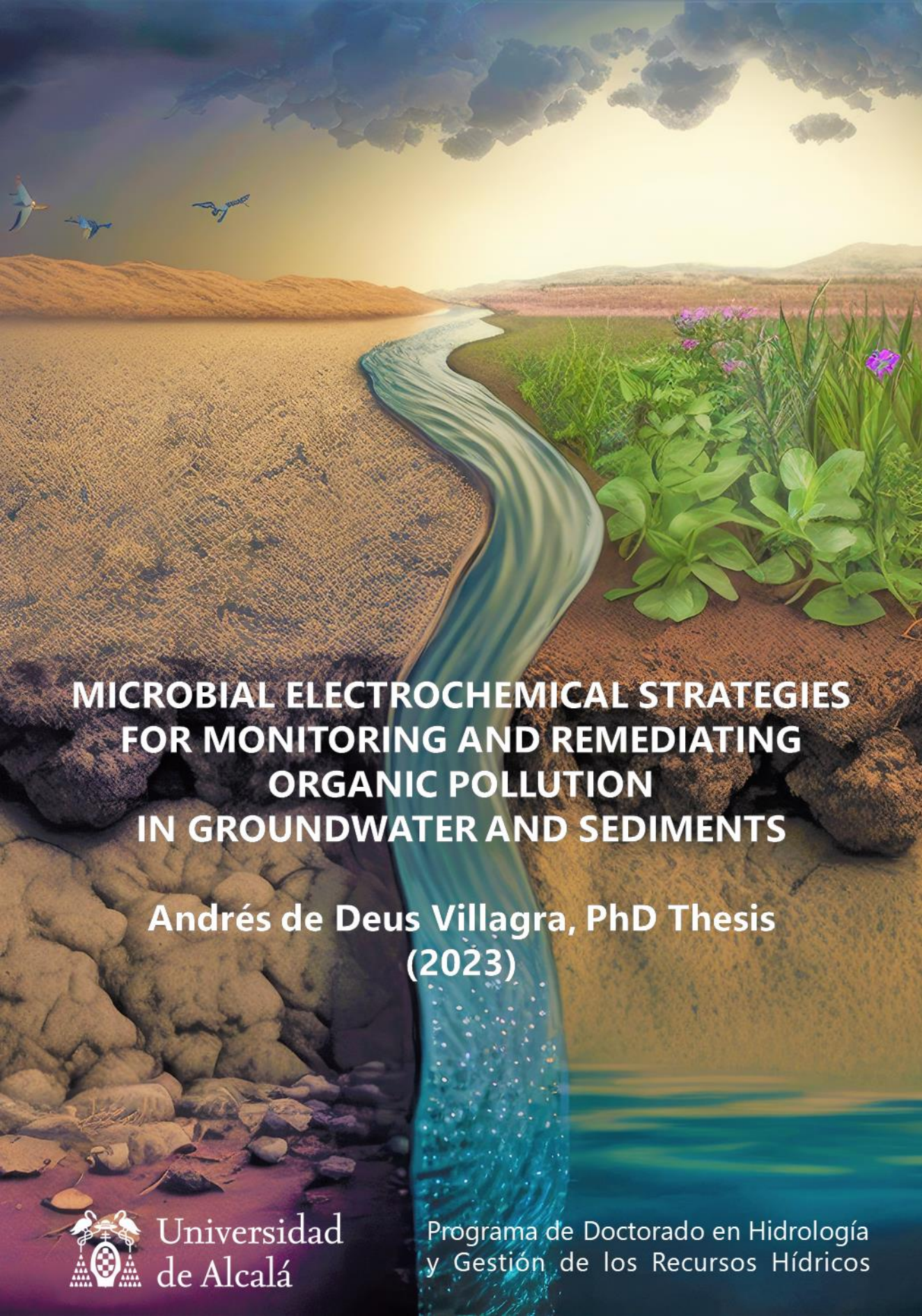

MICROBIAL ELECTROCHEMICAL STRATEGIES FOR MONITORING AND REMEDIATING ORGANIC POLLUTION IN GROUNDWATER AND SEDIMENTS

Andrés de Deus Villagra, PhD Thesis
(2023)

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Programa de Doctorado en Hidrología y Gestión de los Recursos Hídricos

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MICROBIAL ELECTROCHEMICAL STRATEGIES FOR MONITORING AND REMEDIATING ORGANIC POLLUTION IN GROUNDWATER AND SEDIMENTS

Tesis Doctoral presentada por

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Director:

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Alcalá de Henares, 2023

Leyes de Clarke:

1. Cuando un científico distinguido pero de edad avanzada afirma que algo es posible, es casi seguro que tiene razón. Cuando afirma que algo es imposible, es muy probable que esté equivocado.

2. La única forma de descubrir los límites de lo posible es aventurarse un poco más allá de ellos hacia lo imposible.

3. Cualquier tecnología lo suficientemente avanzada es indistinguible de la magia.

Arthur Charles Clarke

A mi hermano, Jorge

Summary

Microbial electrochemistry is a biotechnological field that explores interaction between microorganisms and electrically conductive materials. Such studies have evolved to develop a plethora of environmental applications, known as Microbial Electrochemical Technologies (MET). MET can be used to clean up polluted environments by utilizing electrodes as terminal electron acceptors or donors, which enables microbial metabolism to occur beyond natural conditions. This technology is highly versatile and can be applied to a range of matrices, including wastewater, groundwater, sediment and soil. However, the implementation of MET in real-field applications requires overcoming microbial, technological, and economic challenges. Despite these challenges, MET exhibit great potential as a strategy to enhance environmental remediation.

In this thesis, we have explored the capability of MET in natural environments, for both i) to **detect** groundwater-contaminants like petroleum derived compounds and agrochemical compounds like lindane (**Chapter 2**) and ii) to **remediate** lindane-polluted environments (**Chapter 3** and **Chapter 4**). Through our research, we have demonstrated the ability of these technologies to both detect the presence of contaminants but also to stimulate their degradation, leading to the restoration of natural environments.

Chapter 1 represents an updated state of the art regarding the thesis topic: electrobioremediation and bioelectrochemical detection of contaminants in polluted soil. We indeed provided an overview about environmental pollution specially devoted to aromatic (BTEX) and chlorinated hydrocarbons including their impact in the environment and human health. Furthermore, we reviewed various methods for detecting and removing pollutants from the environment, specially those relevant to our research. In the final section of the chapter, we introduce MET, including their fundamental principles and applications, with an emphasis on how to enhance microbial metabolism of electroactive bacteria for detecting and remediating polluted environments.

Under the following statement *one of the best ways to prevent contamination is to monitor risky locations,* we have explored innovative methods for developing *in-situ* early detection of pollutants in groundwater. Indeed, in **Chapter 2**, we used microbial electrochemical strategies to detect contaminants, such as petroleum hydrocarbons or

agrochemicals, in groundwater at microcosm and mesocosm scales. The biosensor consisted of a 3-electrode configuration with a working electrode polarized at anodic potential (0.6 V vs. Ag/AgCl), inserted inside a piezometer. A microbial community of uncontaminated groundwater was used to colonize the electrode, then we observed a response (<2 hours) to a pulse containing a mixture of pollutants such as BTEX and ETBE. Additionally, we also tested the response to complex mixtures using a kerosene spike. We used a biocathode-based sensor strategy (- 0.6 V vs. Ag/AgCl) to monitor electrical current consumption, associated with dehalogenation, in the presence of the insecticide lindane (gamma-hexachlorocyclohexane).

Electrobioremediation is a strategy to clean-up pollution using a combination of electrochemical tools and microbiology. In **Chapter 3**, we designed and validated at different configurations for removing a widely used pesticide, lindane, from a synthetic and a real polluted soil. Cathodic configuration resulted to show the higher remediation efficiency. In fact, electrode acted as an electron donor and removed lindane ca. 10 times faster than natural attenuation. Moreover, different isomers of lindane were removed using different configurations. Finally, we could demonstrate that even non-flooded polluted soil could be electrobioremediated.

For several years lindane production residues were discharged in Sabiñanigo (Huesca, Spain) and, eventually, landscape was vastly polluted. In this context, we explored strategies ways to clean-up contaminated real soil using *in-situ* electrobioremediation (**Chapter 4**). Over a period of 20 weeks, different electrobioremediation configurations were tested. The results revealed a cathode-based configuration as the most effective to remove HCH contaminants. Different isomers throw up different removal efficiencies. The majority isomer, α-HCH, was almost completely removed; however, the most persistent isomer, β-HCH, was only partially removed. Furthermore, phytoxicity analysis showed that a cathode-based configuration was effective for promoting plant growth. Regarding the composition of microbial community, cathode-based configurations selected cathodophilic bacteria, while anode-based configurations selected anodophilic and aromatic degrading bacteria.

Finally, in **Chapter 5** we have included a general discussion, a series of conclusions after results from the current thesis, and future strategies for optimizing the electrobioremediation actions. The general discussion is presented as a question-answer format, highlighting the favorable impact of electromicrobiology for remediating polluted environments at physical, chemical, and biological level.

Resumen

La electroquímica microbiana es una rama de la biotecnología que explora la interacción entre los microorganismos y los materiales conductores de la electricidad. Este campo ha evolucionado hasta dar lugar a una plétora de aplicaciones medioambientales, conocidas como tecnologías electroquímicas microbianas (MET, por sus siglas en inglés). Las MET pueden utilizarse para limpiar ambientes contaminados utilizando electrodos como aceptores o donadores terminales de electrones, lo que permite que el metabolismo microbiano actúe en condiciones diferentes de las condiciones naturales. Esta tecnología es muy versátil y puede aplicarse a diversas matrices, como aguas residuales, aguas subterráneas, sedimentos y suelos. Sin embargo, la implantación de las MET en aplicaciones de campo reales requiere superar desafíos microbiológicos, tecnológicos y económicos. A pesar de estos retos, las MET presentan un gran potencial como estrategia para mejorar la recuperación del medio ambiente.

En esta tesis, hemos explorado la capacidad de las MET en entornos naturales para i) **detectar** contaminantes de aguas subterráneas como compuestos derivados del petróleo y agroquímicos como el lindano (**Capítulo 2**), y ii) **remediar** entornos contaminados con lindano (**Capítulo 3** y **Capítulo 4**). A través de nuestra investigación, hemos demostrado la capacidad de estas tecnologías no sólo para detectar la presencia de contaminantes, sino también para facilitar su degradación, lo que conduce a la restauración del entorno natural. Nuestros hallazgos ponen de relieve que las MET son una valiosa herramienta para la vigilancia y la recuperación del medio ambiente.

El **Capítulo 1** recoge el estado del arte sobre el ámbito de estudio de la tesis: electrobiorremediación y detección bioelectroquímica de contaminantes en suelos contaminados. De hecho, proporcionamos una visión general sobre la contaminación ambiental especialmente centrada en los hidrocarburos aromáticos (BTEX) y clorados, incluyendo su impacto en el medioambiente y en la salud humana. Además, repasamos varios métodos para detectar y eliminar contaminantes del medioambiente, especialmente aquellos relevantes para nuestra investigación. En la última parte del capítulo, presentamos las MET, incluidos sus principios fundamentales y sus aplicaciones, haciendo hincapié en cómo potenciar el metabolismo microbiano de las bacterias electroactivas para detectar y remediar los entornos contaminados.

Bajo la premisa de que *una de las mejores formas de prevenir la contaminación es vigilar los lugares de riesgo*, hemos explorado métodos innovadores para desarrollar la detección temprana *in-situ* de contaminantes en aguas subterráneas. De hecho, en el **Capítulo 2**, utilizamos estrategias electroquímicas microbianas para detectar contaminantes, como hidrocarburos del petróleo o agroquímicos, en aguas subterráneas a escala de microcosmos y mesocosmos. El biosensor consistió en una configuración de 3 electrodos con un electrodo de trabajo polarizado a potencial anódico (0.6 V vs. Ag/AgCl) instalado en un piezómetro. Tras la colonización mediante la comunidad microbiana de aguas subterráneas no contaminadas, observamos una respuesta (<2 horas) a un pulso con mezcla de contaminantes (BTEX y ETBE). Además, también comprobamos la respuesta a mezclas complejas utilizando un pulso de queroseno. Alternativamente, y para detectar la presencia del insecticida lindano (gamma-hexaclorociclohexano), se recurrió a una configuración de biocátodo (- 0,6 V vs. Ag/AgCl) para monitorizar el consumo de corriente eléctrica asociado a la deshalogenación.

La electrobiorremediación es una estrategia que permite descontaminar mediante una combinación de herramientas electroquímicas y microbiología. En el **Capítulo 3**, diseñamos y validamos diferentes configuraciones para eliminar un insecticida muy utilizado, el lindano, de un suelo contaminado sintéticamente y de un suelo real contaminado. La configuración catódica resultó ser la más eficaz. De hecho, el electrodo actuó como donador de electrones y eliminó el lindano aproximadamente 10 veces más rápido que la atenuación natural. Además, se eliminaron diferentes isómeros de lindano utilizando diferentes configuraciones. Por último, pudimos demostrar que incluso los suelos contaminados no anegados podían ser electrobiorremediados.

Durante largos periodos de operación, se vertieron residuos de la producción de lindano en Sabiñánigo (Huesca, España) y, con el tiempo, el paisaje quedó ampliamente contaminado. En este contexto, exploramos estrategias para limpiar el suelo real contaminado mediante electrobiorremediación *in-situ* (**Capítulo 4**). Durante un periodo de 20 semanas, se probaron diferentes configuraciones de electrobiorremediación. Los resultados revelaron que la configuración basada en cátodos era la más eficaz para eliminar los contaminantes HCH. Los diferentes isómeros mostraron diferentes eficiencias de eliminación. El isómero mayoritario, α-HCH, se eliminó casi por completo; sin embargo, el isómero más persistente, β-HCH, sólo se eliminó de forma parcial. Además, el análisis de fitoxicidad demostró que una configuración basada en cátodos era eficaz para promover el crecimiento de las planta frente al bajo crecimiento natural

en suelo contaminado. En cuanto a la composición de la comunidad microbiana, las configuraciones basadas en cátodos seleccionaron bacterias catodófilas, mientras que las configuraciones basadas en ánodos seleccionaron bacterias anodófilas y degradadoras de aromáticos.

Finalmente, en el **Capítulo 5** hemos incluido una discusión general, una serie de conclusiones a partir de los resultados alcanzados en esta tesis, así como las futuras estrategias para optimizar los tratamientos de electrobiorremediación. La discusión general se presenta en formato pregunta-respuesta, resaltando el impacto favorable de la electromicrobiología para recuperar ambientes contaminados, tanto a nivel físico, como químico y biológico.

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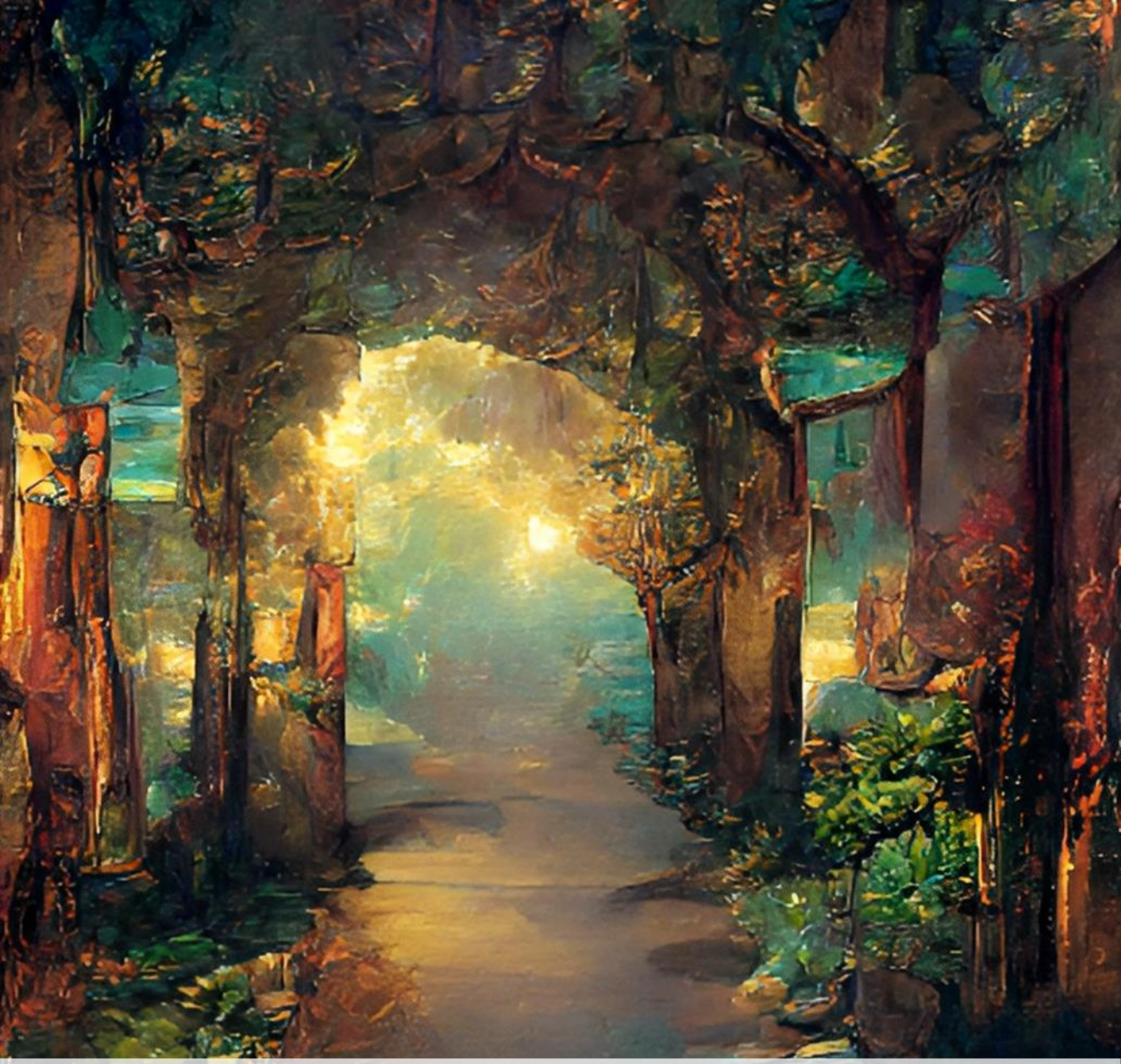

Chapter 1:

Introduction

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1. Contaminants in the environment

Since humanity has gathered in population centers, contamination sites have been generated. In ancient Athens and Rome, landfills and dumping sites were already generated. These sites were chosen far from the city centers because of their effects upon health and well-being [Emmerson, 2020]. During European Middle Ages, the effects became more apparent and domestic waste management was regulated through laws that prevented street dumping. However, these laws were largely ignored and fostered problems such as the Black Death pandemic [Geltner, 2020]. Similarly, smoke emission laws were ignored during the industrial revolution in England, with dramatic changes in some ecosystems [Cook and Shortall, 2022]. In the most recent past, especially since World War II, a wide variety of substances have been generated. Manufacturing these new compounds involves producing large amounts of waste [Vijgen et al., 2011]. Furthermore, in many cases the use of the new substances has induced health or environmental effects [Chartres et al., 2019; Wacławek et al., 2019].

The environment is composed of interconnected parts. The soil-water-air-biosphere relationship maintains a constant dynamic. Changes that modify one imply modifications in the rest. In recent years we have seen several examples of this relationship: the increase in the concentration of CO_2 in the air has promoted the acidification of the oceans [L.-Q. Jiang et al., 2019]; moreover the release of heavy metals through mining processes [Bisone et al., 2016] has generated bioaccumulation of these metals in organisms (including humans) [Mallakpour and Khadem, 2019]. There are many more existing relationships between different media [Berkowitz et al., 2014; Brunner et al., 2017] and many of them affect human health [Konduracka, 2019]. Contamination processes are so defined as environmental disturbance which generate harm to humans, damage into the altered phase or damage in any other phase.

Air and biosphere are two phases with difficult access for the elimination of pollutants. There are very ambitious projects that try to remove CO_2 from the atmosphere in large quantities [XPRIZE Foundation - Elon Musk, 2021], and classical remedies to reduce heavy metals in humans are known [Mehrandish et al., 2019]. However, prevention is the only currently valid strategy to keep the air and biosphere free of contaminants. In soil and water, prevention is a fundamental part of management. Nevertheless,

techniques have also been developed to combat soil and water contamination problems.

Environmental and human health concerns since the existence of landfills, coupled with the technical feasibility of solving contamination problems, places soil at the center of the equation. Soil receives contamination from many different sources (Table 1.1)[Spellman, 2017] and can then spread to water, air and the biosphere. Especially significant are the contamination processes that start in the soil and transfer the contaminant to water, and more specifically to groundwater [Zhang, 2020a]. For this reason, groundwater quality can serve as an indicator of soil quality. On the other hand, most of the contaminants increase their mobility when they come into contact with the groundwater, so they are diluted and increase the rate of affection, which is known as contamination plume [Postigo et al., 2018].

Table 1.1: Sources of contamination in soils.
Extracted from Spellman (2017) [Spellman, 2017]

Sources of contamination in soils
Gaseous and Airborne Particulate Pollutants
Infiltration of Contaminated Surface Water
Land Disposal of Solid and Liquid Waste Materials
Stockpiles, Tailings, and Spoil
Dumps
Salt Spreading on Roads
Animal Feedlots and Animal Feeding Operations
Fertilizers and Pesticides
Accidental Spills
Composting of Leaves and Other Wastes

1.1. Principal organic contaminants

Not all contaminated sites are affected by the same type of pollution. The pollutants that reach the soil and groundwater can be extremely different and can be grouped according to their nature: chemical, physical and biological pollutants. Physical contamination comprises damages caused by high/low temperatures, vibrations or other mechanical or electromagnetic disturbances, including radionuclide emissions.

Biological contamination is formed by disease-causing agents [Postigo et al., 2018], but the most extended contamination is the chemical contamination.

Around 7 million chemicals exist, of which 100,000 have been released into the environment [Zhang, 2020b]. Although most of these compounds are not contaminants, some of those that do contaminate bring dramatic effects. These contaminants are usually divided into organic and inorganic. Inorganic contaminants involve heavy metals (Fig. 1.1), metalloids As and Se, inorganic ions and nanomaterials (metal compounds and carbon nanotubes). Most of the contaminated soil and groundwater contain organic pollutants (Fig. 1.1). Their classification by functional groups provides insight into the origin, toxicity, degradation and other environmental considerations of each contaminant.

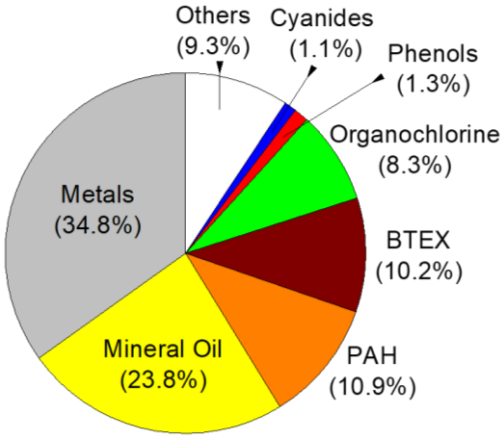


Figure 1.1: Distribution of contaminants in contaminated sites in Europe. Extracted from Tack and Bardos (2020) [Tack and Bardos, 2020]

1.1.1. Aliphatic hydrocarbons

Aliphatic hydrocarbons include all open-chain carbon compounds and non-aromatic cyclic rings. Alkanes or kerosenes are the major compounds in gasolines and other fuel blends [Burri et al., 2004; Edwards, 2002]. Alkenes (olefins) and cycloalkanes (napththenes) are also found in fuels. Apart from fuels, there are many aliphatic compounds formed in industrial processes for other compounds (by-products), such as mineral oils or 4-vinylcyclohexene.

All aliphatic hydrocarbons are slow biodegrading compounds and remove oxygen from the areas they are present [Unimke et al., 2018]. On the one hand, the organisms that

degrade these compounds consume oxygen, and on the other hand, the compounds impermeabilize the area and prevent oxygen from diffusing to lower layers.

1.1.2. Aromatic hydrocarbons

The most widespread monocyclic aromatic compounds are benzene, toluene, ethylbenzene and xylene (known as BTEX), compounds found in the fuel oils. If the aromatic rings join together, they form polycyclic aromatic hydrocarbons (PAH) such as naphthalene or phenanthrene, which are present in fuel oils in lower concentrations.

The problems that arise from releasing aromatics at the environment are the same as aliphatics, with the addition that aromatics increase genetic, biochemical or physiological alterations.

The mixture called total petroleum hydrocarbon (TPH) is referred to compounds present in fuel oils, crude oil and other mixtures derived from petroleum. TPH contamination usually includes a large number of aromatic aliphatic and other organic compounds, although the proportion depends on the initial mixture and diffusion medium.

1.1.3. Halogenated hydrocarbons

Halogen compounds include in their structure one or more halogen elements (F, Cl, Br, I and At). Cl is the most present halogen in the earth and therefore it is the most found in halogenated organic compounds, forming organochlorines. These compounds have special relevance in the design of pesticides, receiving the name of organochlorine pesticide (OCP). All these compounds usually have high toxicity, low water solubility, high density and high persistence. Their degradation usually occurs by dehalogenation, a reductive pathway that substitutes Cl for H.

Aliphatic halogenated compounds are mostly used as solvents in industrial processes. For this reason, chloroform (non-polar solvent) is the most commonly found contaminant in groundwater, although other organochlorines such as chloroform, chloromethane or perchloroethene and compounds with different halogens such as dichlorodifluoromethane or bromodichloromethane are also frequently found [Zhang, 2020a].

If we focus on halogenated cyclic aliphatics, several OCPs can be found such as aldrin, dieldrin, heptachlor and endosulfan; and there are molecules formed in several planes such as mirex or kepone that were also used as OCPs.

Aromatic organochlorines have several uses. The chlorobenzene family is mainly used as a solvent. Polychlorinated biphenyl (PCB) is used as a dielectric and stable industrial fluid. But the use that has generated the most attention in recent years has been agronomic. Aromatic OCPs have been dispersed in many soils and some places still suffer their consequences. Among them are DDT, dicofol, pentachlorophenol, 2,4-D and lindane.

1.1.4. Oxygenated hydrocarbons

Oxygen is one of the most abundant and reactive compounds on earth. Therefore, it forms an enormous number of compounds with a great diversity of oxygen-based functional groups. Some esters such as phthalate esters are added in many beauty and hygiene products. In fuel blends, Pb-compounds has been abandoned and replaced by ethers. The most common are methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME) [Guerra Que et al., 2019]. Although they are less contaminating than Pb-compounds, they are very soluble in water, appearing in groundwater repeatedly [Thornton et al., 2020a; Zhang, 2020a].

If an alcohol group (-OH) is added to an aromatic compound, a phenol is formed. Phenols are one of the most common groups present in contaminated areas (Fig. 1.1). Many phenols are formed as by-products of industries or processes. Especially noteworthy are the poly chlorinated phenols (PCP), by-products of degradation of halogenated aromatics, and 4-Nonylphenol, degradation by-product of nonionic surfactants.

1.1.5. Nitrogen/Phosphorous/Sulfur-containing Organic Compounds

The CHONPS elements (carbon, hydrogen, oxygen, nitrogen, phosphorus and sulfur) are considered to be the most important elements in organisms. On the one hand, some compounds are an unintentional result of industrial processes. Biomass combustion can generate cyanides, a group found mostly among contaminated sites (Fig. 1.1), and animal industries generate amides.

On the other hand, some products are voluntary designed with these functional groups. The functional group "azo" (-N=N-) is present in most of the dyes. There are some sulfur-containing solvents, such as carbon disulfide, widespread in groundwater. Linear alkylbenzene sulphonates (LAS)-like compounds are widely present among detergents. Triazine group such as deethylatrazine, atrazine, simazine or prometon is one of the most common contaminant groups present in groundwater. There are also other aromatic nitrogen compounds used in agriculture such as bentazon or metolachlor, very present in many groundwaters [Zhang, 2020a].

1.2. How do we detect contaminants in the environment?

Soil and water quality are closely related, so contamination that affects the soil eventually reaches the groundwater [Zhang, 2020a]. Groundwater quality monitoring has become doubly important. Firstly, it warns of soil contamination hotspots, and secondly, it provides necessary information for drinking water [Brunner et al., 2017]. With the rise of satellites and prediction models, groundwater monitoring has taken a multi-scale view [Bhunia et al., 2021]. In these techniques, field measurements are still necessary to verify the prediction. Classical analytical techniques are still the most widely used for the measurement of the compounds of interest [Farhadian et al., 2008]. However, modern compounds and the current environmental and health awareness bring about new needs such as measuring groundwater contaminants *in-situ*. To this end, a large number of *in-situ* sensors have been designed that can be classified according to the detector, i.e. the signal that is expressed when the analyte comes into contact.

1.2.1. Optical sensors

The most common sensors are those based on optical techniques. In these, a beam of light is emitted and made to interact with the substrate. In many cases it is necessary to add a signaling molecule for maximize the response. The specific case of biosensors, a biological structure acts as signaling. These biological structures can be molecular structures (enzymes, antibodies, nucleic acids…), whole cells (bacteria, algae…) or aggregates (biofilms, tissues…) [Abegaz et al., 2018].

a) In colorimetry, a beam of light is emitted through the substrate [Liu et al., 2020]. This type of sensor and biosensors has detected cations [Li and Wei, 2018; Park et al., 2014], and anions [Gupta et al., 2014; Tummachote et al., 2019].

b) In fluorescence-based detection, a beam of light is emitted, passes through the substrate and excites the analyte [Shin et al., 2021]. Fluorescence sensors are especially useful for the detection of green algae and cyanobacteria [Shin et al., 2018], and dissolved organic matter [Brandl et al., 2020]. And mainly fluorescence biosensors have been developed to detect pathogens [Ohk and Bhunia, 2013; Yang et al., 2018; Zawadzka et al., 2009].

c) In Surface Plasmon Resonance (SPR), a beam of light is emitted onto a metal surface. The other side of this metal surface is in contact with the substrate [Prabowo et al., 2018]. This type of sensor allows interaction with other types of sensors through the metal surface, such as electrochemical sensors or piezometric sensors. SPR sensors have been capable of detecting heavy metals [Ermakova et al., 2013]. Meanwhile, SPR biosensors are often used with ligand-receptor recognition moieties [Couture et al., 2013] mainly in pathogens detection by antibody-antigen [X. Liu et al., 2016; Masdor et al., 2017] and by oligonucleotide [Arya et al., 2011; Zhang et al., 2012].

1.2.2. Piezoelectric sensors

Gravimetric analytical techniques are ancient, but sensors based on mass modifications have not gained importance until the advent of biosensors and specific antibodies. Piezoelectric biosensors are based on the pressure variation generated by receptor-ligand bonds. Two main models of piezoelectric biosensors are used.

a) The quartz crystal model utilizes variations upon the crystal [Na Songkhla and Nakamoto, 2021]. In this way, biosensors have been developed for many pathogen bacteria [Lian et al., 2015; Shi et al., 2017] and viruses, including Cov-SARS-2 (causing COVID-19) [Narita et al., 2021].

b) Cantilever model utilizes the variations caused by leaving the sampling edge of the sensor unclamped [Fritz, 2008]. This model has also been used for detection of pathogens [Sharma and Mutharasan, 2013; Zhang and Ji, 2004].

1.2.3. Electrochemical sensors

Electrochemical systems transform chemical energy into electrical energy. Electrochemical sensors measure this generation of electrical energy, which can be kinetic (current intensity) or potential (electrical potential). Here, the number of sensor elements is reduced, because the electrodes act as both a receiver and a transducer.

Like other types of sensors, biological structures can be added for the enhancement of this type of electrochemical sensors. These techniques have been greatly benefited by the discovery and use of electroactive microorganisms. Electroactive microorganisms have made it possible to design many microbial electrochemical techniques (MET), including microbial electrochemical sensors. In these sensors, further detailed in Section 2.3.5, microorganisms are in direct contact with an electrode in order to harvest an electrical current in response to the metabolism of a diversity of analytes. Therefore, microbial electrochemical sensors obtain the advantages of electrochemical sensors (reduction of necessary elements) and electroactive microorganisms (used instead signaling molecules) [Hossain and Mansour, 2019].

a) Amperometric sensors fix a potential difference between the working electrode and a reference electrode. Therefore, variations in current intensity will be due to the occurrence of analytes interacting with the electrode surface [Su et al., 2011]. This technique proved to be useful for detecting drugs [Ganta et al., 2019], agro-chemicals [Noori et al., 2018; Prathap et al., 2016], and it is widely used measure BOD [Jouanneau et al., 2014]. The addition of enzymes on electrodes has allowed the design of biosensors that detect insecticides [Arduini et al., 2006; Deo et al., 2005], diphenyl compounds [Zehani et al., 2015], surfactants [Nomura et al., 1998], and remediation treatment by-products as catechol [Nistor et al., 2002]. In addition, BOD detection has led to the development of several commercial biosensors [Ejeian et al., 2018].

b) In potentiometry, the potential of the working electrode is measured with respect to the reference electrode. Classically, ion-selective electrodes are used [Su et al., 2011] as in the case of measurement of pH [Chung et al., 2017], cations and anions [Urbanowicz et al., 2017] and surfactant [Mikysek et al., 2016]. Apart from ion-selective electrode, non-polar molecules have been detected, such as lindane [Anirudhan and Alexander, 2015]. Otherwise, enzymes have been used to detect anionic surfactants in potentiometric biosensors [Khaled et al., 2017], and oligonucleotides have been used

for detecting pathogens [Zhao et al., 2016], toxins, pollutants and drugs [Marrazza et al., 1999].

c) Voltammetric sensors change the potential of the working electrode and measure the current intensity generated at each moment. This analysis results in graphs comparing the current generated at different potentials. Their competitive advantage is that they can differentiate between different analytes as long as they interact with the working electrode under different potentials [Zoski, 2007]. With this technique, sensors have been developed that detect halogenated compounds [Anu Prathap and Srivastava, 2013; Noori et al., 2021], F- ion [Sharma et al., 2015], nitrogenized aromatic compounds [Geto et al., 2019], and other aromatics [Cesarino et al., 2012]. Although voltammetric biosensors has not been so prolific as in other cases, some enzymatic biosensors have determined heavy metals [Muralikrishna et al., 2014].

d) The impedance technique circulates an alternating current with variable frequency through the circuit. This can calculate the change in various electronic parameters with an electrochemical translation. The complexity of the technique has prevented their common use. Some examples of this technique are the determination of herbicides [Panasyuk-Delaney et al., 2001], phenol [Singh et al., 2016], salinity [Chung et al., 2017] and viable cells [Uria et al., 2016a]. Enzyme-based atrazine [Hleli et al., 2006] and oligonucleotide-based heavy metal concentrations [Zhu et al., 2014] have also been measured.

e) Conductimetric sensors measure the conductivity of the medium between two electrodes. This conductivity depends on the addition of some analytes. Conductimetric technique has been monitored cations [Braiek et al., 2016] and engine oil aging [Latif and Dickert, 2011]. Among the conductimetric biosensors, enzymatic sensors have detected herbicides [Anh et al., 2004], heavy metals [Nepomuscene et al., 2007] and dissolved organic carbon [Marrakchi et al., 2007]; and oligonucleotide sensor have detected pathogen bacteria [Xuzhi Zhang et al., 2020].

1.3. Remediation: how do we clean-up a polluted environment?

A contaminated soil can become a source of environmental and health contamination. This is why contaminated soil management plays an important role among the techniques used for environmental management. When contamination is detected in a soil, the parameters of the contaminated soil are studied (type of contaminant, extent of contamination, type of soil, proximity to susceptible points...) and a decision is taken on the treatment to be applied. I) No access to the contaminated point or urgent to restrict its expansion, containment techniques are used to limit the passage of the contaminant (i.e. physical barriers) [Council, 2007]. II) Access to the contaminant, but not possible to eliminate or urgent to stop its expansion, immobilization techniques are used to reduce the mobility of the contaminant [Derakhshan Nejad et al., 2018]. III) Accessibility and technical possibility to remove it, remediation techniques are used. Soil remediation is a multidisciplinary field in which physical, chemical, biological and thermal techniques are interrelated (Table 1.2). There are several techniques for treatment without transporting contaminated soil (Table 1.3) and techniques to treat contaminated soil out of the original place (Table 1.4). In addition, saturated soil has similarities with other media (waterlogged sediments, sludge...), so these techniques can be extrapolated to other environments.

All these techniques can be used separately or together, to improve treatments. The most promising techniques are those based on nanoparticles [Fei et al., 2022] (within the chemical techniques) and those based on biological systems that use living organisms for remediating soils, called bioremediation [Sales da Silva et al., 2020]; moreover, simultaneous use of nanoremediation and bioremediation techniques [Cecchin et al., 2017; Raj Kumar et al., 2017]. Nanoparticles provide more robust techniques, like most chemical treatments (they modify soil conditions, even at the expense of the soil resilience). In contrast, bioremediation requires adaptation but it offers greater versatility (it performs an infinite number of routes simultaneously) and ease of reusing the soil after treatment. Within bioremediation we find different options depending on the necessary operations and the biological intervention in charge of eliminating the pollutant.

Table 1.2: Summary of operational processes for treating soil

Treatment type	Treatment type processes
Biological	Degradation by the activity of living organisms
Chemical	Degradation or mobilization following chemical reactions
Physical	Separation based on physical differences with the soil
Thermal	Removal of movilization using elevated temperatures

Table 1.3: Summary of *in-situ* soil treatments

	***In-situ* treatments**	**Treatment processes**
Biological treatment	Natural attenuation	Processes of different nature (biological, chemical, physical…) remove pollutants spontaneously.
	Bioventing/biosparging	Air or pure oxygen injected into the soil to promote aerobic degradation processes.
	Bioslurping	Vacuum application increases aeration (bioventing) and absorbs a pollutant. First, the gas is separated from the liquid; then, the contaminant is separated from the water.
	Phytoremediation	Plants used to degrade pollutants, by direct plant impact or by biological populations promoted around the the plants.
	Biological permeable barrier	Pollutant mobilization and passage through a barrier filled with biological structures (peat moss, compost…) that degrade or retain the pollutant.
	Bioaugmentation	Inoculation of pollutant-degrader microorganisms which are not present in the soil.
	Biostimulation	Amendment additions (nutrients, co-substrates, electron donors or acceptors…) that promote degrading activity of the microorganisms present in the soil.
Chemical treatment	Chemical washing	Pollutants mobilization by adding water or reagents (chelating agents, surfactants, pH modifiers…) and extraction of the polluted solution.
	Chemical permeable barrier	Pollutant mobilization and passage through a barrier filled with chemical reagents (Zero Valent Iron, iron slag…) that degrade the pollutant.
	Oxidation	Oxidizer reagents (H_2SO_4, $K_2Cr_2O_7$, Fenton reagent…) are added to oxidize the pollutant and decrease its toxicity.
	Reduction	Reducer reagents (NaOH, Zero Valent Iron…) are added to reduce the pollutant and decrease its toxicity.
	Dehalogenation	Reagents (Zero Valent Iron, H_2, methanol, butyrate…) are added to replace halogens in halogenated pollutants.
Physical treatment	Soil flushing	Water or reagents (chelators, surfactants, pH modifiers…) are added to raise the water table up to the polluted zone. The polluted groundwater is then extracted.
	Electrokinetic	Powering an electric potential difference that mobilizes ions and charged contaminant particles.
	Fracturing	Pressurized water injection that fractures impermeable zones, creates new passages ways and allows the pollutant to percolate and not originate in a high concentration points.
	Vapor extraction	Vacuum pump absorbs gases generated by volatile contaminants.
	Physical permeable barrier	Pollutant mobilization and passage through a barrier filled with adsorbent material (active carbon, surfactant-modified zeolites, apatite…) that retains the pollutant.
Thermal treatment	Hot air/steam injection	Air or steam injection at high temperature volatilizes pollutants that are piped away.
	Vitrification	Increasing soil temperature (i.e. using electrodes) until the contaminant becomes as a crystalline structure.

Table 1.4: Summary of *ex-situ* soil treatments

	***Ex-situ* treatments**	**Treatment processes**
Biological treatment	Landfarming	Spreading polluted soil above unpolluted soil. Periodic tilling or moving required to ensure aeration.
	Biopile	Spreading polluted soil as mounds or parallel piles. Periodic tilling or moving required to ensure aeration.
	Composting	Mixing polluted soil with organic amendments (wood chips, animal wastes, manure...) and spreading it as piles or mounds. Periodic tilling or moving required to ensure aeration.
	Bioreactors	Polluted soil is added into a reactor where the microbiome degrades the contaminant.
	Slurry phase	A mixture of polluted soil and water is added into a reactor. The particles are kept in suspension and the microbiome degrades the contaminant.
Chemical treatment	Chemical washing	Pollutants mobilization by adding water or reagents (chelating agents, surfactants, pH modifiers...) and extraction of the polluted solution.
	Dehalogenation	Reagents (Zero Valent Iron, H_2, methanol, butyrate...) are added to replace halogens in halogenated pollutants.
	Oxidation	Oxidizer reagents (H_2SO_4, $K_2Cr_2O_7$, Fenton reagent...) are added to oxidize the pollutant and decrease its toxicity.
	Reduction	Reducer reagents (NaOH, Zero Valent Iron...) are added to reduce the pollutant and decrease its toxicity.
Physical treatment	Separation	Kinetic differences between pollutant particles and soil particles are used to separate them. It can be diameter difference, ballistic/hydrodynamic (weight), ferromagnetism, flotation...
	Solvent extraction	Solvent (water, methanol, acetone...) addition and liquid-solid separation.
	Vapor extraction	Vacuum pump promotes pollutant volatilization that are piped away.
	Electrokinetic	Powering an electric potential difference that mobilizes ions and charged contaminant particles.
Thermal treatment	Thermal desorption	High temperature promotes pollutant volatilization that are piped away.
	Incineration	High temperature under aerobic conditions mineralizes the pollutant to CO_2.
	Pyrolisis	High temperature in anaerobic conditions decomposes the pollutant into by-products, gas and solid (coke).
	Vitrification	Increasing soil temperature (i.e. using electrodes) until the contaminant becomes as a crystalline structure.

1.3.1. Bioremediation techniques

Bioremediation techniques comprise all tools capable of using living organisms to degrade contaminants and reduce their toxicity [Sales da Silva et al., 2020]. Some of them are described below:

a) Landfarming treatment spreads the contaminated soil above an uncontaminated soil. It is one of the most basic treatments due to its low cost and technical simplicity. However, its efficiency is low and requires periodic tilling, moving and mixing to ensure aeration [Ortega et al., 2018].

b) Biopile treatment spreads contaminated soil in parallel mounds or piles. Water, nutrients or reagents can be added to enhance microbial treatment. It also requires periodic tillage, movement and mixing to ensure aeration [Whelan et al., 2015].

c) In composting treatment, contaminated soils are mixed with organic amendments (wood chips, animal waste, manure...) and the mixture is spread as piles or mounds. Water, nutrients or reagents can also be added to enhance microbial treatment and requires periodic tillage, movement or mixing to ensure aeration [Aguelmous et al., 2019; Grasserová et al., 2020].

d) Solid phase bioreactors are enclosed volume reactors that promote biological reactions inside. The bioreactor is filled with contaminated soil and maintained under conditions that enhance microbiological degradation of the contaminant. Conditions can be monitored and regulated more easily than in other systems. For this purpose, compounds that improve the microbial treatment are measured and added. It can operate in aerobic or anaerobic conditions [Mosca Angelucci and Tomei, 2016].

e) Slurry phase bioreactor fill a reactor with contaminated soil mixed with water. In this way, the particles are kept in suspension and the microorganisms degrade the contaminant. It is also easy to regulate the conditions and can operate in aerobic or anaerobic conditions [Balseiro-Romero et al., 2019; Mosca Angelucci and Tomei, 2016; Quintero et al., 2006].

f) Natural attenuation is a technique in which no modification is applied to the soil. Time is left and the soil resilience allow natural processes (mainly biological, but also chemical or physical) to remove contaminants spontaneously, without input of anthropogenic matter or energy [Safdari et al., 2018].

g) Bioventing injects air or pure oxygen into the soil to promote aerobic degradation processes. It can be done in dry or non-flooded soil, or it can be done in flooded soil, where it is called biosparging [Xiao and Zytner, 2019].

h) Bioslurping, also called multiphase extraction, applies vacuum to increase aeration, which promote aerobic degradation processes, and absorb liquid and gas contaminant. Then, a liquid-gas separation and finally a liquid-water contaminant separation are performed [Kim et al., 2014].

i) Phytoremediation comprises any remediation technique which uses plants to degrade contaminants. To achieve this, depending on the plant and the pollutant, this technique can take actions in different ways [Kumar Yadav et al., 2018] such as:

i.1) Phytodegradation or phytotransformation, the plant eliminates or transforms the contaminant into a non-toxic by-product, within its tissue or on the plant surface [Nebeská et al., 2021].

i.2) Phytoextraction, the plant absorbs and accumulates the contaminant [Asgari Lajayer et al., 2019].

i.3) Phytovolatilization, the plant absorbs the contaminant and excretes it as a non-toxic gas through the aerial parts [Guarino et al., 2020].

i.4) Phytostimulation, the plant secretes root exudates that promote the degradation processes of the microorganisms [Souto et al., 2020].

j) Biological permeable barrier treatment, first requires the mobilization of the pollutant, and then it is passed through a barrier filled with biological structures (peat moss, compost...) that degrades the pollutant [Yeh et al., 2010].

k) Bioaugmentation is the inoculation of contaminant-degrading microorganisms which are originally not present in the soil. The use of this technique requires knowledge of the microbial population present in the soil, to ensure that allochthonous bacteria are needed; and the isolation of a microbial population or species with degradative properties, to inoculate microorganisms that will act against the contaminant [Gutiérrez et al., 2020].

l) Biostimulation adds amendments that promote degrading activity of the microorganisms present in the soil. This technique is useful in the case of the microbial populations are capable of degrading the contaminant under specific conditions [Sales da Silva et al., 2020; Siles and García-Sánchez, 2018; Song et al., 2019; X. Wang et al., 2020a], but those conditions are not present in the soil. Amendments can be added, such as nutrients [Villalba Primitz et al., 2021], co-substrates [Bianco et al., 2020]. However, some of these compounds persist in sediment and soil due to the absence of a suitable electron acceptor or donor [Boopathy, 2004; Megharaj et al., 2011; Wang et

al., 2016; Widdel and Rabus, 2001]. Some strategies aimed to overcoming these limitations, as addition of electron acceptors [M. Chen et al., 2020; García Frutos et al., 2010; Herrero et al., 2019; Kabelitz et al., 2009; Suh and Mohseni, 2004; Wu et al., 2020], addition of electron donors [Askarian et al., 2017; Chen et al., 2001; Fennell et al., 1997; Guzmán-López et al., 2021] or addition of mediators that transport electrons between donor and acceptor [M. Chen et al., 2020; Lovley, 2000; Mazarji et al., 2020; Y. Zhang et al., 2020].

I.1) Electrobioremediation: *in-situ* electrochemical stimulation

Since 2010, coupled with the advancement of microbial electrochemistry, a new biostimulation strategy was born [T. Zhang et al., 2010a]. In electrobioremediation, some microorganisms use electrodes as inexhaustible electron donor or acceptor [Tucci et al., 2021b]. This remediation strategy is key for achieving the research goals of this thesis and it deserves a section by itself (Section 2.3.6).

1.4. Contaminants investigated in this thesis

Considering the different problems of environmental contaminants and the opportunities offered by new technologies explained in the following section (Section 2), two main groups of compounds are studied in this thesis:

1.4.1. Ptroleum hydrocarbon contaminants: BTEX

BTEX, the name for the set consisting of the most common and simplest aromatic compounds: benzene, toluene, ethylbenzene and xylene isomers (Fig. 1.2 and Table 1.5). They are the compounds that most influence the octane number of fuel oils [Burri et al., 2004]. They are also used in paints, processing industries, and other industrial raw materials [González et al., 2017; Sarafraz-Yazdi et al., 2010].

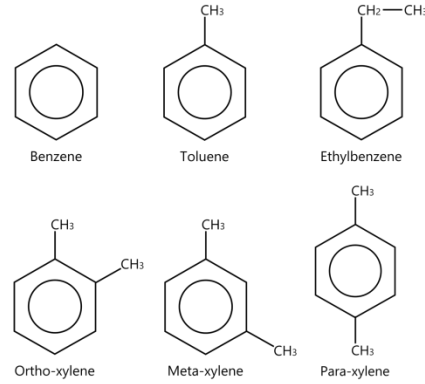


Figure 1.2: BTEX formulae

Table 1.5: BTEX physic-chemical characteristic

Compound	Benzene	Toluene	Ethyl-benzene	Ortho-xylene	Para-xylene	Meta-xylene
Molecular formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}	C_8H_{10}
Molecular mass (g/mol)	78.11	92.13	106.16	106.16	106.16	106.16
Density (g/ml)	0.87	0.87	0.87	0.88	0.87	0.86
Melting point (ºC)	5.50	−95.00	−94.97	−25.00	−47.40	13.00
Boiling point (ºC)	80.10	110.60	136.20	144.40	139.30	137.00
Vapor pressure (mmHg)	95.19	28.40	4.53	6.60	8.30	3.15
Water solubility (mg/L)	1791.00	535.00	161.00	175.00	146.00	156.00
Henry's constant ($kPa \cdot m^3/mol$)	0.557	0.660	0.843	0.551	0.730	0.690

Extracted from El-Naas (2004) [El-Naas et al., 2014]

a) Bottlenecks

All the BTEX uses cause eventually environmental discharge by means of accidents [Anjos et al., 2021; Sun et al., 2018] or by voluntary actions [Atamaleki et al., 2022; Dobaradaran et al., 2021]. This environmental spreads have resulted in 10.2% of contaminated sites containing BTEX (Fig. 1.1).

BTEX degrading microorganisms, consume oxygen [Benedek et al., 2018], and lead to oxygen depletion. In addition, oxygen depletion is further aggravated by the impermeable effect of these compounds. BTEX prevent oxygen diffusion to lower layers and could reside in an anaerobic environment for decades [Page et al., 2013]. Similarly, they induce a depletion of nitrate, sulphate and other nutrients and shift in pH values [Ossai et al., 2020; Yu et al., 2022].

Furthermore, aromatic compound cause teratogenic, carcinogenic, and mutagenic [Kim et al., 2013; Rota et al., 2014; White et al., 2016]. Specifically, BTEX exposure has been associated with problems in liver, nervous system, heart, kidneys and a greater the risk of non-lymphocytic leukemia [Khajeh and Zadeh, 2012; Nagaraju et al., 2019].

b) Detection in the environment

Considering the problems caused by BTEX and its ability to spread, a great effort has been shown for developing sensors to detect it. Most BTEX sensors are designed for gaseous media and atmospheric monitoring [Clément and Llobet, 2020; Król et al., 2010; Mirzaei et al., 2018; Rydosz, 2018]. BTEX detection in liquid media has been mostly performed by analytical techniques, both in water [Alsalka et al., 2010; Amy Tan et al., 2012; Anbia and Irannejad, 2013; Fakhari et al., 2012; Fernandes et al., 2014; Hosseinzadeh et al., 2011; S. Liu et al., 2016] as in organic medium [Sciarrone et al., 2010; S. Zhang et al., 2010], including food oils [Toledo et al., 2010].

In addition to analytic techniques, some BTEX sensors have been developed. We can find several studies of chemical sensors for water [Bender et al., 2013; Cooper et al., 2015; Sothivelr et al., 2017] biosensors for water [Hernández-Sánchez et al., 2016] with whole-cell designs [Belkin, 2003; Paitan et al., 2004] and biosensors for soils

c) Remediation of BTEX-polluted environment

BTEX remediation, most often together with other petroleum hydrocarbons, has been proved by several techniques. BTEX can be degraded under aerobic conditions, natural attenuation has been one of the most widely used processes for BTEX remediation, with the clear advantage of the lowest cost [Verginelli et al., 2018]. Moreover, alternative bioremediation techniques have been used with the advantage of being an easy, environmental-friendly, sustainable, and cost-efficient method [Ossai et al., 2020].

Biostimulation demonstrated to be the most effective treatment for petroleum hydrocarbon degradation compared to other *in-situ* treatments [Simpanen et al., 2016]. Biostimulation and other bioremediation techniques have been tested on several occasions (Table 1.6)

Table 1.6: Methods for petroleum hydrocarbon bioremediation

Bioremediation technique		References
In-situ	Biostimulation	[Wu et al., 2016] [Abdulsalam et al., 2010] [Agarry and Latinwo, 2015] [Adams et al., 2015]
	Bioaugmentation	[Nwankwegu and Onwosi, 2017] [Abdulsalam et al., 2010]
	Bioventing	[Trulli et al., 2016] [Agarry and Latinwo, 2015]
	Biosparging	[Kao et al., 2008]
	Phytoremediation	[Gouda et al., 2016] [Agamuthu et al., 2010]
Ex-situ	Slurry reactor	[Zappi et al., 2017]
	Landfarming	[Brown et al., 2017]
	Composting	[Atagana, 2010]

Other non-biological treatments have demonstrated to remove BTEX from petrol-contaminated environments. Vapor extraction [Ma et al., 2016], chemical washing [Kang et al., 2012], solvent extraction [Li et al., 2012], chemical oxidation [Phillips et al., 2006] and pyrolysis [Vidonish et al., 2016] were validated among other strategies.

1.4.2. Chlorinated contaminants: Lindane

Lindane is the gamma isomer of hexachlorocyclohexane (γ-HCH), an OCP (Fig. 1.3 and Table 1.7). Although it is a non-aromatic cyclic compound, is sometimes referred as halogenated aromatic hydrocarbons because of its degradation pathways and general similarity to the chlorobenzene family (it is occasionally named benzene hexachloride). It was used as a pesticide since 1940, either in pure form (pure lindane) or together with the other isomers (technical lindane) [Katsoyiannis et al., 2016].

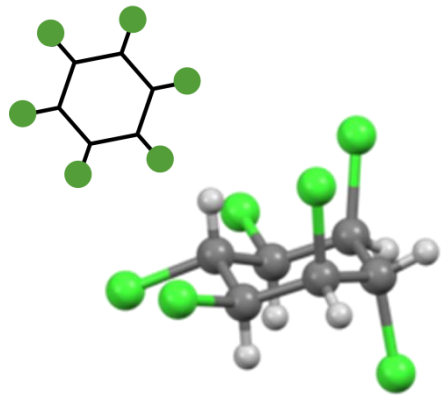


Figure 1.3:
2-D and 3-D lindane structure

Table 1.7: Lindane physical-chemical characteristic

Lindane ($C_6H_6Cl_6$)	
Molecular mass [a]	290.83 g/mol
State [a]	Crystalline solid
Colour [a]	White
Density [b]	1.89 g/cm^3 (19ºC)
Melting point [c]	112ºC
Boiling point [b]	323.4ºC (760 mmHg)
Vapor pressure [b]	3.3×10^{-5} mmHg (20-25ºC)
Water solubility [c]	6-17 mg/L (20-30ºC)
Ethanol solubility [a]	6.4 g/100 g
Ether solubility [a]	20.8 g/100 g
log K_{ow} [c]	3.7
log K_{oc} [b]	3.00-3.57
log K_{aw} [c]	-4.0 to -4.1
log K_{oa} [c]	7.85
log K_{haa} [c]	5.96
EPA toxicity classification [b]	Class II

Extracted from [a][Madaj et al., 2018], [b][J. M. Saez et al., 2017] and [c][Wacławek et al., 2019]

a) Lindane: Health and toxicity

Lindane causes problems associated to both manufacture and use. The waste ratio in the production is 8-12 kg waste per 1 kg lindane [Bodenstein, 1972; De la Torre et al., 2018]. These residues included other hexachlorocyclohexane isomers, chlorobenzenes, chlorophenols and other chlorinated ring derivatives [García-Cervilla et al., 2020]. Dioxin production as PCDD or PCDF has also been detected at some sites [Götz et al., 2012].

In 1953 it was identified for first time as a possible human toxicant [Danopoulos et al., 1953; Wacławek et al., 2019] and since then it has been kept under control. Currently, it is recognized to increase the risks of causing cancer, Alzheimer's and other central nervous system problems, immunosuppression, endocrine problems, reproductive system problems [Salam and Das, 2012] and bioaccumulation [Sun et al., 2016; Wacławek et al., 2019]. For all that, its use was banned in Europe at the 2009 Stockholm Convention [Madaj et al., 2018]. Indeed, it was listed as a persistent organic pollutant (POP) along with its alpha (more abundant and carcinogenic) and beta (more persistent and estrogenic) HCH isomers [Dadhwal et al., 2009].

b) Detection in the environment

Lindane detection in water is particularly difficult due to its low solubility. However, because of the hazards of lindane, various monitoring methods have been designed to detect it. Classically, lindane has been detected by colorimetric techniques [Phillips et al., 2001; Tu, 1976] or by analytic techniques [Imai et al., 1989; Sahu et al., 1990], mainly GC-MS [Covaci et al., 2002; Kumari et al., 2020] and GC-ECD [Covaci et al., 2002].

However, the most recent studies have shown electrochemical detection methods [Noori et al., 2020]. Lindane is more easily reduced than oxidized [Birkin et al., 2004; Cao et al., 2008]. Therefore, all sensors have been based on detecting reduction reactions. In most cases they used volammetric techniques. [Anu Prathap et al., 2015; Anu Prathap and Srivastava, 2013; Birkin et al., 2004; Fayemi et al., 2016; Kumaravel et al., 2013; Peverly et al., 2013; Prathap et al., 2016; Thanalechumi et al., 2019], although some studies used amperometric techniques [Merz et al., 2011; Prathap et al., 2016] and potentiometric techniques [Anirudhan and Alexander, 2015]. Nevertheless, only a few sensors have been tested in samples of contaminated water [Anu Prathap et al., 2015; Anu Prathap and Srivastava, 2013; Fayemi et al., 2016; Prathap et al., 2016; Thanalechumi et al., 2019].

c) Remediation of lindane-polluted environment

Diferent remediation methods for the removal of lindane and its production and degradation by-products have been assayed in soil, both *ex-situ* [Álvarez et al., 2015; Camacho-Pérez et al., 2013; Peng et al., 2015; Quintero et al., 2006; Raimondo et al., 2020a; Salam et al., 2017; Usman et al., 2014; Varo-Arguello et al., 2012], and *in-situ* remediation strategies [Abhilash and Singh, 2008; Phillips et al., 2006].

Several techniques of lindane chemical remediation have been explored [Wacławek et al., 2019]. Oxidative treatments such as hydroxyl radicals [Senthilnathan and Philip, 2010], sulfate radicals [Usman et al., 2017] or electrochemical oxidation [Dominguez et al., 2018] have been successfully tested. However, halogenated compounds may promote toxins generation in oxidation reactions [Evans and Dellinger, 2005]. Otherwise, reduction treatments such as ZVI [Dominguez et al., 2016] or H_2 [Zinovyev et al., 2004] have been validated.

Although biological degradation of HCH is assumed to be for efficient under anaerobic conditions [Mehboob et al., 2013], most studies have focused on pure cultures of

aerobic microorganisms [Kumar and Pannu, 2018; W. Zhang et al., 2020]. The degradation pathways appear to be different in both cases. The most studied pathway is performed by aerobic microorganisms and starts with a dehydrochlorination (non-redox reaction) followed by a dehydroxychlorination [Nagata et al., 2007] (Fig 1.4). Whereas, the anaerobic microorganisms pathway starts with a dechlorination (reduction reaction) followed by a dehydrogenation [Quintero et al., 2005] (Fig. 1.5). In parallel to aerobic/anaerobic studies, cosubstrate-based studies have demonstrated to be effective in lindane degradation. This is the case of sugarcane [Abhilash and Singh, 2008; Raimondo et al., 2020b, 2020a; Salam et al., 2017], tea extract [Wang and Liang, 2018], *Agave tequilana* leaves [Guillén-Jiménez et al., 2012] and root exudates[Álvarez et al., 2012].

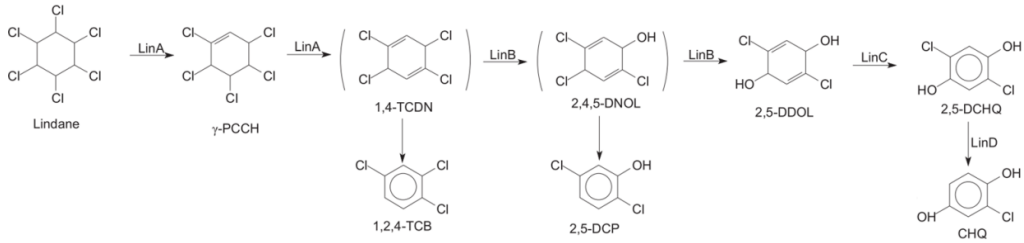


Figure 1.4: Aaerobic pathway of lindane degradation. Extracted from W. Zhang (2020) [W. Zhang et al., 2020]

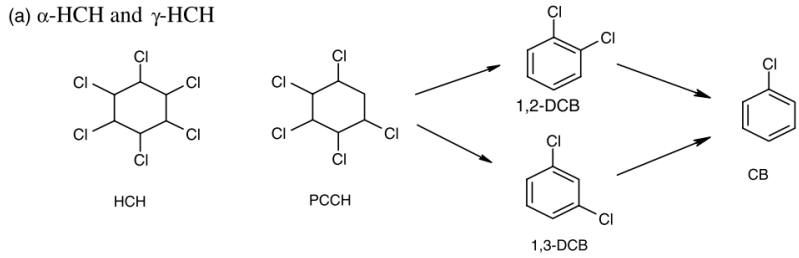


Figure 1.5: Anaerobic pathway of lindane degradation. Extracted from Quintero (2005) [Quintero et al., 2005]

2. Microbial Electrochemical Technologies

2.1. Extracellular Electron Transfer

2.1.1. Electroactive microorganisms

In 1911, M.C. Potter concluded that "the disintegration of organic compounds by micro-organisms is accompanied by the liberation of electrical energy" from observations in cultures of *Saccaromyces cerevisiae* and *Escherichia coli* exposed to different sources of organic matter [Potter, 1911]. However, it was not until 1988 that the process by which microorganisms are able to release electrons to a insoluble material (Fe and Mn oxides) was discovered [Lovley and Phillips, 1988], and, consequently, the term Extracellular Electron Transfer (EET) was born [Hernandez and Newman, 2001]. More than a decade after EET discovery, in 2001, it was revealed the capacity of some microorganisms to donate electrons directly to the electrode [Reimers et al., 2001a]; in 2003, *Geobacter sulfurreducens* appeared as the first microorganism capable of directly transfer electrons to an electrode [Bond and Lovley, 2003].I In 2004, some microorganisms were reported to accept electrons from an electrode [Gregory et al., 2004]. Microorganisms capable of performing EET are called electroactive ones. Most of these microorganisms are mainly bacteria and some archaea [Koch and Harnisch, 2016; Logan et al., 2019]. However, some eukaryotic organisms capable of performing EET have been found, such as yeasts [Hubenova and Mitov, 2015; Potter, 1911] and algae [McCormick et al., 2015].

2.1.2. Interaction microorganism-electrode

In EET process, electrodes replace the insoluble material naturally present in the sediments [Reimers et al., 2001a], to play the role of an electron acceptor [Bond and Lovley, 2003] or donor [Gregory et al., 2004]. There are two main mechanisms to explain how the microorganism-electrode interaction occurs. It can be Direct EET (DEET) or Mediated EET (MEET).

DEET is described according to different hypotheses. The predominant hypothesis is that electrons are transferred from inside the cell to the outermost membrane through cytochromes located on the outer membrane. This hypothesis has been tested in the two main model electroactive microorganisms, the anaerobic Gram-negative bacterium *Geobacter sulfurreducens* [Busalmen et al., 2008; Esteve-Núñez et al., 2011; Snider et al., 2012]. Another hypothesis for DEET function, inferred from indirect evidences, is the production of conductive pili, extensively studied in *G. sulfurreducens* [Gu et al., 2021;

Reguera et al., 2005]. Initially it was concluded that electron transfer must be via a cloud of π bonds present in aromatic residues [X. Liu et al., 2021; Malvankar et al., 2015]; currently a pili with a linearly polymerized outer membrane cytochrome is also proposed [Yalcin et al., 2020].

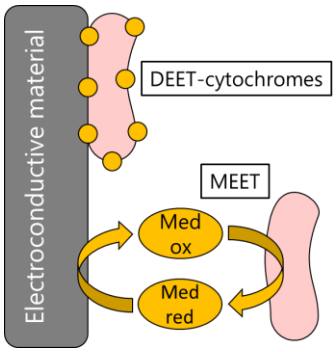


Figure 1.6: EET directly contrasted hypothesis scheme

MEET occurs through soluble redox mediators. S. oneidensis has been shown to produce flavin [Kotloski and Gralnick, 2013], a redox mediator, to carry electrons from the cell to the electrode. This mechanism with flavins has also been found in other bacteria such as Pseudomonas aeruginosa [Glasser et al., 2017] and farther taxonimic Gram-positive Listeria monocytogenes [Light et al., 2018]. Other redox mediators, such as phenazines, phenoxazines or quinines, are also present in MEET processes [Schröder, 2007].

2.1.3. Interaction microorganism-microorganism

EET occurs between a microorganism and an electrode (or insoluble compound in general), but it can also occur between a microorganism that release electrons and a microorganism that accepts electrons. This process is known as Direct Interspecies EET (DIET). DIET was first demonstrated by co-culture of G. sulfurreducens and G. metallireducens. For this, ethanol was used as the sole electron donor (assimilable only by G. metallireducens), and fumarate as the sole electron acceptor (reducible only by G. sulfurreducens) [Summers et al., 2010]. The same process has been promoted in methanogenic environments [McGlynn et al., 2015; Wegener et al., 2015].

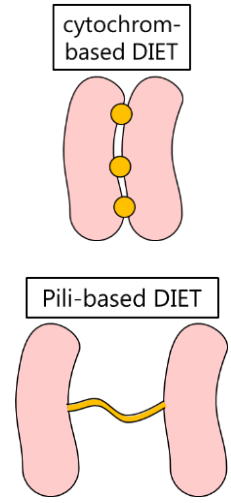


Figure 1.7: DIET schemes

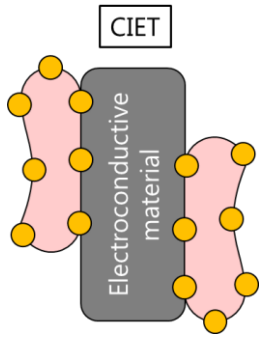


Figure 1.8: CIET scheme

Otherwise, when EET between different species of microorganisms occurs through an electroconductive material, the process is called Conductive-mediated Interspecies EET (CIET) [Nielsen et al., 2010; Rotaru et al., 2021]. In this case, CIET was demonstrated by the degradation of a compound (acetate) that became into unreactive compound in absence of electroconductive material [Rotaru et al., 2018].

2.2. Electrochemical modus operandi

EET process has fostered the generation of different applications that promote microorganism to react with electrodes, known as microbial electrochemistry. Electrochemistry can promote biological reactions in different ways, depending on the used electrodes, their arrangement and their redox reactions.

2.2.1. Polarized systems

A polarized system is a device in which the anode and cathode are connected through a power supply and at least one of the two electrodes is colonized by an electroactive biofilm. In this case, non-spontaneous reactions are desired by using external energy. There are two main different designs within the polarized system.

a) Two electrodes polarized devices

The most basic version of a polarized system host two electrodes, anode and cathode, connected through a power supply. The bioanode, where the organic matter is oxidized, is separated from the cathode by an ion exchange membrane (Fig. 1.9). The reaction of the cathode that causes the most interest is the generation of H_2 [Kadier et al., 2016], although CH_4, formic acid or H_2O_2 generation [Hua et al., 2019] and heavy metals reduction [Bagchi and Behera, 2020] are also studied. This reactor has the advantages of simplicity of design and the possible elimination of the ion exchange membrane, since the anode-cathode potential difference will be setup by the power source supply. However, cathodic target reactions, the most interesting reactions, could compete with oxygen reduction, so anaerobic cathodic chamber is necessary.

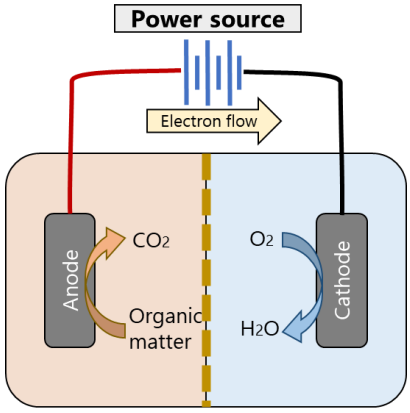


Figure 1.9:
Two electrodes polarized system scheme

b) Three electrodes polarized devices

In a three electrodes system a potential difference can be fixed between an electrode, working electrode, and a reference electrode (electrode with invariable redox potential) placed in the vicinity of the working electrode. Conversely, the potential of the counter electrode is varied to ensure that the potential of the working electrode remains fixed. This potential fixation is achieved by connecting the three electrodes to a potentiostat (Fig. 1.10). Three electrode systems are designed to oxidize or reduce target compounds or groups of compounds. This mode of polarized system has been used in H_2 and acetate synthesis [Chatterjee et al., 2019], dechlorinations [Zhang et al., 2018], petroleum derived compound degradation [H. Wang et al., 2020b; T. Zhang et al., 2010a], agro-chemicals compounds degradation [Rodrigo Quejigo et al., 2018, 2016], sulfide oxidation [Daghio et al., 2018b] or nitrate reduction [Ceballos-Escalera et al., 2022; Tejedor-Sanz et al., 2020].

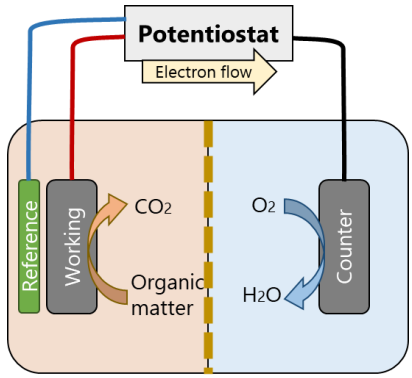


Figure 1.10:
Three electrodes polarized system scheme

2.2.2. Non-polarized systems

A non-polarized system is a device in which the anode and cathode are connected through a resistance. Both electrodes promote spontaneous reactions, producing electron flow and consequently energy production where at least one of the two electrodes is colonized by an electroactive biofilm. Since the concept of non-polarized system was stated [Potter, 1911], the classic design have consisted of two chambers (anodic and cathodic) separated by an ion exchange membrane [Liu and Logan, 2004] (Fig. 1.11). In the anodic chamber, the organic matter (electron donor) is oxidized by bacteria, resulting CO_2, electrons and protons as by-products. These electrons are transferred from the anode to the cathode by an external electric circuit, while protons are transported to the cathodic chamber across the ion exchange membrane by a concentration gradient. In the cathodic chamber, oxygen accepts those electrons and, in combination with the protons, it is reduced to water on the cathode surface. Later, alternatives were tested to obtain more efficient cathodes [Anjum et al., 2021] and to remove the ion exchange membrane [Al Lawati et al., 2019; Gambino et al., 2021]. On the other hand, non-polarized systems have also been developed biocathode to reduce CO_2 [Kannan and Donnellan, 2021] or nutrients with N, P and S [Palanisamy et al., 2019].

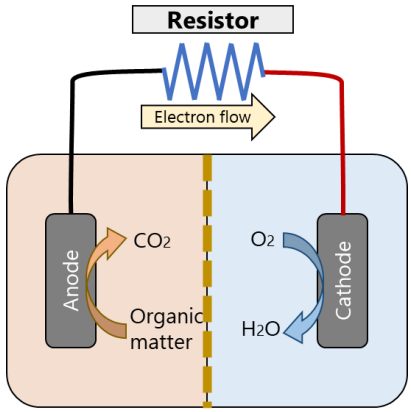


Figure 1.11: Non-polarized system scheme

2.2.3. Snorkel systems (One electrode)

Snorkel system is a device consisting of just one electrode. One extremity of the electrode support anodic reactions, while the other extremity support cathodic ones, so a redox gradient is generated along the whole electrode material (Fig. 12). When this

device was first defined, it was compared to a short circuit non-polarized system by their ends anode and cathode [Erable et al., 2011]. However, it is now understood that the redox gradient favors the emergence of different microenvironments that promote different metabolic activities [Aelterman et al., 2008; Dennis et al., 2016; Prado et al., 2020]. This system has been used especially to oxidize organic matter [Aguirre-Sierra et al., 2016; Erable et al., 2011; Prado et al., 2019], petroleum derived contaminants [Cruz Viggi et al., 2015] or agro-chemicals compounds [Domínguez-Garay et al., 2018a]; and to reduce NO_3^- [Yang et al., 2015].

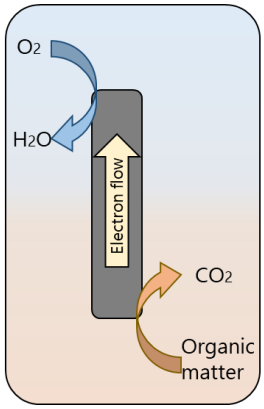


Figure 1.12: Snorkel system scheme

2.3. Microbial electrochemical technologies: applications

2.3.1. Energy production: MFC and SMFC

The discovery of electroactive bacteria immediately triggered the interest in electricity production as first application to be achieved [Davis and Yarbrough, 1962]. Therefore, the use of non-polarized systems leads into Microbial Fuel Cell (MFC), and MFC studies resulted in a large number of improvements applied to non-polarized systems. Reactors, electrode materials, ion exchange membranes, co-cultures (culture consortia), start-up method were optimized to maximized electricity production [Li and Sheng, 2011]. At present, methods to improve energy production are still been researched [Saba et al., 2017]. However, energy production has not yet reached desirable levels as energy development while other applications have been appearing and demonstrating their feasibility.

- Soil and sediment MFC

A particular case is the energy harvesting from soil or sediment using SMFC. In Soils [Gustave et al., 2019] or Sediments [Reimers et al., 2001a] MFC (SMFC to both cases [Li et al., 2022]), the anode is buried in the soil or sediment, where electroactive bacteria oxidize organic matter releasing electrons; the cathode is placed in the aerial part, where oxygen is spontaneously reduced; and electrons flow from the anode to the cathode with the consequent energy production [Zabihallahpoor et al., 2015]. Here, the soil or sediment between the two electrodes replaces the membrane (Fig. 13). Some techniques have tried to increase the amount of energy extracted from the process such as soil pH modifications [Sajana et al., 2013], oxygen increasing in cathode [Majumder et al., 2014] or soil resistivity decreasing [Domínguez-Garay et al., 2013]. The organic matter concentration present in the soil or sediment is also key for energy harvesting [Rezaei et al., 2007]. In order to increase the organic matter of the substrate, SMFC fueled by plants or Planted MFC (PMFC) have been developed [Maddalwar et al., 2021]. First, root exudates increase the presence of organic matter in the soil or sediment and improve anode efficiency. Second, oxygen concentration increases in the superficial zones and improves the cathode efficiency.

Further progress has also been made in scaling up this technology [Ewing et al., 2014], but SMFCs suffer from limitations (high resistance) to become competitive among renewable energy sources.

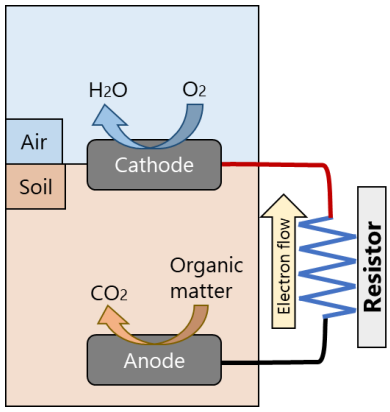


Figure 1.13:
SMFC scheme

2.3.2. Water electrobioremediation

From the discovery of microbial electrochemistry, wastewater treatment was the very first target [Jadhav et al., 2022; Srivastava et al., 2020]. In the last two decades, a number of reactor designs have been developed in order to remove organic pollutants.

The main concern of wastewater is the presence of organic pollutants. Therefore, most of the investigations are focused on removing COD or BOD [Capodaglio and Bolognesi, 2020]. Furthermore, N and P [Srivastava et al., 2020], dyes [Kumar et al., 2021; Solanki et al., 2013], petroleum derived hydrocarbons [Priyadarshini et al., 2021] and drugs [Zakaria and Dhar, 2022] have been removed by means of bioelectrochemical systems. Nevertheless, the latest studies seek to eliminate contaminants in parallel to recover them in a harmless and reusable form [Devda et al., 2021; Jadhav et al., 2017; Kumar et al., 2021].

Bioelectrochemical systems have been used for nitrogen removal from wastewater by using different microbial processes depending on the N speciation: ammonia oxidation to N_2 gas, catalyzed by nitrifying bacteria [Aguirre-Sierra et al., 2020; Koffi and Okabe, 2021] or anammox [Shaw et al., 2020], coupling aerobic ammonia oxidation to bioelectrochemical denitrification with a cathode working as electron donor [Virdis et al., 2010], or direct denitrificatication [Chu et al., 2021; Tejedor-Sanz et al., 2016].

First reactors were intended to use MFCs for water remediation and simultaneous energy production. They were able to remove organic matter [Kargi and Eker, 2007]. Further on, polarized systems have been used to remove NO_3^- [Hussain et al., 2016; T. Zhu et al., 2016], SO_4^{2-} [K. Wang et al., 2017] and S^{2-} [Dong, 2017] among several contaminants. Advances in wastewater treatment have led to the development of new reactors such as filter-press reactors for wastewater treatment [Borjas et al., 2015] or different wetland-based reactors [Srivastava et al., 2020].

Microbial Electrochemical Fluidized Bed Reactor (ME-FBR) is a promising example of innovative reactor designs [Tejedor-Sanz and Esteve-Nuñez, 2020] (Fig.1.14). Fluid-like electrodes minimize limitations related with mass transfer and allow electroactive planktonic bacteria to grow [Borsje et al., 2021; Tejedor-Sanz et al., 2017, 2016]. ME-FBR have been validated with organic matter and nitrogen removal through a bioanode [Yeray Asensio et al., 2021; Tejedor-Sanz et al., 2018]and a biocathode [Tejedor-Sanz et al., 2020].

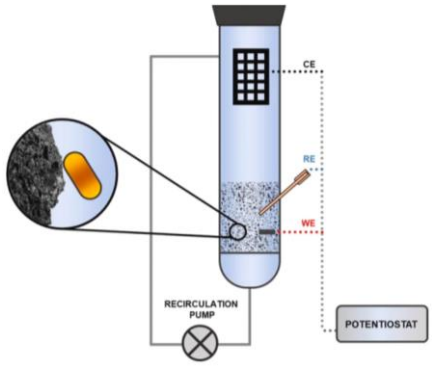


Figure 1.14: Fluidized bed reactor scheme. WE is working electrode, RE is refence electrode, CE is counter electrode. Extracted from Asensio (2021) [Y. Asensio et al., 2021]

A hybrid concept was born by merging microbial electrochemistry field with treatment wetlands, a nature-based solution for cleaning-up wastewater. The result are the so-called METland® [Aguirre-Sierra et al., 2016] (Fig.1.15). This technological solution has been widely studied for urban wastewater treatment [Prado de Nicolás et al., 2022], including removal of emerging pollutants [Pun et al., 2019], ammonium oxidation [Aguirre-Sierra et al., 2020], electroconductive materials [Prado et al., 2019], increase electron sink [Prado et al., 2020], and sustainability of construction [Peñacoba-Antona et al., 2021b, 2021a]. The result of decade on intensive research is the commercialization of the solution through the spinoff METfilter.

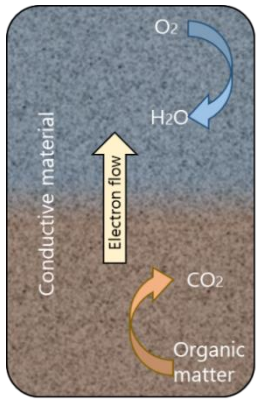


Figure 1.15: METland scheme

Alternatively, electrobioremediation has been tested in groundwater, with successful results in removal of NO_3^- removal [Ceballos-Escalera et al., 2021; Cecconet et al., 2018; Puggioni et al., 2021], petroleum derived hydrocarbons [Cecconet et al., 2020], halogenated compounds [Aulenta et al., 2007; Lai et al., 2017] and radionuclides [Gregory and Lovley, 2005]. In the process of optimization, the classical dual-chamber system has been modified as far as designs for *in-situ* wells [Tucci et al., 2022, 2021a].

2.3.3. Desalination: microbial desalination cells

Another application related to water treatment is desalination. For this purpose, the Microbial Desalination Cell (MDC), a reactor with three chambers separated by ionic membranes, was designed [Borjas et al., 2015; Cao et al., 2009; Ewusi-Mensah et al., 2021; Ramírez-Moreno et al., 2021, 2019] (Fig.1.16). This arrangement has been modified and new designs have appeared [Al-Mamun et al., 2018] that are capable of coupling other applications of bioelectrochemistry within MDC such as removal of nitrogen, heavy metals (including transition metals boron and arsenic) and carbonates, pH modification, production of H_2 [Imoro et al., 2021], phenol removal [Pradhan et al., 2015] and petroleum derived compound removal [Tawalbeh et al., 2018]. MDC have reached a maturity stage that have allowed desalination of 150 L/h during several months in a pilot system [Salinas-Rodriguez et al., 2021].

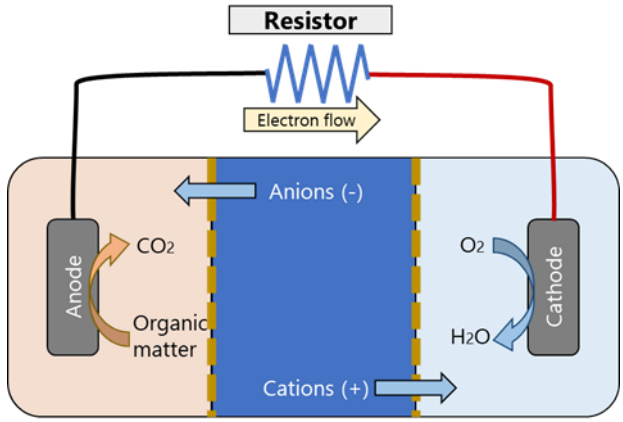


Figure 1.16: MDC scheme

2.3.4. Microbial electrosynthesis

Microbial electrochemical systems also address the needs of producing compounds of interest. Thus, microbial electrosynthesis aims the production of value-added compounds. These reactors have been validated for the generation of H_2 [Chatterjee et al., 2019; Tang, 2021], CH_4 [Dykstra and Pavlostathis, 2020] and other electrofermentation derived compounds [Schievano et al., 2016] such as medium chain fatty acids [Chu et al., 2021], short chain fatty acids and alcohols [Chandrasekhar et al., 2021].

2.3.5. Microbial Electrochemical Sensors

Microbial electrochemial sensors, initially called whole-cell biosensors [Rawson et al., 1989], have been defined in Section 1.2.3 as electrochemical sensors that use electroactive microorganisms for detection purpose. Among that microorganisms, sensors have been colonized by pure culture, especially *Pseudomonas* cultures [Su et al., 2011] but also other bacteria [Tront et al., 2008] and some eukaryotes [Shitanda et al., 2009; Tag et al., 2007], or by mixed culture [Jiang et al., 2018a].

These sensors have been shown to be capable of quantifying a wide range of compounds [Jiang et al., 2018a]. Several tested compounds, organic matter in the form of BOD [Kumlanghan et al., 2008], COD [Di Lorenzo et al., 2009] and COD into a constructed wetland [Corbella et al., 2019], acetate [Liu et al., 2014] and other VFAs [Jiang et al., 2018a], has been quantified; and toxic such as heavy metals [Chouteau et al., 2005; Liu et al., 2014; Tag et al., 2007; Tekaya et al., 2014; Yüce et al., 2010; Zlatev et al., 2006], surfactants [Taranova et al., 2002], petroleum derived compounds [Rasinger et al., 2005], agro-chemicals compounds [Chouteau et al., 2005; Lei et al., 2005; Odaci et al., 2008; Shitanda et al., 2009; Tekaya et al., 2014], phenolic compounds [Timur et al., 2007a, 2007b] and drugs [Kumar et al., 2008; Zeng et al., 2017] have been detected.

From operation point of view, most of these sensors are based on non-polarized systems reactors [Velasquez-Orta et al., 2020] because of their construction simplicity. However, polarized system systems offer important advantages in order to have an accurate signal. Two electrode polarized systems have the advantage of controlling the electron flow direction, but they are limited in the potential control (no determine each electrode potential). This have been investigated in some studies [Jin et al., 2017; Yuan and Kim, 2017]. In contrast, three electrodes polarized systems have the advantage of fixing the potential of an electrode to detect a target compound or group of compounds. For this reason, many microbial electrochemical sensor based on three electrode polarized system have emerged [Corbella et al., 2019; Fernandez-Gatell et al., 2022; Hua et al., 2019; Jiang et al., 2018a].

From a sensor configuration perspective (detailed in Section 1.2.3), amperometry is the most used technique [Jiang et al., 2018a; Su et al., 2011], but other strategies such as potentiometry [Kumar et al., 2008; Liu et al., 2014], voltammetry [Timur et al., 2007b] and conductimetry [Chouteau et al., 2005; Tekaya et al., 2014] have also been implemented.

The potential of this microbial electrochemical sensor is very promising, at least, in the detection of organic pollutants. Several patents [Huang et al., 2012; Kiely et al., 2019] have been filed and 3 independent products are now commercially available and manufactured by Nanoelectra S.L. (fundamental pillar of this thesis), HYDREKA SAS and SENTRY™, and compared in Table 1.8 and Fig. 1.17.

Table 1.8: comercial microbial electrochemical sensors

Comercial sensor	**IoT Biosensing**	**NODE biosensor**	**MET sensor**
Manufacturing Company	Nanoelectra S.L.	HYDREKA SAS	SENTRY™
Operation mode	Polarized (three electrodes)	Non polarized	Non detailed
Electrochemical technique	Chronoamperometry	Chronoamperometry	Non detailed
Image	Fig. 1.17 A	Fig. 1.17 B	Fig. 1.17 C
Web page	nanoelectra.com	sentrywatertech.com	hydreka.com

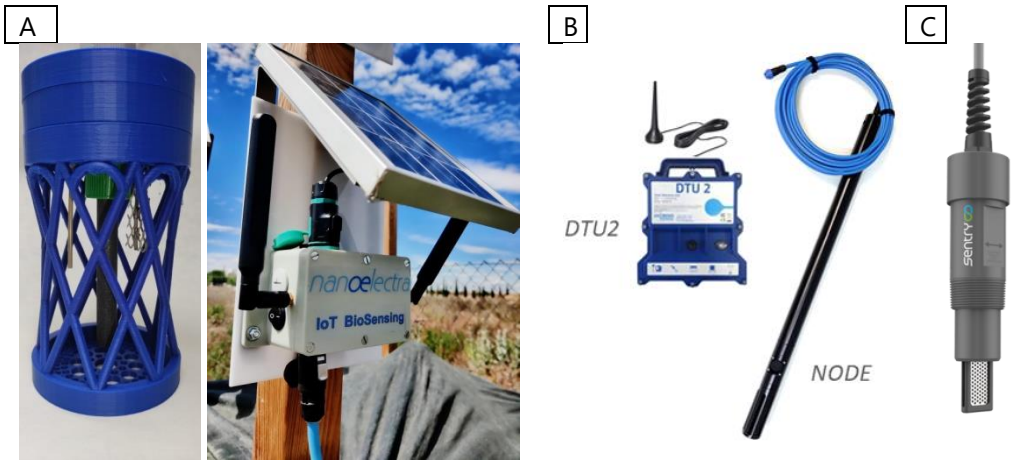


Figure 1.17: A) IoT Biosensing (Nanoelectra S.L.); B) NODE biosensor (HYDREKA SAS); C) MET sensor (SENTRY™)

Petroleum derived compounds are one of the most widespread contaminants group (Fig.1.1). This spread and its dangerous mobilization in water have highlighted key points for the development of microbial electrochemical sensor for its detection. Different non-polarized systems have determined concentrations of hydrocarbons [Nandimandalam and Gude, 2019a] and engine oil [Dai et al., 2019], while three electrodes polarized system have determined BTEX [Rasinger et al., 2005; Santoro et al.,

2016] and naphthenic acid [Chung et al., 2020]. In addition, there are many examples in which degradation systems undergo modifications in electrochemical behavior [Hao et al., 2020; Kronenberg et al., 2017] that tend to suggest that the development of these sensors is still in its infancy .

Organochlorine compounds represent a substantial part of soil and groundwater contamination (Fig. 1.1). Like microbial electrochemical sensors for petroleum-derived compounds, microbial electrochemical sensors for organochlorines have been driven by the environmental problems they can cause. In this case, non-polarized systems have been used to detect PCBs [Kim et al., 2007] and three electrodes polarized system have been used for 2-chlorophenol [Odaci et al., 2008], paraquat, diuron [Tucci et al., 2019] and 2,4-D [Odaci et al., 2008] detection. Meanwhile, considering the possibilities offered by bioelectrochemical systems for the degradation of organochlorine compounds [Zhang et al., 2018], organochlorine microbial electrochemical sensors is still at an early stage of development.

Lindane detection using microbial electrochemical sensor have only tested in few studies. *Escherichia coli* was reported to detect amperometrically lindane isomers and one by-product after overexpression of LinA2 gene [Anu Prathap et al., 2012]. *Streptomyces* strain M7 detected and quantified lindane via impedometric techniques [López Rodriguez et al., 2015].

2.3.6. Soil and sediment electrobioremediation

Soil and sediment electrobioremediation can be understood as an electrochemical biostimulation, as described in Section 1.3.1 of this thesis dissertation. Electrobioremediation may overcome the lack of electron donor or acceptor by using electrodes directly buried in soil or sediments. Since the first assay for removing aromatic pollutants in sediment [T. Zhang et al., 2010a], this technology has been successfully tested in variety of contaminants in soil and sediments [Tucci et al., 2021b].

Many of these contaminant degradations have been associated to different enhancement strategies. The development of different devices has been one of the optimization methods. Multi-anode devices [Li et al., 2016a, 2015; Zhang et al., 2015] ensure electroactive microorganisms not to be limited limited for bioremediation. Otherwise, cylindrical devices [Huang et al., 2011; Lu et al., 2014b, 2014a; H. Wang et al., 2020a; Wang et al., 2019, 2012] maximize the anode-soil and cathode-air contact surface and minimize the anode-cathode distance.

Unfortunately, most of the environmental applications for microbial electrochemical systems have been conducted in waterlogged soils or sediments under flooded conditions [Domínguez-Garay et al., 2013; Li and Yu, 2015; Rodrigo Quejigo et al., 2016; Sherafatmand and Ng, 2015; Yan et al., 2012]. High moisture provides a low resistant in the soil and favors electrochemical reactions [Habibul et al., 2016; Li et al., 2016d]. However flooding is not a common situation for soil and only 5-8% of the world's lands are wetlands [Fennessy and Wardrop, 2016] of which only half are constantly flooded [Davidson et al., 2018]. Moreover, it is not feasible to flood all contaminated soil so common bioelectrochemical designs are certainly limited to operate in standard soils.

Several studies have tested the non-flooded soil conditions in electrobioremediation. Non-polarized systems for petroleum derived compounds improve remediation as increase the moisture [Wang et al., 2019, 2012]. And polarized system at constant moisture remove petroleum derived compounds [Li et al., 2010] and PCP [Harbottle et al., 2009]. Techniques for improve soil moisture have been hardly studied. A moisture gel layer placed around the anode and in contact with the soil was tested to remove petroleum derived compounds [H. Wang et al., 2020a]. In this sense, previous studies in our group came up with a new concept by designing a bioelectrochemical system to operate in non-flooded soil conditions by integrating an out-of-soil cathode using a ceramic barrier tool for separating anodic and cathodic processes (Fig. 1.18) [Domínguez-Garay and Esteve-Núñez, 2018]. This system demonstrated their capability for remediating atrazine-polluted soil and is a key methodology in the present thesis

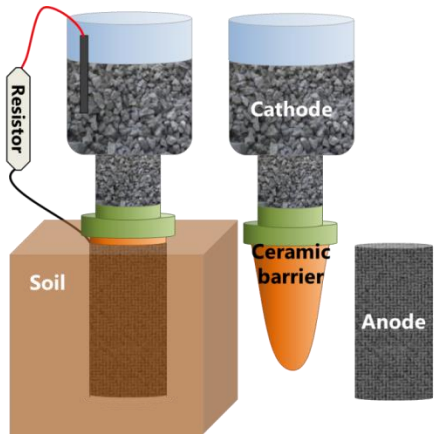


Figure 1.18: Design for operating microbial electrochemical device in non-flooded soils. Figure adapted from [Domínguez-Garay and Esteve-Núñez, 2018]

In parallel, reagent or material additions have been tested as strategy for maximizing degradation. Similar to any microorganism culture, nutrients [Sherafatmand and Ng, 2015; Wang et al., 2012; Xia et al., 2015] and co-substrates [Bhande et al., 2019; Camacho-Pérez et al., 2013; Cao et al., 2016; Zhao et al., 2018] have been used to enhance the growth and metabolism of electroactive and related bacteria. Agricultural amendments as biochar [Cai et al., 2020; Li et al., 2019] or plant pieces [Song et al., 2015; Song and Jiang, 2018; D. Zhu et al., 2016] have been added for improve soil characteristics and microorganism activity. Solid conductive or metal-oxidized as carbon fiber [Li et al., 2016c, 2016b; X. Li et al., 2018b; Xiaolin Zhang et al., 2020; Zhao et al., 2019] and Fe-oxides [Liu et al., 2017; Xu et al., 2017; Yan and Reible, 2015, 2012; Yan et al., 2012; H. Yu et al., 2017; Zhou et al., 2014] promote the electroactive microorganism growth. Moreover, surfactants assist in some contaminants biodegradation [Barba et al., 2019; Cao et al., 2016; X. Li et al., 2018b; Lu et al., 2014a; Niqui-Arroyo and Ortega-Calvo, 2007; Ramírez et al., 2015; Xu et al., 2015]. Finally, acid [J. Zhang et al., 2020] could release immobilized metals and sand [Li et al., 2015] reduce soil electrochemical resistance.

a) Petroleum hydrocarbon electrobioremediation

Petroleum-derived compounds are present in most of the contaminated sites (Fig.1.1). This spread has made it necessary to develop a large number of systems for their degradation. Among the developed systems, electrobioremediation systems have emerged in recent years [Tucci et al., 2021b]. Reciprocally, electrobioremediation systems have been improved, in most studies, by the treatment of petroleum hydrocarbons, resulting in numerous papers for remediating aromatic compounds (Table 1.9) and petroleum-derived mixtures (Tables 1.10a and 1.10b).

Table 1.9: Aromatic compound electroremediation in soils and sediments

Contamination	Electrochemical configuration	Amendment or artificial matrix	Reference
Benzene, toluene, naphthalene	Polarized	Growth media	[T. Zhang et al., 2010a]
Benzo[a]pyrene	Non-polarized	-	[Yan et al., 2015]
Benzo[a]pyrene	Non-polarized	-	[Yan et al., 2017]
Phenanthrene	Polarized	Mineral medium	[Niqui-Arroyo et al., 2006]
Phenanthrene	Polarized	Mineral medium	[Yan and Reible, 2015]
Phenanthrene and naphthalene	Polarized	Fe-oxide (sidertite)	[Yan and Reible, 2012]
Phenanthrene and pyrene	Non-polarized	-	[Liang et al., 2020]
Phenanthrene and pyrene	Non-polarized	Fe-oxide (amorphous Fe oxide)	[Yan et al., 2012]
Phenanthrene and pyrene	Non-polarized	-	[B. Liu et al., 2019]
Naphthalene, 2-methylnaphthalene, phenanthrene	Non-polarized	Mineral medium	[Hamdan et al., 2017]
Naphthalene, acenaphthene and phenanthrene	Non-polarized	Nutrients (N and S)	[Sherafatmand and Ng, 2015]
PAHs	Non-polarized	-	[Nastro et al., 2019]
PAHs	Non-polarized	-	[B. Yu et al., 2017]
PAHs	Polarized	Surfactant (Brij 35) and mineral medium	[Niqui-Arroyo and Ortega-Calvo, 2007]
PAHs	Polarized	Mineral medium	[Sharma et al., 2020]

Abbreviations: PAHs, polyaromatic hydrocarbons

Table 1.10a: Petroleum-derived mixture electroremediation in soils and sediments (Part 1)

Contamination	Electrochemical configuration	Amendment or artificial matrix	Reference
Crude oil	Polarized	Artificial groundwater	[H. Wang et al., 2020b]
Crude oil	Snorkel	-	[Aulenta et al., 2021a]
Crude oil	Snorkel	Artificial seawater	[Marzocchi et al., 2020]
Crude oil	Snorkel	Artificial seawater	[Barbato et al., 2022]
Crude oil	Snorkel	-	[Cruz Viggi et al., 2015]
Llight crude oil	Polarized	-	[Cappello et al., 2019]
Llight crude oil	Polarized	-	[Bellagamba et al., 2017]
Llight crude oil	Polarized	-	[Li et al., 2010]
Llight crude oil	Snorkel	Fresh brackish medium	[Viggi et al., 2017]
Diesel	Non-polarized	Artificial groundwater	[Wang et al., 2019]
Diesel	Non-polarized	Artificial groundwater	[Mao et al., 2016]
Diesel	Non-polarized	-	[Lu et al., 2014b]
Diesel	Polarized	Surfactant (SDS) and mineral medium	[Ramírez et al., 2015]
Diesel	Polarized	Artificial groundwater	[Mena et al., 2016]
Diesel and engine oil contamination	Non-polarized	Surfactant (Triton X-100)	[Lu et al., 2014a]

Abbreviations::SDS, Sodium Dodecyl Sulfate.

Table 1.10b: Petroleum-derived mixture electroremediation in soils and sediments (Part 2)

Contamination	Electrochemical configuration	Amendment or artificial matrix	Reference
Chemical and petroleum hydrocarbon	Non-polarized	Methanol	[Zhao et al., 2018]
Hydrocarbons	Non-polarized	Refinery wastewater and growth medium	[Morris and Jin, 2012]
Petroleum hydrocarbon	Non-polarized	Polyacrylamide hydrogel and nutrients (N and P)	[H. Wang et al., 2020a]
Petroleum hydrocarbon	Non-polarized	Surfactant (Tween 80)	[Nandy et al., 2022]
Petroleum hydrocarbon	Non-polarized	-	[Li et al., 2014]
Petroleum hydrocarbon	Non-polarized	-	[Zhang et al., 2015]
Petroleum hydrocarbon	Non-polarized	-	[X. Li et al., 2018a]
Petroleum hydrocarbon	Non-polarized	Carbon fiber	[Li et al., 2016b]
Petroleum hydrocarbon	Non-polarized	Carbon fiber	[Li et al., 2016c]
Petroleum hydrocarbon	Non-polarized	Carbon fiber	[Xiaolin Zhang et al., 2020]
Petroleum hydrocarbon	Non-polarized	Carbon fiber & surfactants (β-cyclodextrin, SDS, CTAB, lecithos or GMS)	[X. Li et al., 2018b]
Petroleum hydrocarbon	Non-polarized	Biochar	[Li et al., 2019]
Petroleum hydrocarbon	Non-polarized	Sand	[Li et al., 2015]
Petroleum hydrocarbon	Non-polarized	Nutrients (N and P)	[Wang et al., 2012]

Abbreviations: SDS, Sodium Dodecyl Sulfate; CTAB, Cetrimonium bromide; GMS, Glycerol monostearate

b) Electrobioremediation of Agro-chemical pollutants

Soil agro-chemical degradation have been studied thanks to non-polarized systems for herbicides such as atrazine [Domínguez-Garay et al., 2018a; Domínguez-Garay and Esteve-Núñez, 2018; H. Wang et al., 2017; Wang et al., 2018], metolachlor [Y. Li et al., 2018] or hexachlorobenzene; fungicides such as hexachlorobenzene [Cao et al., 2016, 2015; Wang et al., 2018]; and pesticides such as lindane [Camacho-Pérez et al., 2013]. Furthermore, mediated by polarized system systems, degradation of herbicides such as isoproturon [Rodrigo Quejigo et al., 2018, 2016], oxyfluorfen [Barba et al., 2019, 2018, 2017] or 2,4-D [Barba et al., 2018]; and pesticides such as pentachlorophenol [Cai et al., 2020; Harbottle et al., 2009].

Most of the electrobioremediation cases are non-polarized systems [Tucci et al., 2021b] because of their simplicity in construction. However, polarized systems have been particularly useful in remediation of halogenated compounds [Barba et al., 2018; Cai et al., 2020; Harbottle et al., 2009; Liu et al., 2017; H. Yu et al., 2017], due to the reductive pathways favoring dehalogenation [Fincker and Spormann, 2017].

Lindane biodegradation is an example where reductive pathways are required. Anaerobic conditions, the natural condition with most reducing properties, enhance lindane degradation [Camacho-Pérez et al., 2012]. Co-substrates, which release electron during degradation, also increase the lindane degradation [Álvarez et al., 2012; Salam et al., 2017]. Anaerobic conditions and co-substrate additions highlight the greater lindane removal in reducing conditions. Even in non-polarized reactors with bioanodes, better results have been observed if oxygen permeability is reduced [Camacho-Pérez et al., 2013]. Anaerobic conditions and low coulombic efficiency indicated that the lindane degradation reaction occurred mainly in the anaerobic (and reducing) medium, independently of the bioanode.

3. Objetives

The present thesis aims to evaluate the capabilities of microbial electrochemistry to remediate and detect contamination discharged in soils and groundwater. With this goal, we have tested a soil-persistent halogenated compound with low water solubility (lindane) and different persistent hydrocarbons with higher water solubility and mobility (BTEX, ETBE, vinylcyclohexene and mixtures of them). The experiments were first focused on the detection of these compounds by microbial electrochemical strategies. Second, we focused on the electrobioremediation of lindane and its isomers in soils and sediments at lab scale, highlighting the degradation in non-flooded soil. Finally, we studied the electrobioremediation of lindane and isomers at outdoor pilot field scale, where the resulting sediment was evaluated in depth through the bacterial community and germination toxicity.

Therefore, the following specific objectives were proposed:

3.1. To design a microbial electrochemical sensor and to evaluate the response to the presence of BTEX, ETBE, kerosene, vinylcyclohexene and lindane in groundwater at lab scale and outdoor mesocosm.

In Chapter 2, a microbial electrochemical sensor was designed, constructed and validated through electrochemical response after exposure to different contaminants. First it was validated at laboratory scale using BTEX, vinylcyclohexene and lindane pulses. Then it was validated in a mesocosm using BTEX, ETBE, vinylcyclohexene and kerosene pulses.

3.2. To design an electrobioremediation setup for lindane removal in different edaphic environments.

In Chapter 3, different configuration of electrobioremediation devices were studied. The main efforts were to maximize the degradation of lindane, to rebuild the device for extrapolation to different environments and to optimize the system in non-optimal environments for electrobioremediation.

3.3. To validate the electrobioremediation setup for outdoor lindane removal at a real polluted site.

After studying the different systems in chapter 3, in chapter 4 we explored different electrobioremediation configurations. They were implemented in order to find the configuration with the highest remediation results in the contaminated area of Sabiñanigo (Huesca).

3.4. To verify the bioelectroactive redox conditions for BTEX, ETBE, vinylcyclohexene, keronsene and lindane degradation.

Chapters 2, 3 and 4 validated the electrochemical configurations capable of degradating the studied compounds. Chapter 1 shows that the proposed redox reactions (oxidation or reduction) for the different pollutants (BTEX, ETBE, kerosene, vinylcyclohexene and lindane) are consistent with the previous literature. In chapters 2 and 3 we confirmed that reduction reaction was the one leading to a larger lindane removal.

3.5. To analyze the electrochemical response of electrobioremediation devices in soil and sediment.

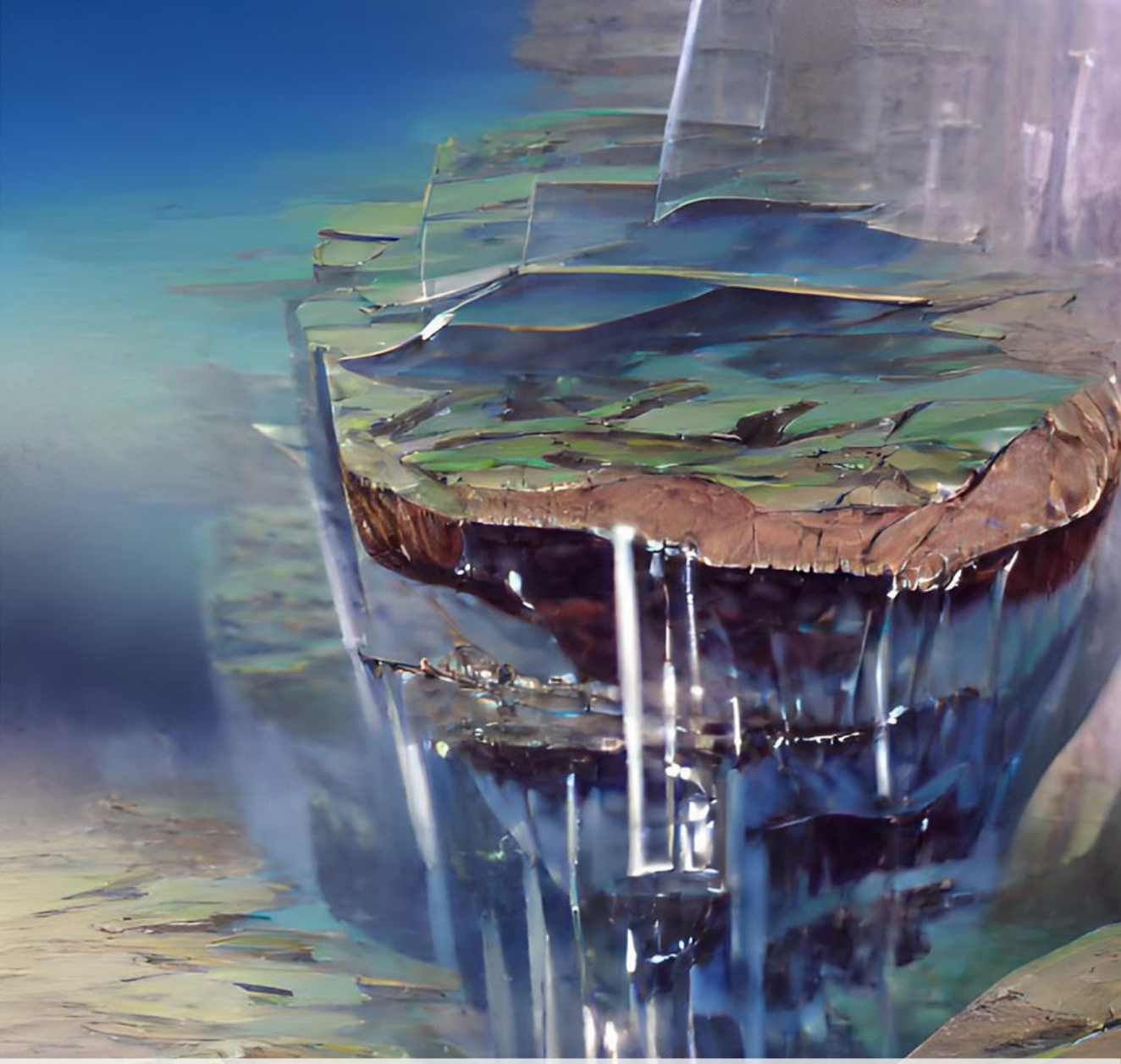
Chapters 2 and 3 analyzed the devices used in electrobioremediation. We have analyzed response in terms of redox potentials, electrical currents and cyclic voltammetries to make correlation between such variations, setup configurations and the edaphic matrix.

3.6. To analyze the ecotoxicological impact of electrobioremediating lindane-polluted soil

In chapters 2 and 3, soil, we analyzed sediment and water at the end of the electrobioremediation task to observe the impact of the treatment. In chapter 2, we analyzed physicochemical characteristics (pH and conductivity) at the end of the assay. In chapter 3, we analyzed the soil toxicity at the end of the experiment by germination phytotoxicity test.

3.7. To analyze the influence of lindane-polluted soil electrobioremediation on bacterial community

Chapter 3 included the study of the microbiological community at the end of the experiment. The 16-S gene was analyzed by Illumina and the bacteria present were compared with bacteria with degradative capacities (lindane and other pollutants) and with electroactive capacities or related to them (DIET, CIET...).



Chapter 2:

Microbial electrochemical biosensor for real-time detection of pollutant hydrocarbons in groundwater

Chapter 2: Microbial electrochemical biosensor for real-time detection of pollutant hydrocarbons in groundwater

Abstract

Anthropogenic contamination with petroleum hydrocarbons and agrochemical sectors is a serious environmental problem, especially in environments limited in electron acceptors in which natural attenuation is not sufficient to cope with contamination. The monitoring of risk sites is the most suitable strategy for prevention. In this work we have investigated the detection of contaminants in groundwater by means of a microbial electrochemical biosensor at microcosm and mesocosm scale. For this purpose, we used a 3-electrode configuration (working electrode polarized at 0.6V vs. Ag/AgCl) inserted inside a piezometer. After a period of colonization, using as sole inoculum the microbial community of the uncontaminated groundwater, we observed a response (<2 hours) to a pulse containing i) a pollutants mixture of benzene, toluene, ethylbenzene and xylene (BTEX) and i) ETBE. Additionally, we also tested the response to complex mixtures using a kerosene spike. Alternatively, a biocathode -based sensor strategy (-0.6V vs. Ag/AgCl) was followed to monitor electrical current consumption (associate to dehalogenation) in presence of the insecticide lindane (gamma-hexachlorocyclohexane).

1. Introduction

Environmental limitations in contaminated sites such as the bioavailability of the contaminants, availability of electron acceptors, salinity or lack of essential nutrients [Burns et al., 1996; McFarland et al., 2008], limits that natural attenuation for removing pollutants, making human intervention necessary [Wilson and Jones, 1993]. Thus, monitoring sites with a high risk of contamination is a common practice in order to reduce economic costs and environmental problems [Farhadian et al., 2008].

In the early 2000s [Bond et al., 2002; Reimers et al., 2001b], a new field so-called electromicrobiology was born allowing to merge two concepts: the microbial metabolism of organic pollutants and the extracellular electron transfer. The result of such coupling can generate electrical current from oxidative metabolism of contaminants by electroactive bacteria. The technologies designed after such electromicrobial concepts are known as Microbial electrochemical technologies (MET) and constitute a new field where electrodes can act as an inexhaustible electron donor or acceptor [Logan et al., 2019]. Those MET devoted to enhance the removal of contaminants gave birth to the term electrobioremediation [X. Wang et al., 2020b]. Indeed, electrobioremediation are among the most successful applications from MET field, including soil bioremediation [Daghio et al., 2017; Domínguez-Garay et al., 2018b; Domínguez-Garay and Esteve-Núñez, 2018], marine sediment [Tucci et al., 2021b], groundwater [Pous et al., 2015] and wastewater [Mosquera-Romero et al., 2023]. In fact, the electric current produced is a kinetic measurement directly related to the concentration of the contaminant [Hamelers et al., 2011]. For this reason, microbial electrochemistry has been proposed as on-site monitoring tool for pollutants in different environments [Hassan et al., 2021; Sevda et al., 2020].

For instance, different electrochemical biosensors have been developed in the wastewater field [Ejeian et al., 2018]. They can detect biodegradable organic matter like biological oxygen demand (BOD) [Peixoto et al., 2011; Qi et al., 2021] or more specific chemicals like acetate [Estevez-Canales et al., 2015], or other volatile fatty acids [Jiang et al., 2018b; Y. Jiang et al., 2019; Schievano et al., 2018], petroleum-derived pollutants [Nandimandalam and Gude, 2019b] or Cr(VI) [Chung et al., 2016]. The presence of toxic chemicals like heavy metals [Yogarajah and Tsai, 2015; Yu et al., 2020], mycotoxins [Y. Chen et al., 2020] or formaldehyde [Dávila et al., 2011] can also be detected when a

steady state electrical current is suddenly affected. Not just water matrix but microbial electrochemistry have also been tested to monitor soil and sediment microbial metabolism [Logroño et al., 2016; Wardman et al., 2014]. These microbial electrochemical sensors have been widely developed under microbial fuel-cell (MFC) configuration [Chouler et al., 2018; Cui et al., 2019; Di Lorenzo et al., 2014; Jiang et al., 2018b; W. Liu et al., 2019; Nandimandalam and Gude, 2019b]. However, microbial electrolysis-cell (MEC) based biosensors are also an interesting option for *in-situ* environmental monitoring, providing a continuous measurement [Adekunle et al., 2019; Hua et al., 2019]. Moreover, the use of genetic engineered strain of *Geobacter* to condition the production of electricity to a regulatory circuit is certainly a possibility [Ueki and Lovley, 2010] and, more recently, *E. coli* was used as chassis to detect thiosulfate using an abiotic electrochemical reaction [Atkinson et al., 2022].

One of the most interesting environments for validating microbial electrochemical sensors is groundwater polluted with petroleum-based hydrocarbon. Groundwater is an important freshwater source, so preservation of these environments is substantial as they become scarce. However, the increasing chemical contamination of groundwater worldwide creates the need for real-time water quality monitoring [Al-Hashimi et al., 2021; Lamastra et al., 2016]. Organic contaminants such as petroleum-based hydrocarbons are common groundwater pollutants [Li et al., 2021], with benzene, toluene, ethylbenzene and xylene (BTEX) as the most used anthropogenic organic compounds [Kao et al., 2006; Shemer and Belkin, 2022]. Some oxygenated ether fuels such as ETBE are also ranged in this category [Que et al., 2019]. Although they differ in their solubility and adsorption in soil, they all have in common their recalcitrant properties and their negative effect on the environment, on human health and therefore on the global economy [Baghani et al., 2019; Durmusoglu et al., 2010; Poulsen and Kueper, 1992].

In addition, long exposure of BTEX and ETBE is harmful for the environment due to their toxic and recalcitrant nature, indicating the need for early detection of petroleum hydrocarbon spills [Brassington et al., 2007]. However, conventional sampling methods do not allow *in-situ* and real-time contaminant detection in groundwater, so analytical methods are not a sufficient monitoring tool [Logeshwaran et al., 2018]. Hence, the microbial electrochemical sensors can be considered as an alternative for monitoring these specific environments. A number of electroactive bacteria have been described as part of electrobioremediation tasks in marine sediments polluted with petroleum

hydrocarbons [Tucci et al., 2021a], so the existence of such bacteria suggests that microbial electrochemical sensors can be a suitable option.

However, petroleum derived compounds are not the only problematic organic compounds when they get uncontrolled in the environment and need to be monitored. Many agrochemicals are hazardous if they reach human consumption, including some that are currently not used but are persistent in the environment (POPs) such as DDT or lindane [United Nations, 2019; Vijgen et al., 2011]. Meanwhile, lindane is susceptible to biological reduction, while it is difficult to oxidize [Mehboob et al., 2013; Santos et al., 2018].

In this work, a new microbial electrochemical biosensor for monitoring presence of hydrocarbons in groundwater was developed. The biosensor was validated with some of the main pollutants from i) oil&gas industry, (eg. BTEX, ETBE, vinylcyclohexene, complex mixtures as kerosene) and ii) agrochemical industry (eg. lindane)

2. Materials and Methods

2.1. Experimental set-up

2.1.1. Microcosms set-up

A microbial electrochemical system was design and constructed to be operated as biosensor. The system was built following a scheme of three electrodes. A carbon rod (ClipCarbono S.L.) surrounded by carbon felt (Mersen S.L.) was used as a working electrode, while a platinized titanium mesh (INAGASA, S.L.) was used as a counter electrode. The reference electrode used was an Ag/AgCl 3M electrode (Hanna Instruments S.L.).

In order to simulate a real environment, a microcosm was set up in a 250 ml glass bottle. The bottle was filled with groundwater collected from the mesocosm (composition in Table 2.1) and then the biosensor was submerged. The groundwater was constantly stirred and bubbled with nitrogen gas (Fig. 2.1 A).

NEV-4 potentiostat (Nanoelectra, S.L.) was used to fix the working electrode potential at 0.6 V (vs. Ag/AgCl 3M), except lindane detection at -0.6 V, and to record the electrical current every second.

2.1.2. Mesocosms set-up

A three electrodes system was also design and constructed to be operated as biosensor in a mesocosm. In this case, a carbon fiber cylinder (ClipCarbono S.L.) surrounded by carbon felt (Mersen S.L.) was used as a working electrode. A carbon rod (ClipCarbono S.L.) in direct contact with the carbon felt was used as current collector. And a platinized titanium mesh was used as a counter electrode. The reference electrode used was an Ag/AgCl 3M electrode (Hanna Instruments S.L.).

Mesocosm system was performed to reproduce the real operating conditions of a biosensor in a piezometer (Fig. 2.1 B-D). For the construction of the mesocosm, a methacrylate cylinder filled with clay loam soil (collected at 40°30'49"N 3°20'16"W; analysis data in Table 2.2), was used to house a piezometer inside it. Thus, we can mimic

the natural impact of soil or sediment in groundwater. The mesocosm was filled using tap water reaching a real groundwater composition (Table 2.1).

A 4G remotely-controlled potentiostat (LP, Nanoelectra S.L.), was used to control the working electrode potential, at 0.6 V (vs. Ag/AgCl 3M), to record the electrical current every second, and to transmit the data. The working electrode was poised at and the current intensity was recorded every second.

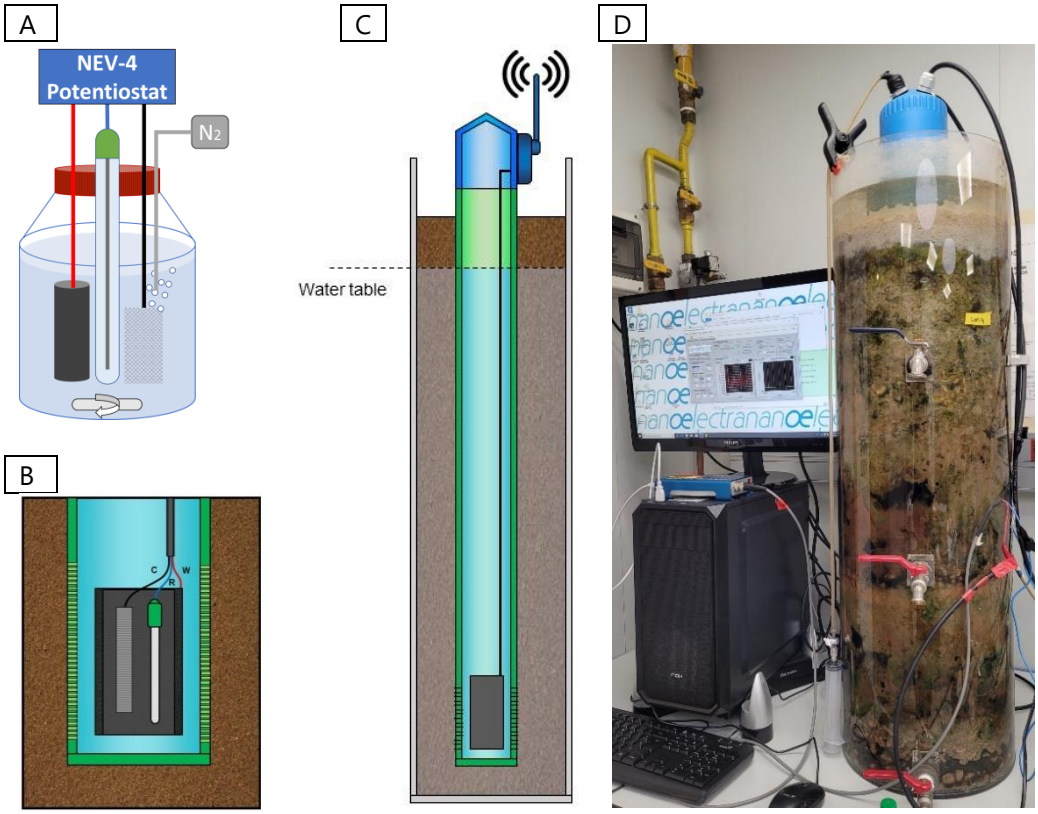


Figure 2.1: Scheme of a Microcosm (A), detailed biosensor inside groundwater piezometer (B), Mesocosm (C), and photo of Mesocosm (D).

Table 2.1: Physic-chemical groundwater analysis

pH	7.95
EC (µS/cm)	250
COD (mg/l)	149
Cationic composition (mg/l)	
Na^+	44.4
NH_4^+	8.6
K^+	37.9
Ca^{2+}	39.4
Mg^{2+}	13.0
Anionic composition (mg/l)	
Cl^-	1.77
NO_2^-	0.54
NO_3^-	1.37
PO_4^-	0.76
SO_4^{2-}	1.98

Abreviations:
EC, electric conductivity;
COD, chemical oxygen demand.

Table 2.2: Physic-chemical soil analysis

pH	8.94
EC (µS·/cm)	91.6
Organic matter (%)	1.70
CEC (cmol/kg)	14.8
Granulometry (%)	
Clay	29.9
Silt	46.1
Sand	24.0

Abreviations:
EC, electric conductivity;
CEC, cation exchange capacity.

2.2. Microcosms experimental procedures

An electroactive microbial community was tested regarding their bioelectrochemical response to BTEX, vinylcyclohexene and lindane. Once the steady state was reached, a pollutant pulse was spiked into the stirred groundwater.

2.2.1. BTEX and Vinylcyclohexene

A microbial community selected for degrading BTEX coupled to anode respiration as sole electron acceptor reactions was tested in 5 independent microcosms polluted with single contaminants from BTEX (benzene, toluene, ethylbenzene, and xylene) and also the whole mixture. Pollutants were spiked with single contaminants (250 ppm) after colonization under pollutant exposition and steady state current production.

Additionally, 4-vinylcyclohexene was also spiked (50 ppm). After the pulse, the electric current was recorded every second.

2.2.2. Lindane

Lindane sensing was tested. In contrast to all previous compounds, the biodegradation of lindane occurs mostly under reducing conditions [Mehboob et al., 2013; Santos et al., 2018] to dehalogenate the molecule. Therefore, the electrode polarization was posied at -0.6 V (vs. Ag/AgCl). Lindane shown a low solubility in water, so microcosm systems were set up to provide lindane dissolved in Tween80. First, microcosm was spiked with lindane-free solvent to evaluate the microbial response to Tween80. Then, a 1 ml spike lindane dissolved in Tween80 was spiked (100 ppm of lindane, final concentration in groundwater) at 18 days and data were collected up to day 51.

2.3. Mesocosm experimental procedures

2.3.1. Biosensor colonization and acclimation

The biosensor was immersed 70 cm below upper layer of water in the piezometer. The native microorganisms present in the soil were the sole inoculum for the bioanode. A BTEX pulse of 4 ml was added to the groundwater to select an electrobioremediation community on the bioanode.

2.3.2. Pulse-response experiments

System performance was assessed in terms of electric current generation and contaminant concentration in the groundwater. In all pulse-response experiments, the biosensor was polarized until it reached a steady state in which the current was stable (variations below 20 μA). Once the steady state was reached, a pollutant pulse was spiked on the upper water layer of the piezometer, so that the diffusion processes through the groundwater and soil adsorption were simulated. Different pulses to analyze different compounds were spiked. Biosensor was serially tested with 4 ml of BTEX mixture, ETBE, kerosene and 4-vinylcyclohexene. After the pulse, the electric current was recorded every second and water was sampled in the vicinity of the biosensor for chemical analysis.

2.4. Analytical methods

A gas chromatograph (GC) system (Agilent 7890A) coupled to a mass spectrometer (MS) with a triple quadrupole analyzer (Agilent 7000 GC/MS Triple Quad) was used for samples analysis. The system was equipped with an automatic multipurpose autosampler (Gerstel), a thermal desorption unit (TDU) and a cooled injection system (CIS).

The GC column used was a TRB-624 capillary column (30m length x 0.25 mm i.d. x 1.4 µm film thickness) (Teknokroma). Helium was used as carrier gas at a constant flow of 1.2 mL/min. Injection (1 µL; sample diluted with methanol) was carried out under programmable temperature vaporizing (PTV) mode by applying consecutive temperature rates in the TDU and the CIS units: 120 ºC/min from 40 ºC until 280 ºC (maintained during 1 min), and 12 ºC/s from -150 ºC until 280 ºC (maintained during 5 min), respectively. The oven temperature was programmed as follows: 35 ºC (2 min); 20 ºC/min until 180 ºC; 50 ºC/min until 260 ºC (2 min). Interface temperature was set to 250 ºC.

Mass spectrometer operated under electron ionization mode (EI), and the source temperature was maintained at 250 Cº. The acquisition was performed under Selected Ion Monitoring (SIM).

Water samples were diluted with methanol (at least ratio 1/10) before direct injection into the GC-MS system.

2.5. Cyclic Voltammetries

Cyclic voltammetries were performed in mesocosms system using a NEV-4 potentiostat (Nanoelectra S.L.) at scan rate of 1 mV/s from -0.8 V to 0.8 V.

2.6. Chemicals

All the chemicals for synthetic groundwater preparation were purchased by Sigma Aldrich. BTEX, 4-vinylcyclohexene, ETBE and kerosene were provided by Repsol. Lindane was purchased by Sigma Aldrich.

3. Results and discussion

The bioelectrochemical response of an electroactive community to specific pollutants from oil&gas and agrochemical sectors was validated under both microcosm and mesocosm groundwater environments.

3.1. Cyclic Voltammetries

Microcosm assays were conceived as a first step to verify if bioelectrochemical response to specific pollutants was really observed.

3.1.1. BTEX colonization and pulse-response signal

The results of BTEX spikes in the microcosm systems showed a different response for each compound (Fig. 2.2). The biosensor exposed to toluene obtained electrical current as high as 80 µA. Meanwhile, the rest of the biosensors increased their electrical current after exposition to benzene (35 µA), ethylbenzene (30 µA), xylene (20 µA) and the whole BTEX mixture (25 µA). The increment in electrical current for all biosensors suggests that all were colonized.

After colonization, the groundwater in the microcosms was renewed and the biosensors were polarized until current stability in order to monitor current after a new round of pollutant spiking. (Fig. 2.2 and Table 2.3). Toluene exposed biosensor was the last to respond (ca. 3 days from the spike), but it showed the highest current rate (ca. 7 µA/day) for more than 10 days. Next, xylene exposed biosensor presented the second highest rate (ca. 6 µA/day) and the shortest period for a sustain increment in current (5.3 days). Xylene exposed biosensor and the BTEX exposed biosensor had a similar response time (ca. 2 days since spiking). In contrast, BTEX mixture showed lower current (3.5 µA/day). Finally, the benzene and ethylbenzene biosensors were the firsts to react to the spike (0.2 and 0.3 days from the spike), but their response presented the lowest current rate (2.4 and 2.1 µA/day). All biosensors responded bioelectrochemically to spikes as shown by the current intensity increment. We do not know exactly what microbial communities are involved in the process but we can hypothesize that an interaction between electroactive- and aromatic hydrocarbon degrading bacteria

should be involved [Aulenta et al., 2021b]. Furthermore, the common observation of bacteria from genus *Geobacter* in soils would suggest A DEET interaction [Rodrigo Quejigo et al., 2018; T. Zhang et al., 2010a].

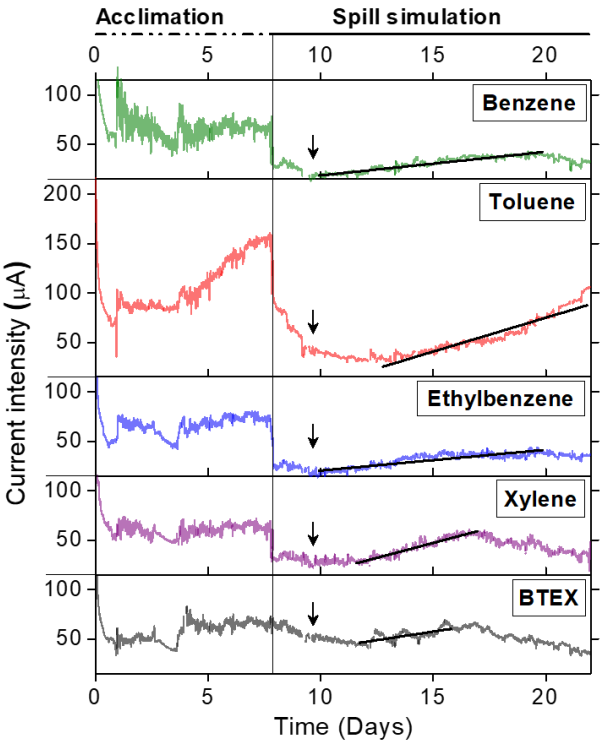


Figure 2.2: Biosensor current response in presence of BTEX pollutants. Arrows represent the spike and the overdrawing lines represent the current variation average (rate).

Table 2.3: Biosensor current response in presence of BTEX pollutants in microcosm

Spike	Time to react (days)	Response duration* (days)	Average current variation* (µA/day)	Maximum current (µA)
Benzene	0.2	10.0	2.4	43
Toluene	3.1	9.2	6.9	105
Ethylbenzene	0.3	9.9	2.1	43
Xylene	1.9	5.3	6.1	60
BTEX mix	2.1	4.0	3.5	69

* Calculated along the maximum current response

Chronoamperometries were able to predict how microcosm response was biological since time response was not instantaneous. However, to ensure the impact of the BTEX abiotic tranformation, a cyclic voltammetry was performed before and after BTEX addition to groundwater. The resulting voltagrams showed that the signal of both was similar (Fig. 2.3). In fact, BTEX voltagram appeared to slightly poison the electrode which decreased its amplitude [Ouhadi et al., 2010]. So, we could conclude that the current harvested is not caused by abiotic BTEX reaction.

Another observation that can confirm an effective colonization was the increase in the amplitude of the cyclic voltammetry [Choi and Chae, 2013], ergo an increase in the capacitance, together with the presence of some redox peaks (Fig. 2.3). Peaks relate to oxidation at 0.0 V and reduction at -0.2 V were similar to peaks found in previous electroactive biofilms [Carmona-Martínez et al., 2013a].

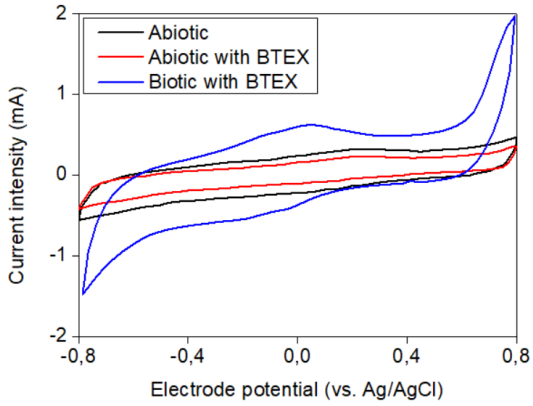


Figure 2.3: Cyclic voltammetry of i) abiotic anode in groundwater (black line) and ii) abiotic anode in groundwater with BTEX (blue line) and iii) bioanode in groundwater with BTEX (red line). Scan rate 1 mV/s.

3.1.2. Vinylcyclohexene

The previous results regarding detection of hydrocarbons and hydrocarbon mixtures prompted to test the biosensor with more recalcitrant compounds like 4-vinylcyclohexene [Hort and Luengas, 2020; Neumann and Dror, 1998] (Fig. 2.4). In this test a slightly current increase was observed after the pollutant spike.

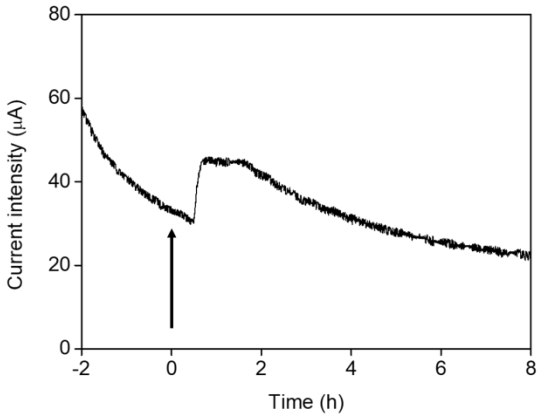


Figure 2.4: Chronoamperometry of biosensor exposed to 4-vinylcyclohexene in microcosm. Pulse was spiked in time=0.

3.1.3. Lindane

All previously tested compounds were be more easily oxidized than reduced [Bacosa et al., 2010; Daghio et al., 2018a; Hort and Luengas, 2020; Neumann and Dror, 1998; Nicholls et al., 2020; Palma et al., 2018]. In order to test the electrochemical microbial sensor with xenobiotic chemical subjected to a first reductive attack, lindane was tested [Mehboob et al., 2013; Santos et al., 2018]. Lindane was assayed in microcosms mixed with solvent, Tween80, to increase its solubility in groundwater. Furthermore, Tween80 have been demonstrated to increased lindane degradation [García-Cervilla et al., 2021; Juliana Maria Saez et al., 2017]. To ensure that Tween80 are innocuous to the biosensor, this detergent was added in absence of lindane without a significant current consumption response (Fig. 2.5). A slight increase in current was observed between days 9 and 11. On day 18, lindane was spiked mixed with Tween80. Then, the assay revealed two large variations in the current. First the current increased slightly between days 24 and 28, similarly to the sole spike of Tween80. Then, an increase in current consumption was again observed on day 37. In this case the drop was much more profuse (from -10 μA to -80 μA) and lasted 10 days (until day 47). Eventually, current was stable until day 51 so we can conclude such current consumption was is probably due to the reduction of lindane.

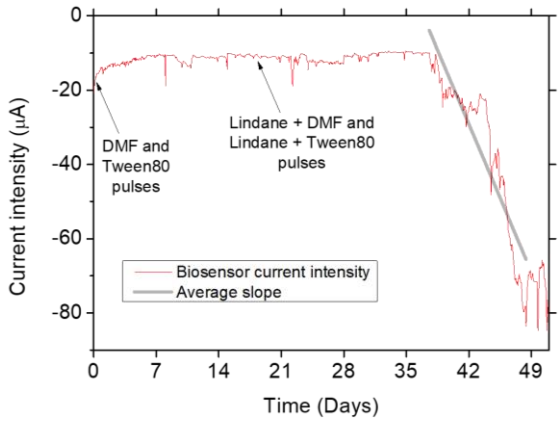


Figure 2.5: Chronoamperometry of biosensor exposed to lindane. Lindane-free Tween80 was spiked at time=0 as control; lindane with Tween80 was spiked 18 days after assays started.

3.2. Mesocosm colonization and acclimation

The current production showed the biosensor colonization process (Fig. 2.6). The bioanode of biosensor was polarized for 12 days with BTEX as main carbon and electron donor to promote extracellular electron transfer to the bioanode. During this process, the current intensity increased from 30 µA to ca. 200 µA. In a first stage (I, 1.5 days), a rapid increase in the current (capacitive current) followed by a decrease and stabilization was observed. This process corresponds to the redistribution of charges on the electrode surface after polarization [Aoki et al., 2020; Streeter and Compton, 2008]. During next stage (II, 1.5-7.5days), the current increased from 30 µA to 75 µA. The stage II corresponds to the attachment process, characterized by an increase in current as bacteria adhere to the electrode and biofilm formation begins. After 7.5 days (III), current increased faster from 75 µA to reach 225 µA, this phase corresponds to exponential phase [Choi and Chae, 2013; Guo et al., 2013]. After ca. 10 days of incubation, we identified stage IV, where current was stable in values from 200 µA to 225 µA. During this stage, the current was stable because degradation rate was the limiting factor. By last, during stage V, current decreased, due to depletion of contaminant and, consequently, depletion of electron donor for electroactive bacteria.

The whole process corresponds to the colonization of the biosensor by electroactive bacteria biodegrading BTEX (Fig. 2.6). This process depends on a large number of variables such as the inoculum size, the species present in it [Bakonyi et al., 2018; Gacitúa et al., 2018], the temperature [Patil et al., 2010], the pH [Patil et al., 2011], the salinity [Guo et al., 2021], the potential [Carmona-Martínez et al., 2013b; Pinto et al.,

2018] and the nutrient and substrate concentration [Bakonyi et al., 2018]. In the environment where our biosensor was located, there was a limitation in electron acceptors (no oxygen detected 3 cm under water sheet). Using BTEX as the main carbon and electron source, and the anode as the electron acceptor, we force the microbial community to strong selective pressure as previous studies demonstrated [Daghio et al., 2018a; Palma et al., 2018]. In this way, colonization of the biosensor was achieved or favored by contaminant-oxidizing electroactive bacteria [Doyle and Marsili, 2015; Lueders, 2017]. Some of the microorganisms with the highest pollutant degradation capacity have been found in environment typically not polluted with specific xenobiotics like BTEX [Ramos et al., 1995]. On the other hand, it has been shown that electroactive bacteria are widely distributed in all kinds of natural environments [Koch and Harnisch, 2016; Uria et al., 2016b]. It is then consistent with the fact that, just by polarizing the electrode, it is possible to select hydrocarbon-oxidizing electroactive bacteria in non-polluted soils.

The biofilm formation process (Fig.2.6, II) described in this work took a longer period compared to growth culture in optimal conditions [Zhang et al., 2011]; however, it was a shorter period compared to other groundwater hydrocarbon systems [Tucci et al., 2021a]. Even a longer colonization period was required in some mix culture studies with growth medium [Choi and Chae, 2013; Guo et al., 2013]. Hydrocarbon-oxidizing electroactive bacteria selection is possible from uncontaminated groundwater, since acclimation in contaminated groundwater favors a broader hydrocarbon-oxidizing microbial community colonization [Lueders, 2017].

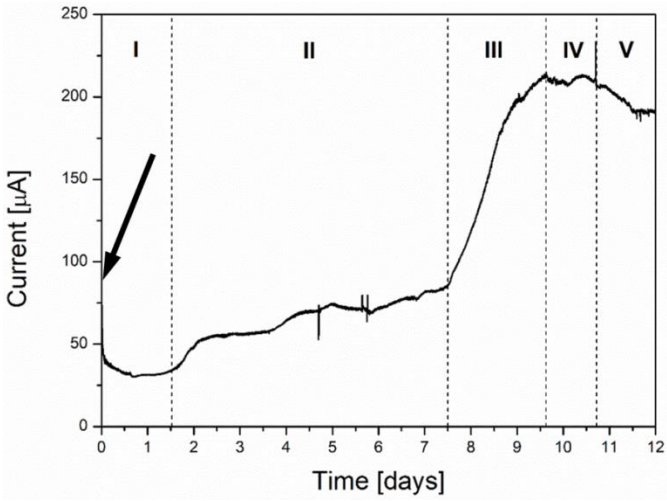


Figure 2.6:
Chronoamperometry of biosensor at 0.6 V (vs. Ag/AgCl 3M).
Roman numerals indicate estimation of different stages in a biofilm formation process:
I electrochemical capacitive processes,
II biofilm acclimation,
III exponential growth phase,
IV stationary phase,
V pollutant depletion.

3.3. Pulse-response mesocosm experiments

Once the biosensor was colonized, the biosensor response in the presence of contaminants was tested. For this purpose, we performed a pulse of contaminant in the vicinity of the bioanode and both the current production and contaminant concentration were recorded.

The first assayed contaminant was a mixture of BTEX, the same pollutants used to promote primary colonization. After a period where the current was stable, the pulse of 4 ml BTEX was performed on the top of the water body (Fig. 2.7). Current increased from 250 µA to exceed 400 µA in 10 h. Such increase corresponded to the higher concentration of pollutant detected in the vicinity of the biosensor. This process requires compounds solubilization in water and their diffusion to the deepest area of the piezometer.

After confirming colonization, a BTEX mixture spike was added and current growth was observed in a short period of time (Fig 2.7). The current took barely 1 hour to start to increase (22 µA/h). In comparison with the first scenario pre-colonization (Fig. 2.6), the biosensor behavior was considerably different reducing the response from 7 days to 1 hour.

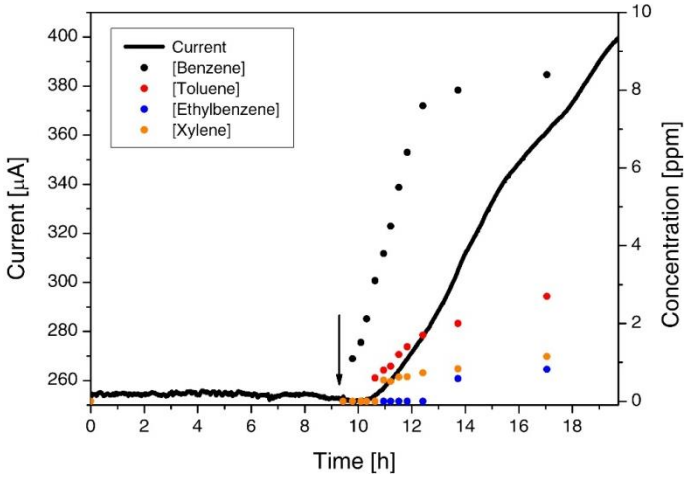


Figure 2.7: Chronoamperometry of biosensor after BTEX pulse in the piezometer. The biosensor was poised at 0.6 V (vs. Ag/AgCl 3M).

Additonally, an ETBE pulse of 4ml was performed in the piezometer, in order to test the detection of other organic contaminants (Fig. 2.8). Although the mixed culture on the anode was selected with BTEX, the pulse of ETBE produced an immediate bioelectrochemical signal, without acclimation to the specific pollutant. The current was higher than the one observed in response to BTEX; this is consistent with the greater water solubility of ETBE compared to BTEX. The groundwater analysis in the vicinity of the biosensor revealed an ETBE concentration 200-fold higher than BTEX, so a higher microbial electrical current response is reasonable to expect.

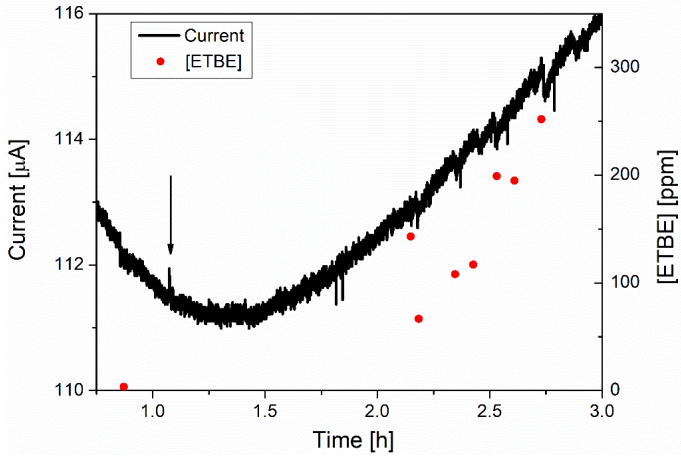


Figure 2.8: Chronoamperometry of biosensor after a ETBE pulse in the piezometer. The biosensor was poised at 0.6 V (vs. Ag/AgCl 3M).

Aerobic microbial consortia obtained from natural environments, such as groundwater, have been reported to be capable of degrading oxygenated compounds like ETBE and MTBE [Nicholls et al., 2020]. Alternatively, there are also some examples of anaerobic microorganisms able to degrade ETBE and MTBE [van der Waals et al., 2018]. Our work shows for the first time the bioelectrochemical response to ETBE-type pollutants. This observation is remarkable, not just in a biosensing context, but also suggests a potential as *in-situ* electrobioremediation action. The bioelectrochemical technologies would enhance the bioremediation of ETBE-type pollutants using the electrode as electron sink, suppressing the electron acceptor limitation that occurs in contaminated environments [Thornton et al., 2020b; T. Zhang et al., 2010b].

Once we demonstrated the biosensor capacity for detecting specific organic pollutants we validated the behavior of the same microbial community with complex mixtures of hydrocarbons present in gasoline and kerosene. The response to a 4 ml pulse of kerosene showed a number of stages (Fig. 2.9). The delay in response and changes in the current variation could be due to the time of solubilization of kerosene in water.

Kerosene is a mixture of numerous compounds [Burri et al., 2004; Coleman et al., 1984; Edwards, 2002], so different rates observed in stages II to IV may correspond to the different solubilization rand diffusion values for every kerosene component, that eventually would access the surface of the biosensor at different rates. Previous studies have reported that in complex hydrocarbon mixtures such as kerosene, aromatic hydrocarbons are more soluble in water than aliphatic hydrocarbons. Particularly, light aromatic hydrocarbons have a greater solubility than naphthalene-type hydrocarbons. These different contaminant solubilities have an impact in their bioelectrochemical detection time in groundwater; actually, the most soluble hydrocarbons are the first to generate a current signal because they easily reach the biosensor. Moreover, the short-chained aromatic hydrocarbons are easier to degrade by microorganisms. Considering the fast response to the kerosene pulse, these short-chained hydrocarbons were probably the first to be degraded by the biosensor biofilm [Daghio et al., 2017]. Taking the hydrocarbon solubility and its biodegradability as influencial parameters for the detection of complex hydrocarbon mixture, the final stable phase (VI) of the chronoamperometry may not be due to a depletion of carbon. In fact, this current stability may be explained by the lower solubility of some kerosene hydrocarbons, which could be limiting the access for microorganisms to degrade them.

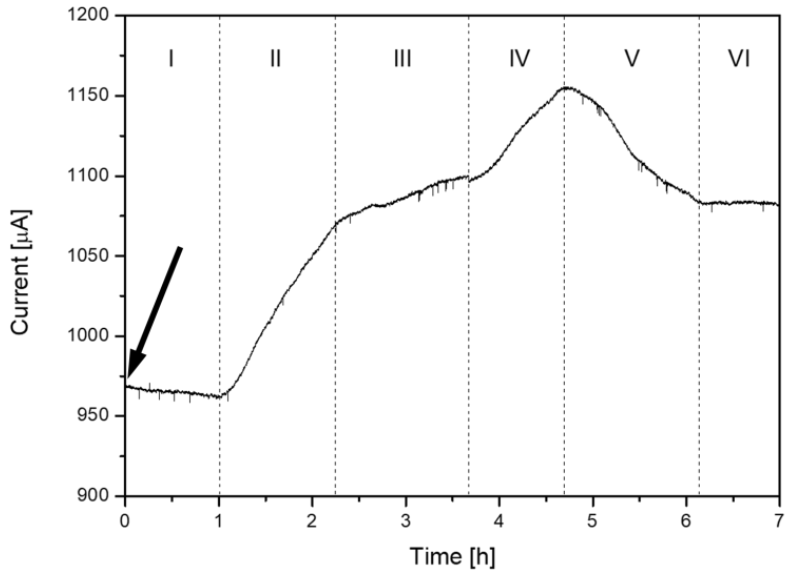


Figure 2.9: Chronoamperometry of biosensor in response to a kerosene pulse. The biosensor was poised at 0.6 V (vs. Ag/AgCl 3M). Roman numerals indicate different stages in response to the kerosene pulse.

Finally, 4-vinylcyclohexene spike resulted in a negative response 1.5 hours after the spike (Fig. 2.10) in contrast with the results previously shown under microcosm scale (Fig. 2.4). Considering that microbial communities in microcosm and mesocosm have a different profile then mesocosm bioanode is probably not including those bacteria responsible of 4-vinylcyclohexene oxidation.

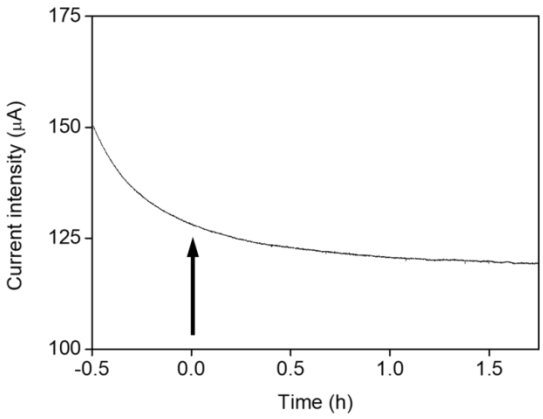


Figure 2.10:
Biosensor chronoamperometry in response to a 4-vinylcyclohexene pulse. The biosensor was poised at 0.6 V (vs. Ag/AgCl 3M). Pulse was spiked in time=0.

4. Conclusion

In this study, we have successfully validated the use of microbial electrochemistry tools for detecting petroleum hydrocarbons at microcosm and mesocosm scale in groundwater. In fact, our results suggest that natural microbial community from uncontaminated groundwater is sufficient to select for pollutant-degrading electroactive bacteria. Furthermore, we observed an early detection of BTEX and ETBE, precisely in less than 2 hours after a potential pollutant spill. We demonstrate the versatility of our biosensor for detecting the presence of complex mixture of i) hydrocarbon present in kerosene (just 1 hour after the spill) and ii) lindane. Our biosensor strategy is based on achieving electrical current from pollutant biodegradation. This finding is remarkable, not just in a biosensing context, but also suggests a potential use for *in-situ* electrobioremediation. If electrodes can play a role as electron acceptor for groundwater microorganism capable of oxidizing petroleum hydrocarbons, then we are facing a potential use of electrochemical barriers for suppressing the electron acceptor limitation that occurs in contaminated environments [Thornton et al., 2020b; T. Zhang et al., 2010b].

We believe our results show the functionality of a biosensor based on microbial electrochemistry for *in-situ* detection of different petroleum hydrocarbons, avoiding the need for conventional sampling and lab analysis. Thus, we can anticipate a future for such applications considering that the electrical current magnitude is valid and useful as it is (eg. microampere range) and, in contrast with other MET-based systems like electrobioremediation, bioelectrosynthesis or energy production, no need for scale up process is required.

Chapter 3:

Electrochemical-based strategies to enhance bioremediation of lindane polluted soils

Chapter 3: Electrochemical-based strategies to enhance bioremediation of Lindane polluted soils.

Abstract

Lindane, γ-hexachlorocyclohexane (γ-HCH), was widely used in agriculture as insecticide since the 1940s generating vast polluted areas. In this context, electrobioremediation is a novel strategy to stimulate microbial metabolism of pollutants by using electrochemical tools and a number of positive experiences with chlorinated xenobiotics have been previously reported. The aim of this chapter is to assess the optimal electrobioremediation configuration to remove lindane from a natural polluted soil and a artificially polluted soil. Thus, anodic, cathodic and snorkel configurations were tested for every edaphic matrix in comparison with natural attenuation. The results revealed a preferential removal always under a cathodic configuration where electrode behaves as electron donor to favour reductive pathways. In fact, lindane was removed from a real polluted soil at rates ca. 9-fold faster (ca. 0.9mg/(kg_{soil}*day)) than natural attenuation (ca. 0.1 mg/(kg_{soil}*day)). Lindane-degrading microbial communities were electrode-dependent because disconnecting the electrode polarization for 50% resulted in 2-fold reduction of the removal rates. Different isomer degradations were optimized in different configurations, α-HCH by cathodic, β-HCH by anodic and δ-HCH by cathodic and anodic configurations. Electrodes potential and current density varied depending on configuration (anode/cathode) and soil matrix. Furthermore, the implementation of a electrochemical design capable to operate in non-flooded soil revealed a 98% lindane removal at cm distance from electrode, opening a door to carry out bioremediation actions in outdoor environments.

In the energy saving experiment, 50% of saving promotes 50% of time delay to reach maximum degradation. Whereas, non-flooded soil experiment highlighted the moisture significance, and remarked the cathode as optimal lindane removal configuration.

1. Introduction

The concern for persistent organic pollutants (POPs), such as organochlorine pesticides (OCPs), has grown exponentially in recent years. OCPs are widely used in agriculture but not easily degraded by natural processes in the environment, so they persist even decades after prohibitions regarding their use [Camenzuli et al., 2016; Mishra et al., 2012; Vizcaíno and Pistocchi, 2010].

Lindane ($C_6H_6Cl_6$), specifically the gamma isomer of hexachlorocyclohexane (γ-HCH) was one of the most widely OCPs used as a broad spectrum insecticide in agriculture [Katsoyiannis et al., 2016; Li, 1999]. Its production resulted in the generation of a massive amount of waste; indeed, Europe host 63% of the world lindane wastes [Vijgen et al., 2011]. Solid residues from lindane are eventually accumulated in soil due to its low biodegradability [Madaj et al., 2018], resulting in environmental and health problems, increasing the risks of causing cancer, Alzheimer's and other central nervous system problems, immunosuppression, endocrine problems, reproductive system problems [Salam and Das, 2012] and bioaccumulation [Sun et al., 2016; Wacławek et al., 2019]. Indeed, lindane and the isomers α-HCH and β-HCH were included in the list of Persistent Organic Pollutant (POP) and Stockholm Convention banned its use and production since 2009 [Madaj et al., 2018].

Although most of organic pollutants present in soils and sediments can be degraded by microorganisms under proper conditions [Sales da Silva et al., 2020], some of these compounds persist in sediment and soil due to the absence of a suitable electron acceptor or donor [Boopathy, 2004; Widdel and Rabus, 2001]. In the particular case of lindane the most studied degradation pathway is performed by aerobic microorganisms attacking the molecule through a dehydrochlorination (non-redox reaction) followed by a dehydroxychlorination [Nagata et al., 2007]. In contrast, anaerobic microorganisms use pathways based on dechlorination (reduction reaction) followed by dehydrogenation [Quintero et al., 2005].

In spite of the recalcitrant nature of Lindane, a number of authors have reported bioremediation experiences. Some of them have been *in-situ* tested, as sugarcane bagasse application, resulted in 53% lindane removal [Abhilash and Singh, 2008], or daramend technology, reaching 75% HCH degradation [Phillips et al., 2006]. However, most of cases have studied *ex-situ* remediations. Sludge reactors are capable of removing more than 90% lindane in presence of winery sludge [Quintero et al., 2006]

and sucrose [Varo-Arguello et al., 2012]. Furthermore, merging biostimulation (maize plants or sugarcane bagasse) with bioaugmentation (*Streptomyces or Candida*) strategies have demonstrated to reach a high removal of lindane removal [Álvarez et al., 2015; Raimondo et al., 2020a, 2020b; Salam et al., 2017].

More recently, insoluble electrodes have been proved to be effective as electron donor or electron acceptor as part of new concept so-called electrobioremediation [X. Wang et al., 2020a]. Since Zhang et al (2010) reported the first example of hycrocarbon electrobioremediation using graphite electrodes [T. Zhang et al., 2010a], several authors have followed a electromicrobial-based strategy to remediate environments polluted by chlorinated organics [Chun et al., 2013; Liu et al., 2013; Yu et al., 2016], herbicides[Domínguez-Garay et al., 2018a, 2016; Domínguez-Garay and Esteve-Núñez, 2018; Rodrigo Quejigo et al., 2016] and pesticides [Cao et al., 2015]. Furthermore, electrobioremediation of lindane have been succesfully tested in a slurry reactor where a sulfate reducing inoculum pre-exposed to lindane was grown in a Microbial Fuel Cell [Camacho-Pérez et al., 2013].

Unfortunately, most of the environmental applications for microbial electrochemical systems have been conducted in waterlogged soils [Domínguez-Garay et al., 2018a, 2013; Rodrigo Quejigo et al., 2016] or sediments [Sherafatmand and Ng, 2015; Yan et al., 2012] under flooded conditions. Actually, flooding is not a common situation for common soil and, indeed, it is not feasible to flood all soil environments that need bioremediation. In this sense, previous studies in our group came up with a new concept by designing a bioelectrochemical system to operate in non-flooded soil conditions by integrating an out-of-soil cathode using a ceramic barrier as membrane [Domínguez-Garay and Esteve-Núñez, 2018].

The aim of the current work was to apply electrochemical tools for stimulating the biodegradation of lindane and its isomers in both flooded and non-flooded polluted soils in order to assess the area of *in-situ* influence the electrode.

2. Materials and Methods

2.1. Chemicals

Lindane (>97%, Sigma Aldrich) and Sodium Acetate Anhydrous (99%, Carlo Erba) were used in experiments. Methanol (99.9%, Sigma Aldrich), n-hexane (>95%, Sigma Aldrich) and MQ-water were used in lindane and rest of HCH extraction.

2.2. Soil collection

Lindane-polluted soil ($SOIL_{polluted}$ in this chapter) was sampled from a soil runoff sedimentation pond at Sabiñanigo, Huesca (42°29'12" N; 0°21'41" W). Furthermore, non-polluted soil was sampled in a rural road edge near to Madrid (40°30'29"N; 3°20'14"W) and spiked by pure lindane to reach 10 mg/kg ($SOIL_{spiked}$ in this chapter). $SOIL_{spiked}$ was air-dried and sieved (<2 mm) before any further experimental setup. Both $SOIL_{spiked}$ and $SOIL_{polluted}$ were initially analyzed (Table 3.1).

Table 3.1: Physical-chemical characteristics for $SOIL_{spiked}$ and $SOIL_{polluted}$ *

Parameter		$SOIL_{polluted}$		$SOIL_{spiked}$	
pH		8.91		8.63	
EC		123	µS/cm	191	µS/cm
Organic matter		0.835	%	2.13	%
Granulometry	Clay	17.5	%	26.2	%
	Silt	62.3	%	28.7	%
	Sand	20.2	%	45.1	%
Kjeldal nitrogen		0.52	mg/kg	0.84	mg/kg
CEC		7.01	cmol/kg	11.9	cmol/kg

*$SOIL_{spiked}$ and $SOIL_{polluted}$ samples were air-dried and sieved (<2mm) before analysis.
Abbreviations: EC, electrical conductivity; CEC, Cation exchange capacity

2.3. Experimental Setups

A number of microcosms were designed and constructed in order to test biodegradability of lindane in presence of different electrochemical configurations.

2.3.1. Experimental setup 1

Initially, a $SOIL_{spiked}$ sample (4 kg dry weight) was equally distributed in 4 HDPE bottles (High-Density PolyEthylene, Deltalab 19412). A different electrochemical configuration was set up in each bottle (Fig. 3.1): i) Cathode configuration, 2 graphite plate electrodes (30 x 60 x 4 mm, Mersen JP945) were first located at the bottom of the soil (cathode) and at the water layer (counter electrode) and, eventually, connected to a power source (5 V constant); ii) Snorkel configuration, an electroconductive cylinder made of carbon fiber (Ø=40 mm, L=9 mm, ClipCarbon) was vertically located in the soil; iii) Electrode-free soil as control for natural attenuation.

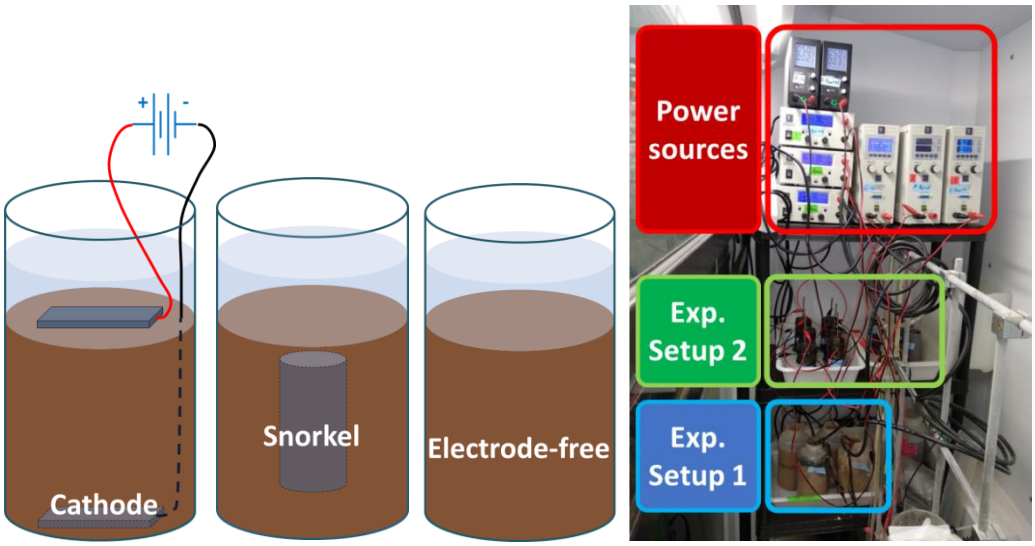


Figure 3.1: Scheme of experimental set up 1 configurations and image of experimental set up 1 and 2.

The four systems were waterlogged with tap water, so all electrodes were underwater. Samples were taken at 2cm from the external perimeter on days 0, 15, 30, 60 and 90 using a 15 mm diameter and 150 mm vertical sampler. Samples were frozen (-22ºC) for further analysis.

2.3.2. Experimental setup 2

In this design, one carbon fiber cylinder plays a double role, electrode and soil container. This set-up consisted of a hollow carbon fiber cylinder (Ø=40 mm, L=9 mm, ClipCarbon) sealed at the bottom by a rubber stopper. A platinized titanium mesh (40 x 25 mm, INAGASA) was used as a counter electrode. The mesh was buried vertically 30 mm in the soil and its edges were covered with rubber to avoid contact with the

internal wall of electroconductive cylinder. Finally, cylinder and mesh were connected to a power source (5 V constant) and the microcosm was always flooded with tap water.

Firstly, the polarized microcosm was tested with the $SOIL_{spiked}$ and the $SOIL_{polluted}$. Microcosms with $SOIL_{spiked}$ were filled with 150 g (dry weight), while microcosms with $SOIL_{polluted}$ were filled with 200 g (dry weight). The four different systems were labeled according to the electrochemical nature of the carbon fiber cylinder (Fig. 3.2): i) Anode, cylinder connected to the positive pole; ii) Cathode, cylinder connected to the negative pole; iii) Snorkel, no counter electrode and no polarization and iv) Electrode-free, a PVC cylinder was used instead of the carbon fiber cylinder as a natural attenuation control. Three replicates of each system were tested. The microcosms were electrochemically monitored once a week: cylinder potential (vs. Ag/AgCl, Hanna) and current intensity was measured. Moreover, 10 g of soil samples were extracted and frozen (-22ºC) for further analysis. pH and Electrical Conductivity (EC) were measured at the end of the experiment.

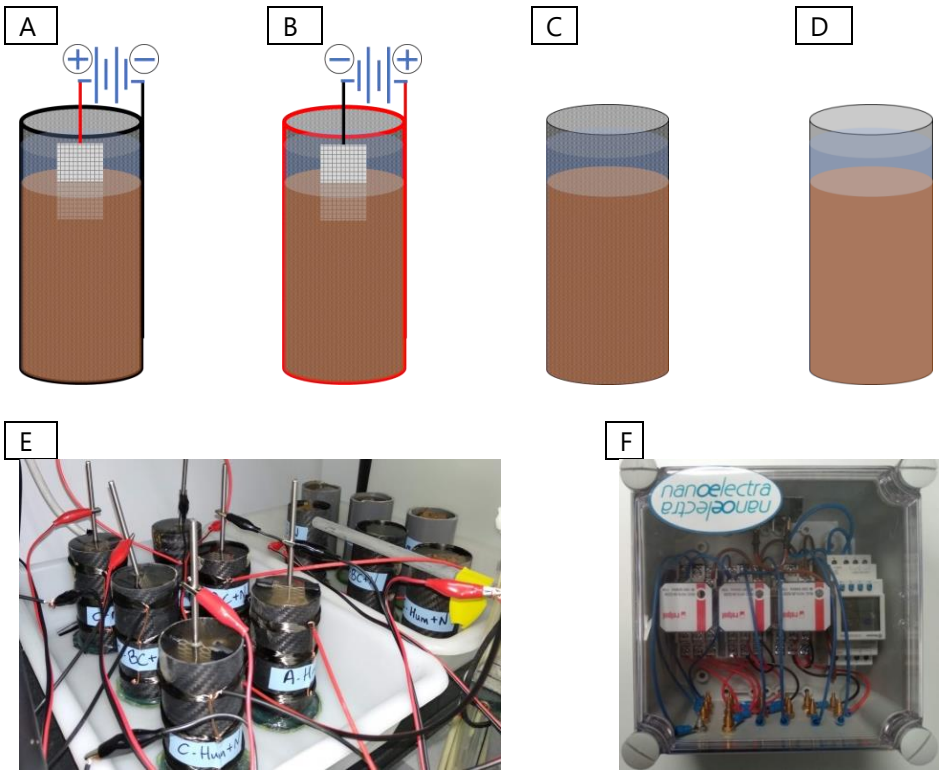


Figure 3.2: Scheme of experimental set up 2 configurations (A, Cathode; B, Anode; C, Snorkel; D, Electrode-free) and image of experimental set up 2 on working (E) and the automatic relay controlled by timer (F).

2.3.3. Experimental setup 3

Similar setup than experimental setup 2 but testing new conditions using $SOIL_{spiked}$: v) Anode-Off, including alternative and programmed on-off polarizations every 24 hours and vi) Cathode-Off, including alternative and programmed on-off polarizations every 24 hours vii) Cathode-Anode, where the polarity is reversed each 24 h. $SOIL_{spiked}$ microcosms were sampled once a week, 10 g were extracted after stirring and frozen (-22°C) for lindane analysis.

2.3.4. Experimental setup 4

In order to test the microbial bioremediation under non-flooded conditions, we designed and constructed a bioelectrochemical system based on previous design [Domínguez-Garay and Esteve-Núñez, 2018]. A cylindrical chamber (Ø=220 mm, L= 200 mm) hosted 3.5 kg (dry weight) of the $SOIL_{spiked}$. In the center, a cone-shape ceramic barrier (Ø=35 mm, L=70 mm, Aquasolo© C4414 Aquacenter) was embedded and filled with carbon coke. Above this, an out-of-soil chamber was installed to expand the coke surface and improve the ceramic barrier effect. Around the ceramic barrier, hollow perforated carbon fiber cylinder (Ø=40 mm, L=90mm, ClipCarbono) was buried. Both, the electroconductive cylinder and the coke-based counter electrode were connected to a power source (5 V constant). The out-of-soil chamber was filled with tap water 15 cm above soil level. Four different configurations were tested (Fig. 3.3): i) Anodic stimulation, fiber carbon cylinder as anode; ii) Cathodic stimulation, fiber carbon cylinder as cathode, and iii) Snorkel configuration, carbon fiber cylinder was not connected to any counter electrode.

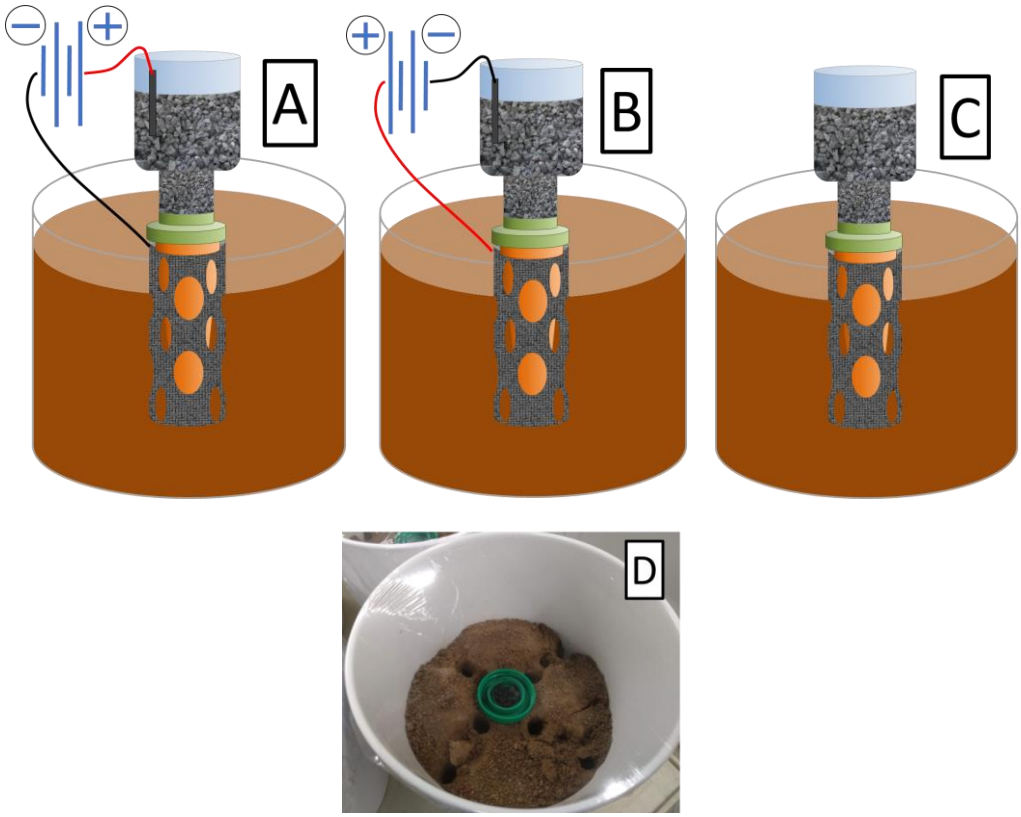


Figure 3.3: Scheme of experimental set up 4 configurations (A, Cathode; B, Anode; C, Snorkel) and image (D) of experimental set up 4 before fractionating at virtual grid.

Samples were taken on days 18, 32, 46 and 60 by vertical sampling of 15 mm diameter and 150 mm lenght. A 3-D lindane concentration map was draw at the end of the experiment. The soil matrix was fractionated by different heights and radius following a virtual grid. On one side, the system $SOIL_{spiked}$ was sampled at various distances from the cone: 0-20, 20-40 and 40-60 mm. Then each section was divided by heights: 0-30, 30-60 and 60-90 mm from the bottom of the cylinder. Such strategy will generate a 3D profile with the concentration of lindane all soil volume. The samples were frozen for further lindane analysis.

2.4. Lindane and hexachlorocyclohexane isomers analysis

To analyze HCH isomers, the frozen samples was defrosted and air-dried. Then, solid-liquid extraction from soil samples were carried out following reported methods [Fuentes et al., 2011]. 5 g of soil were weighted and extracted by 10 ml of a mixture of deionized water, methanol and hexane (proportion 4:1:5). The sample was shaken in a vortex (1 min), sonicated (10 min) and centrifuged (4000 rpm for 10 min). 1 ml of the organic layer was filtered (PVDF 0.22 µm) and collected in a 2 ml vial.

Then, samples were analyzed using a gas chromatograph (GC) system (Agilent 7890A) coupled to a mass spectrometer (MS) with a triple quadrupole analyzer (Agilent 7000 GC/MS Triple Quad). The system was equipped with an automatic multipurpose autosampler (Gerstel) and a thermal desorption unit (TDU) and a cooled injection system (CIS). The GC column used was an HP-5ms capillary column (30m length x 0.25 mm i.d. x 0.25 µm film thickness) (J&W Scientific, Agilent). Helium was used as carrier gas at a constant flow of 1 mL/min. Injection (1 µL) was carried out under programmable temperature vaporizing (PTV) mode by applying consecutive temperature rates in the TDU and the CIS units: 120 ºC/min from 40 ºC until 280 ºC (maintained during 1 min), and 12 ºC/s from -40 ºC until 280 ºC, respectively. The oven temperature was programmed as follows: 70 ºC (2 min); 20 ºC/min until 220 ºC; 50 ºC/min until 300 ºC (2min). Interface temperature was set to 250 ºC.

Mass spectrometer operated under electron ionization mode (EI), and the source temperature was maintained at 250 ºC. The acquisition was performed under selected reaction monitoring (SRM) using nitrogen as collision gas. Table 3.2 shows the transitions selected for the determination of lindane (a quantitative, Q, and a qualitative, q), as well as the collision energies and the dwell time applied, and the corresponding chromatographic time. Finally, the limited detection reached in all isomers was 0.1 mg/kg.

Table 3.2: Detection parameters used for lindane and HCH isomers in GC-MS

HCH isomer	Retention time (min)	Q/q	Precursor ion (m/z)	Product ion (m/z)	Collision energy (eV)	Dwell time (ms)
α-HCH	9.772	Q	219	183	10	150
		q	217	181	5	
β-HCH	10.019	Q	219	183	10	
		q	217	181	5	
γ-HCH (lindane	10.084	Q	219	183	10	
		q	217	181	5	
δ-HCH	10.286	Q	219	183	10	
		q	217	181	5	

Abbreviations: Q, quantitative determination; q, qualitative determination

3. Results and Discussion

Electrobioremediation of lindane in both naturally polluted soil ($SOIL_{polluted}$) and artificially polluted soils ($SOIL_{spiked}$) was validated under a number of different configurations capable to reduce the contamination after the treatment.

3.1. Electrode polarization enhances lindane degradation in flooded soils

The first set of experiments (Experim. setup 1) was devoted to proof our electrobioremediation strategy for removing lindane in artificially polluted flooded-soils ($SOIL_{spiked}$). The absence of any electrode in the polluted soil led to a slight lindane removal in the first 30 days of treatment, confirming that natural attenuation is not an effective method for an efficient removing lindane in soils [Abhilash and Singh, 2008; Hou et al., 2022]. However, lindane presence in extractions was severely decreased after 60 day, due to either true biodegradation or soil adsorption. In contrast with natural attenuation, the presence of an electrode acting as a cathode (electron donor) strongly accelerated lindade removal (80% by day 30 and >99% by day 60). Our results are consistent with previous non electrochemistry-based reports that suggest how lindane is preferably removed under reducing environments [Joo and Zhao, 2008; Quintero et al., 2006; Schilling et al., 2019]. An alternative non-polarized configuration, so-called

snorkel, was also tested. This approach does not require two independent electrodes but a single piece of electroconductive material capable of generating a natural redox gradient inside a soil matrix [Erable et al., 2011; Marzocchi et al., 2020]. Actually, snorkel has been previously reported for remediating hydrocarbon polluted soil [Aulenta et al., 2021a; Viggi et al., 2017]. In our system, snorkel configuration revealed a higher removal efficiency (ca. 30%) than control but not so efficient as revealed by cathodic stimulation. Snorkel-based biostimulation occurs because the electron transfer between microbial communities are enhanced by the elecondutive material [Logan et al., 2019; Rotaru et al., 2021; Shi et al., 2016]. Such "interconnected" microbial communities promoted lindane degradation but not affect to the soil electrochemical profile.

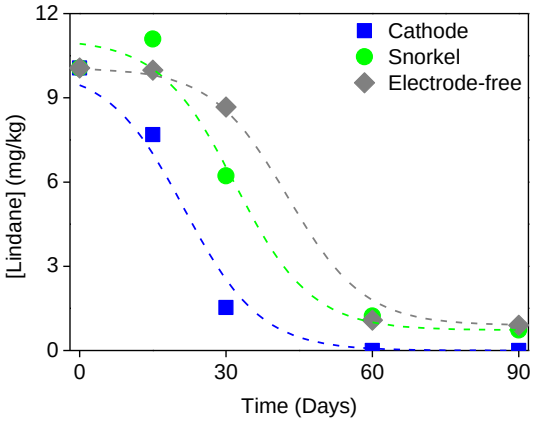


Figure 3.4: Lindane degradation under different configurations (green symbols as snorkel; blue as polarized electrode; and grey as electrode-free control). Dash lines represent sigmoidal fitting.

3.2. Electrochemical behavior of polarized microcosms

The degradation of lindane and the rest of HCH isomers depended on the electrochemical properties of the systems. Regarding redox potentials of polarized cylinders, they reached equilibrium after a few days at values for 2.5 V and -2 V for anodic and cathodic configurations, respectively, when $SOIL_{spiked}$ was used (Fig. 3.5 A, red triangles and blue squares).

However, potentials for $SOIL_{polluted}$ took 1 day to reach equilibrium. Anode system reached equilibrium at 2 V (Fig. 3.4 B, red triangles), while Cathode system reached equilibrium at -1.5 V (Fig. 3.4 B, blue squares). The equilibrium potential was different in $SOIL_{spiked}$ and $SOIL_{polluted}$ due to the difference in salinity (Table 3.1, EC). The higher the salinity of the matrix, the higher potential that the electrode can reach through electrophysical charge interactions [Gerlach et al., 2019; Suss et al., 2014].

On the other hand, the soil reached equilibrium potentials in shorter time because of the lower capacity of its cation exchange layer (Table 3.1, CEC). Therefore, it took shorter time to release all the salts associated with that layer [Kandpal et al., 2005].

Although the potentials varied depending on whether soil or sediment, this difference was not reflected in the current intensity. The current generated by the Anodic configurations (Fig. 3.5, black triangles), was found to be 34 mA ($SOIL_{spiked}$) or 40 mA ($SOIL_{polluted}$) since the first day,then it increased till value ca. 20-25 mA (7-28 days), and eventually dropped to 12 mA on day 35.

The difference in initial currents was influenced by the difference described above between the cation exchange layer (Table 3.1, CEC). The lower the cation exchange capacity, the shorter the time to reach salt balance [Kandpal et al., 2005].

The Cathode systems showed a parabolic trend (Fig. 3.5, black squares). $SOIL_{spiked}$ generated higher current consumption than $SOIL_{polluted}$ throughout the experiment. The reducing potential (ca. from -1.5 to -2 V vs Ag/AgCl) was able to reduce atmospheric carbon dioxide and transform it into carbonates in the soil (Fig. 3.6). The carbonates formation may increase the pH and electrical conductivity (Table 3.3) and thus increased the current. Both pH and electrical conductivity from $SOIL_{spiked}$ were increased, suggesting a higher presence of carbonates. Finally, the bioelectrochemical response decreased for anode configurations after 35 days, proably due to the poisoning of the electrodes by deposition of carbonate salts [Logsdon, 2003; Skafte et al., 2018] (Table 3.3).

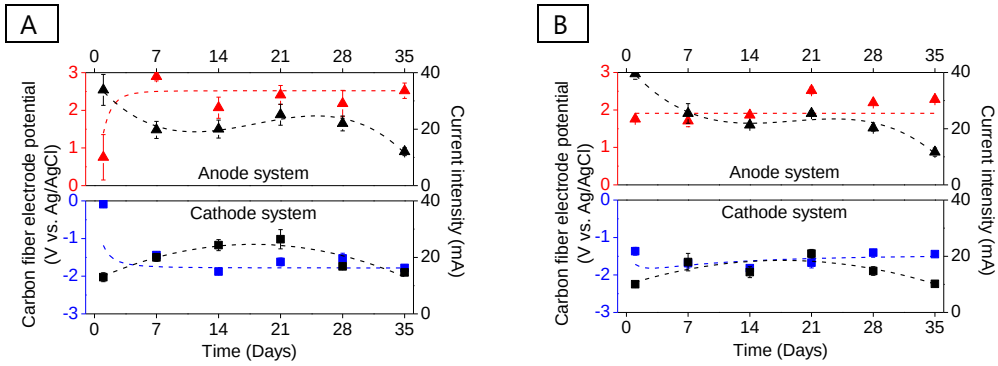


Figure 3.5: Performance of a soil microbial electroylysis cell operated during 35 days using (A) $SOIL_{spiked}$ and (B) $SOIL_{polluted}$. Electrode potential (vs Ag/AgCl) was measured for anodic configuration (red triangles), cathodic configuration (blue squares); current intensity was measured for anodic configuration (black triangles) and cathodic configuration (black squares). Error bars represent standar error and dash lines represent Lognormal fitting for electrode potential and polynomial fitting for current intensity.

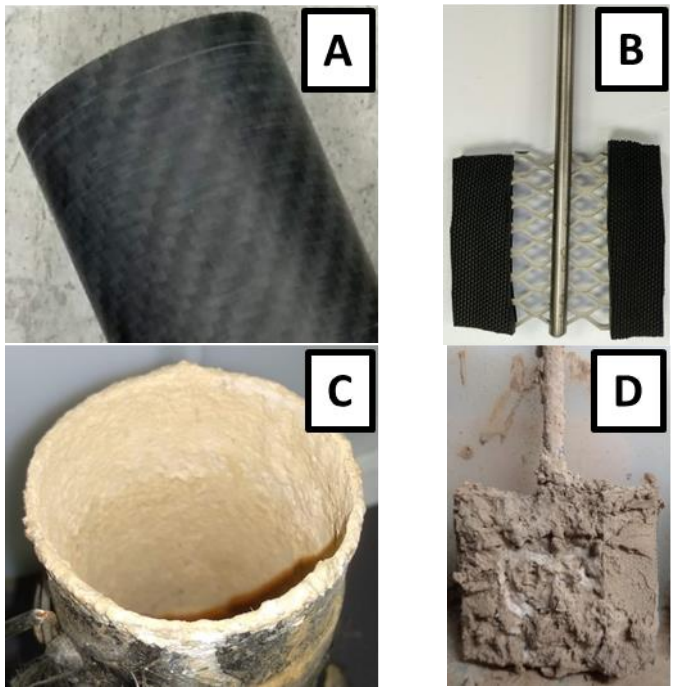


Figure 3.6: Images of a cylindrical carbon fiber electrode (left, A and C) and a titanium platinized mesh electrode (right, B and D) used as cathode, before (upper, A and B) and after operation (lower, C and D).

Table 3.3: pH and EC values after 35 days of treatment soil microcosms.

Sample		pH	EC (µS/cm)
$SOIL_{spiked}$	PVC	7.8 ± 0.2	581 ± 91
	Snorkel	7.8 ± 0.2	500 ± 26
	Anode	8.4 ± 0.6	680 ± 29
	Cathode	12.0 ± 0.1	992 ± 44
$SOIL_{polluted}$	PVC	7.9 ± 0.2	418 ± 38
	Snorkel	7.9 ± 0.1	391 ± 26
	Anode	10.1 ± 0.3	335 ± 48
	Cathode	11.6 ± 0.4	423 ± 65

Values represented as mean ± standard error. Abbreviations: EC, electrical conductivity.

3.3. Polarized Carbon fiber as scalable configuration

Once the proof-of-concept was successfully validated, a more complex approach was performed for testing scalable configurations based on the use of electroconductive carbon fiber hollow cylinders. Thus, the electroconductive cylinders were filled with polluted soil and internal wall was polarized (5V) while lindane removal was monitored. In contrast with natural attenuation control, all systems containing electroconductive material promoted high removal efficiencies after 35 days of incubation, so in order to compare treatments we just focused on performance at day 14^{th} (Fig. 3.7). The mere presence of the carbon fiber (snorkel) created a natural redox gradient capable of stimulating lindane removal (maximum removal rate of 0.42 mg/(kg*day)) in comparison with natural attenuation 0.11 mg/(kg*day)). Furthermore, polarized systems, either anodic or cathodic configurations resulted in maximum removal rates of 0.78 and 0.88 mg/(kg*day) respectively. Thus, cathodic configurations revealed better results after 35 days of incubation and no lindane was detected after extraction protocol. Such configuration uses the electrode as electron donor confirming that reported degradation pathways are preferentially reductive [Bashir et al., 2018; Camacho-Pérez et al., 2012; Elango et al., 2011; Schilling et al., 2019].

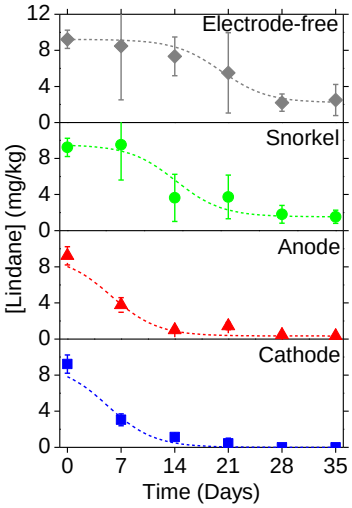


Figure 3.7: Lindane removal in soil microcosm under the following configurations: electrode-free, Snorkel, Anodic and Cathodic one. Error bars represent standar error and dash lines represent sigmoidal fitting.

3.4. Different redox conditions degrade different isomers in real polluted sediment

Polarized electroconductive cylinders were tested for the degradation of HCH, including lindane, present in a real polluted soil ($SOIL_{Polluted}$). The HCH analyses revealed the different behavior of the isomers depending on the degradation pathway.

Comparing the degradation between the initial sample (Table 3.1) and the samples at day 7, some of these differences could be observed. The experimental setup came after homogenization and pasive aeration of the soil. This aeration stimulates 60% removal of β-HCH and 75% of δ-HCH isomers, while α-HCH and lindane isomers hardly changed their concentration after 7 days. This finding confirms how α-HCH and lindane are mainly removed via reductive pathway while β-HCH via oxidative and δ-HCH via oxidative [Phillips et al., 2005; Quintero et al., 2005; Sahu et al., 1990; Schilling et al., 2019].

We have established the beginning of our assay 7 days homogenization&aeration in order to validate the efficiency of the electrobioremediation treatment. Thus, α-HCH (Fig. 3.8 A) was degraded under cathode configuration (>99% at day 28), while the trend for the other configurations showed no clear degradation. This is supported by the fact that α-HCH degradation occur preferably via an anaerobic reductive pathway

[Quintero et al., 2005; Schilling et al., 2019], like those promoted under cathodic configuration.

The β-HCH was the most abundant isomer detected in the polluted soil, probably because it is the most recalcitrant isomer [Bachmann et al., 1988; Nagata et al., 2005; Quintero et al., 2005; Usman et al., 2014]. β-HCH was clearly degraded under anodic configuration, while Cathode and Snorkel ones did not reveal a significant removal. The trend shown by the electrode-free control indicated a slight removal (Fig. 3.8 B). β-HCH is typically reported to degrade following an oxidative route [Lal et al., 2010; Quintero et al., 2005; Schilling et al., 2019], a condition promoted under anodic configuration.

Lindane, γ-HCH, was a minority isomer barely detected in analyses of the polluted soil (ca. 0.05mg/kg). However, all electrochemical configurations tested revealed an enhancement in the removal in comparison with PVC control. Indeed, cathodic configuration was the only one showing a full removal of lindane (Fig. 3.8 C). Actually, lindane biodegradation occurs mostly through a reductive pathway [Bashir et al., 2018; Camacho-Pérez et al., 2012; Elango et al., 2011; Schilling et al., 2019] which is indeed favored by a cathodic configurations where the electrode is acting as electron donor.

Finally, the δ-HCH isomer was degraded by all configurations tested: Snorkel, Anodic and Cathodic ones (Fig. 3.8 D). This isomer was reported to be biodegraded under both oxidative and reductive degradation pathways [Quintero et al., 2005; Schilling et al., 2019], therefore any shift of the redox conditions of the soil could virtually had an impact on its degradation. However, cathodic configurations seems to be the one that degraded the most δ-HCH, which was not detected at day 35.

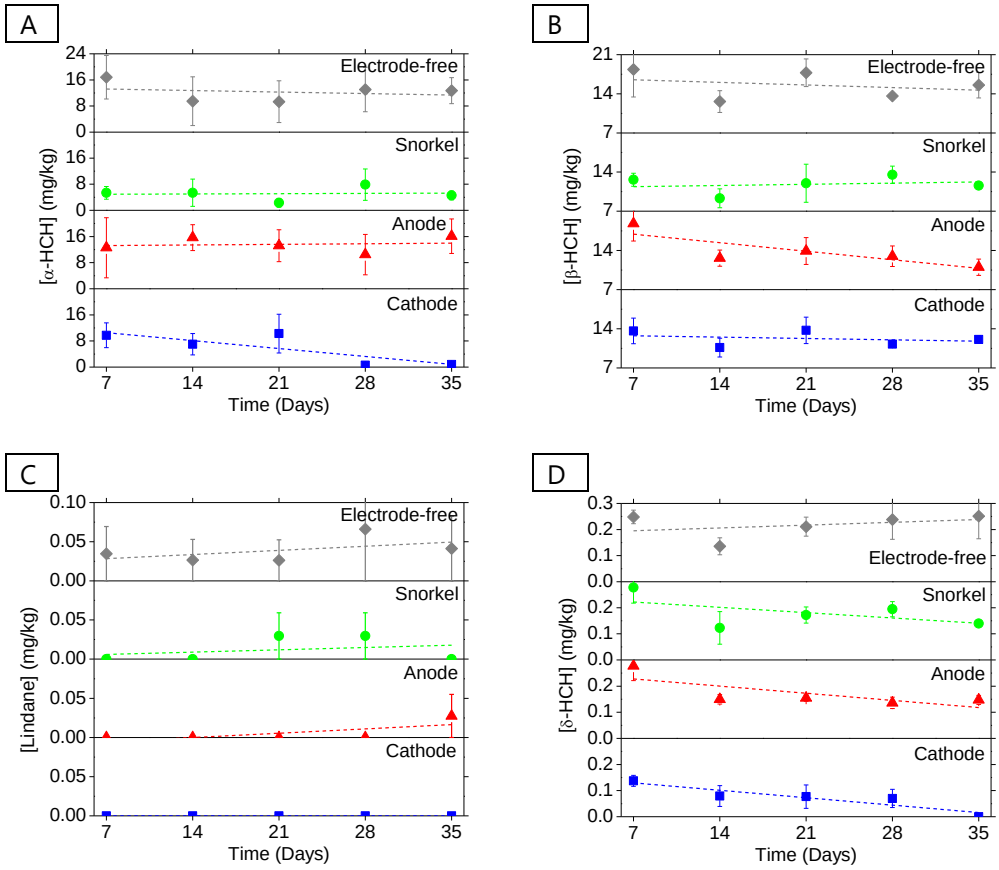


Figure 3.8: Removal of HCH isomers in $SOIL_{polluted}$ microcosm under the following configurations: electrode-free natural attenuation, Snorkel, Anode and Cathode: A) α-HCH, B) β-HCH, C) lindane and D) δ-HCH. Error bars represent standar error and dash lines represent linear fitting.

3.5. Fine tuning electrochemical strategies to reduce energy cost during lindane electrobioremediation

Once electrobioremediation of soil polluted with lindane was proved to be feasible, we focused on shifting the electron flow direction or minimizing the use of energy invested in polarization. We explore two independent strategies: i) on/off polarization during 50% of the assay period to reduce energy cost and ii) reversal polarization to dissolve carbonate deposition on the electrode.

Thus, we have compared our standard configuration (electrodes constantly polarized) with operation conditions where electrode polarization was either interrumpted, or reversed (Fig 3.9). We used the incubation time for reaching 99% removal of lindane as goal to compare all different configurations. Disconecting the cathode by 50% of the time increased removal time from 14 to 21 days. Moreover, reversing the polarization (Cathode-Anode) increased removal to 28 days, same result shown by standard anode polarization. Finally, those configurations, not promoting reductive conditions [Quintero et al., 2005; Schilling et al., 2019] (Anode-based, snorkel and electrode-free soil), showed longer periods for reaching values of removal higher than 90%.

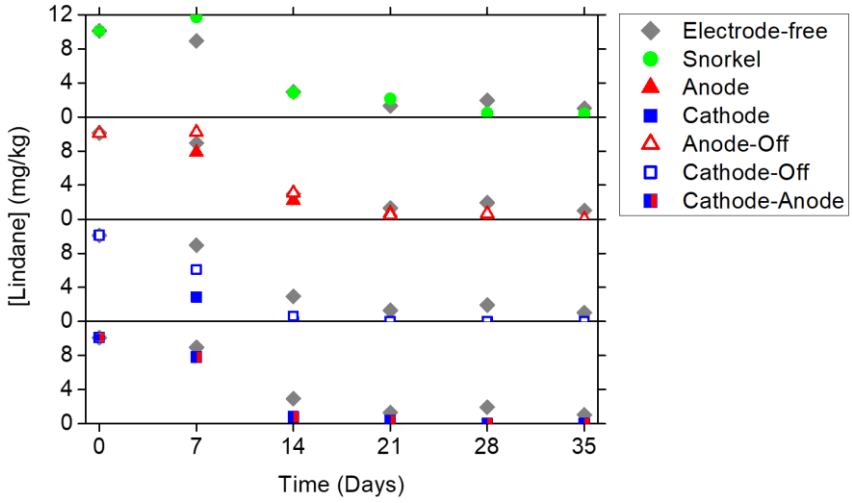


Figure 3.9: Lindane degradation in the energy saving polarized microcosm systems.

3.6. Electrobioremediation of lindane in non-floode soil: 3D assessment

Although flooded soils offer suitable environment for hosting cathode far from anoxic soil, most of the soils on earth are actually under non-flooded conditions [Davidson et al., 2018; Davidson and Finlayson, 2018]. However, previous studies [Domínguez-Garay and Esteve-Núñez, 2018] have reported strategies for operating a microbial electrochemical device under non-flooded conditions. Such device was indeed validated for performing electrobioremediation of the herbicide atrazine. Applying same concept to lindane bioremediation, then a ceramic membrane was used to kept catholyte out of

the soil matrix (Fig. 3.3). The working electrode in contact with the soil was connected through different configurations such snorkel, anodic and cathodic configurations. Although the soil was not fully flooded our set up can guarantee enough level of moisture (average of 10% at the external perimeter of the soil) to support microbial activity and avoid ohmic resistance [Habibul et al., 2016; Li et al., 2016d]. Our observations revealed that lindane removal was dependent on distance to the electrode. The Cathode configuration was the treatment revealing the highest lindane degradation in contrast with the Anode-based configuration (Fig. 3.10 and Fig 3.11). Such observations confirmed previous results under flooded-soil conditions: lindane is mainly degraded mainly via reductive pathway [Quintero et al., 2005; Schilling et al., 2019]. However, in a first period of incubation, cathode-based configuration did not revealed such remediating impact in soil zones far from membrane (30 to 50 mm).

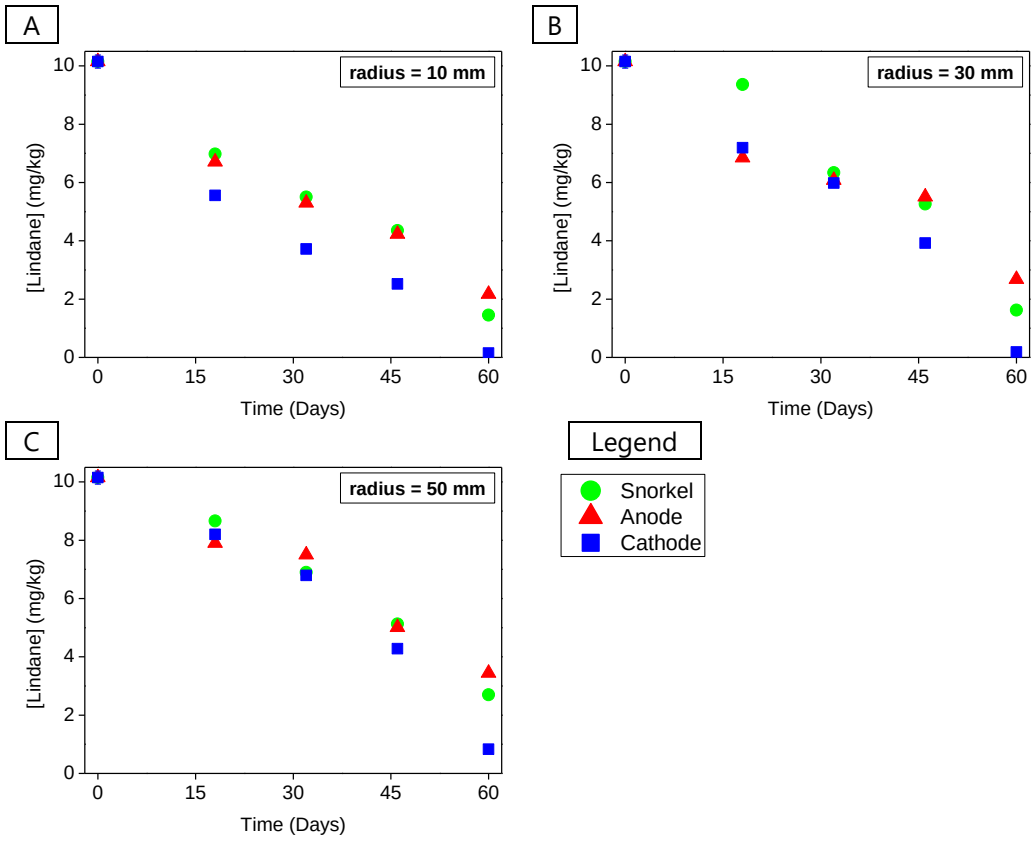


Figure 3.10: Radial distribution (A, 10 mm; B, 30 mm; and C, 50 mm) of Lindane removal

The 3D profile of lindane in the soil exhibited a trend that could be correlated with the expected distribution of moisture in the soil. The moisture was conditioned by the ceramic membrane humectation, the evaporation and the border effect of the pot (no absorption, but with capillary conduct). Precisely, the highest lindane degradation was found at the area below the ceramic membrane, the environment with the highest exposition to the moisture and therefore the first zone reaching reductive redox conditions [Joo and Zhao, 2008; Smith and Dowell, 1974]. Finally, the Cathode configuration revealed an enhancement in lindane removal mediated by electred-based reducing conditions [Bashir et al., 2018; Camacho-Pérez et al., 2012; Elango et al., 2011; Schilling et al., 2019]. Thereby, Cathode was the configuration with the highest impact in bioremediation, keeping lindane presence below 1.2 mg/kg_{soil} even at 6 cm from electrode (Fig. 3.11).

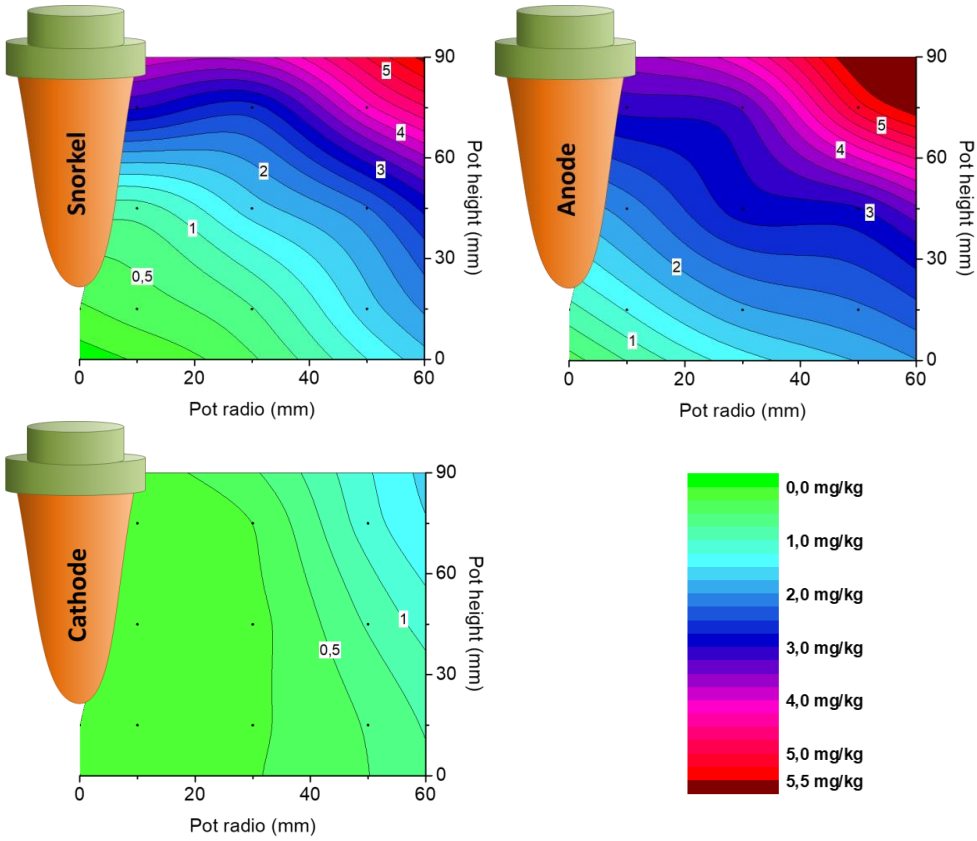


Figure 3.11: Lindane in non-flooded configurations after 60 days of treatment under a) snorkel, b) anodic and c) cathodic configurations. Numbers in curves indicate the isoline for certain lindane content per kg of soil.

4. Conclusions

All our assays to validate electrobioremediation of lindane-polluted soil have revealed that preferential removal was always under a cathodic configuration where electrode behaves as electron donor to favour reductive pathways. In fact, lindane was removed from a real polluted soil at rates ca. 9-fold faster (ca. 0.9mg/(kg_{soil}*day)) than natural attenuation (ca. 0.1 mg/(kg_{soil}*day)). Lindane-degrading microbial communities were electrode-dependent because disconnecting the electrode polarization for 50% resulted in 2-fold reduction of the removal rates.

Alternative electrochemical configurations were also tested, and anodic one resulted in higher lindane degradation than the snorkel systems. This could be due to the fact that the counter electrode was in contact with the soil and may play a role as electron donor similar to the one detected in cathode

Regarding the different HCH isomers, they were metabolized through different treatments according to the preferential degradation pathway reported in literature. α-HCH degraded mostly via reductive pathway, because of the cathode. β-HCH was mostly degraded via oxidative pathway, because of the anode. And δ-HCH was degraded by oxidative and reductive pathways, but mostly reductive.The use of a electrochemical design capable to operate in non-flooded revealed a 98% lindane removal at cm distance from electrode, opening a door to implement bioremediation task in outdoor environments.

Chapter 4:

Electrobioremediation of a real lindane-polluted sediment

Chapter 4: Electrobioremediation of a real lindane-polluted sediment

Abstract

Lindane, the γ-HCH, has been one of the organochlorine pesticides most used in the world. Its production involves waste generation and consequent polluted areas. In Spain, lindane production in Sabiñanigo (Huesca) has contaminated a vast zone for decades of Sabiñanigo (Huesca). This chapter explores the electrobioremediation of a real sediment from such contaminated area. A number of different electrobioremediation configurations were tested during a 20 weeks period. Precisely, anode-based and cathode-based configurations were assayed by using an external power source (5V). Furthermore, natural redox gradient was also investigated by using a snorkel-based configuration. Finally, humic acids and nitrogen-based fertilizers were artificially supplemented to some sediment reactors. The results demonstrate how reducing conditions achieved under a cathode-based configurations were optimal one and capable of removing 75% of Total HCH in just 10 weeks. Regarding HCH isomers, the cathode-based systems degrade up to 97% of α-HCH while β-HCH, the most recalcitrant isomer, was only partially removed. The concentration of γ-HCH isomer, pure lindane, decreased in all systems, including the electrode-free control sediment. Finally, the δ- and ε-HCH isomers, minority isomers, were degraded mainly by cathode-based configurations. Nevertheless, phytoxicity analysis revealed a true remediation task since 81% of *Sorghum saccharatum* seed were germinated after cathode-based treatment in comparison with 17% from electrode-free control sediment. Cathode-based configurations selected cathodophilic bacteria (*Desulfosporosinus* and *Dethiobacter*) while anode-based configurations selected for anodophilic (*Geobacter* genus) and aromatic degrading bacteria.

1. Introduction

Lindane, the gamma isomer of hexachlorocyclohexane (γ-HCH) represent one of the organochlorine pesticides most used around the world since 1940 [Katsoyiannis et al., 2016]. It was used in form of technical lindane (mixture of HCH isomers) or purified lindane. The production of any of these forms leads to residue formation and Europe concentrates the 63% of the world lindane wastes [Vijgen et al., 2011]. The large amount of wastes results in environmental and health problems [Wacławek et al., 2019] so administrations have included isomers α-, β- and γ-HCH in the list of Persistent Organic Pollutant (POP). In Europe, Stockholm Convention banned their use and production since 2009 [Madaj et al., 2018].

In Spain, lindane production was concentrated in several areas. INQUINOSA manufacturing company in Sabiñanigo (Huesca) produced lindane between 1975 and 1988, and continued formulating lindane products until 1992. Waste generation was estimated around 300 and 1500 tons/year of liquid and 6800 tons/year of solids [Fernández et al., 2013]. These wastes generated and stored in a landfill during the manufacturing, imply currently a serious environmental problem. In the former landfill located in Bailín, near to Sabiñanigo, decantation tanks are necessary for reteining the polluted soil. Hydric erosion transports the polluted soil particles from the former landfill to the decantation tank, generating a new residue of polluted soil sediment.

Different degradation methods for the removal of lindane and its associated waste have been assayed in soil, including both *ex-situ* [Álvarez et al., 2015; Camacho-Pérez et al., 2013; Peng et al., 2015; Quintero et al., 2006; Raimondo et al., 2020a; Salam et al., 2017; Usman et al., 2014; Varo-Arguello et al., 2012] and *in-situ* remediation cases [Abhilash and Singh, 2008; Phillips et al., 2006].

Soil microorganisms can degrade a wide variety of compounds, including HCH, under anaerobic conditions [Bashir et al., 2018; Jagnow et al., 1977; Lal et al., 2010; Shin et al., 2019; Song et al., 2019]. However, some of these compounds persist in sediment and soil due to the absence of a suitable electron acceptor or donor [Boopathy, 2004; Megharaj et al., 2011; Wang et al., 2016; Widdel and Rabus, 2001]. Some investigations have proposed the supply of additional electron acceptors [M. Chen et al., 2020; García Frutos et al., 2010; Kabelitz et al., 2009; Suh and Mohseni, 2004], additional electron donors[Askarian et al., 2017; Chen et al., 2001; Fennell et al., 1997] or additional redox

mediators [M. Chen et al., 2020; Lovley, 2000; Mazarji et al., 2020; Y. Zhang et al., 2020] to the environment as a bioremediation strategy.

Such electron acceptor or donor limitation could be overcome using electrodes as part of new strategy for cleaning-up polluted environments for named electrobioremediation [Morris and Jin, 2012; Rodrigo Quejigo et al., 2018]. First example of graphite electrode as insoluble electrode for remediating aromatic polluted slurry was reported more than a decade ago [T. Zhang et al., 2010a]. Since then, several studies have used microbial electrochemical systems to enhance the biodegradation of pollutants of different chemical nature such as petroleum hydrocarbons [Daghio et al., 2016; Morris and Jin, 2012; Zhang et al., 2015], PAHs [Chandrasekhar and Venkata Mohan, 2012; Hamdan et al., 2017; Li and Yu, 2015; Li et al., 2015; Rodrigo et al., 2014; Sherafatmand and Ng, 2015; Wang et al., 2012; B. Yu et al., 2017]; phenol [Huang et al., 2011], nitrobenzene [Liang et al., 2014], chlorinated organics [Chun et al., 2013; Liu et al., 2013; Yu et al., 2016], herbicides[Rodrigo Quejigo et al., 2016] and pesticides [Cao et al., 2015], including lindane in a slurry reactor [Camacho-Pérez et al., 2013].

Moreover, not only pollutant removal but an efficient clean-up was demonstrated by ecotoxicological analysis of a DBT-polluted soil after electrobioremediation as well [Rodrigo et al., 2014]. Similar results were obtained by genotoxicological and phytotoxicological assays in atrazine-polluted soils after microbial oxidation stimulation using an electrode [Domínguez-Garay et al., 2016; Domínguez-Garay and Esteve-Núñez, 2018].

The main purpose of this work was to explore an effective treatment to remove lindane and its isomers from long term lindane-polluted soil sediment (Sabiñanigo, Spain). Additionally, the impact on the microbiology, toxicity and physicochemical properties of the sediment due to the application of different electrode configurations was also measured.

2. Materials and Methods

2.1. Sediment collection and homogenization

Real polluted sediment, originated from soil runoff, was sampled from Sabiñanigo (42°29'12" N; 0°21'41" W). An excavator shovel collected 3.7 m^3 of sediment and homogenized it with a worm screw (Fig. 4.1). Then the sediment was equally distributed in 9 different high density poly-ethylene (HDPE) tanks (112 x 92 x 50 cm) till reaching a sediment depth of 40 cm. All assays were performed in the vicinity of sampling point (120m apart).

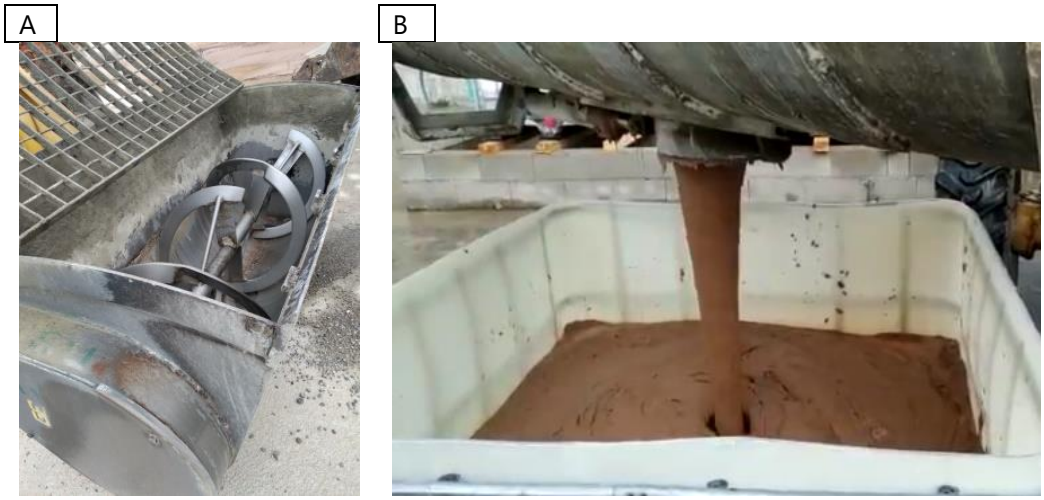


Figure 4.1: Images of A) worm screw homogenizator and B) sediment distribution

2.2. Electrobioremediation configurations

Each sediment tank was filled with tap water till 45 cm level was reached. They were operated under 3 main configurations: i) snorkel, ii) two-electrode; iii) electrode-free as control. All conditions were tested using 25 electroactive replicas per configuration (Fig 4.2 A):

i) Snorkel configuration: 3 independent snorkel reactors were assembled using a cylindrical electrode made of carbon-fiber (Clipcarbono. Length 30 cm, diameter 5 cm), and buried 25 cm below the sediment surface while showing 5 cm in contact with flooded water. One of the snorkel reactors was supplemented with 1.5 L of humic acid (Humipower, arvensis) as amendment (SNO-HA); a second reactor was supplemented with 1.5 L of humic acid plus 3 kg of Universal Blue Fertilizer (NovaTec) (SNO-HA-F). Finally, a third snorkel reactor acted as control non-supplemented (SNO) (Fig. 4.2 B).

ii) Two-electrode configurations: Four independent sediment reactors were constructed, two for testing anodic stimulation and two for cathodic stimulation. The working electrodes consisted of cylindrical carbon-fiber electrode (length 30 cm, diameter 5 cm) vertically buried till 5 cm below sediment surface. The working electrodes were connected to a power source: positive pole for anodic stimulation (ANO) (Fig. 4.2 C) and negative pole for cathodic stimulation (CAT) (Fig. 4.2 D). Furthermore, a titanium platinized meshes (INAGASA) laid over the sediment acted as counter electrodes. These sets of two-electrodes were also amended with humic acids (ANO-HA and CAT-HA).

In addition, another cathode system was developed by matching the surface area of the cathode with the counter electrode. In these devices, both electrodes were made of carbon-fiber cylinders, although the length was shortened (length 10 cm, diameter 5 cm) (S-CAT) (Fig. 4.2 E). The cathodes were vertically totally buried 10 cm below the sediment surface. The counter electrodes were buried 5 cm below the sediment, showing 5 cm in contact with flooded water.

iii) Finally, a polyvinyl chloride (PVC) cylinder (length 30 cm, diameter 5 cm) was used as non-conductive material for control. It was vertically buried 5 cm below the sediment surface (PVC) (Fig. 4.2 F).

All power sources were connected at 5 V and the water level was maintained 5 cm over the sediment. The assay lasted 20 weeks.

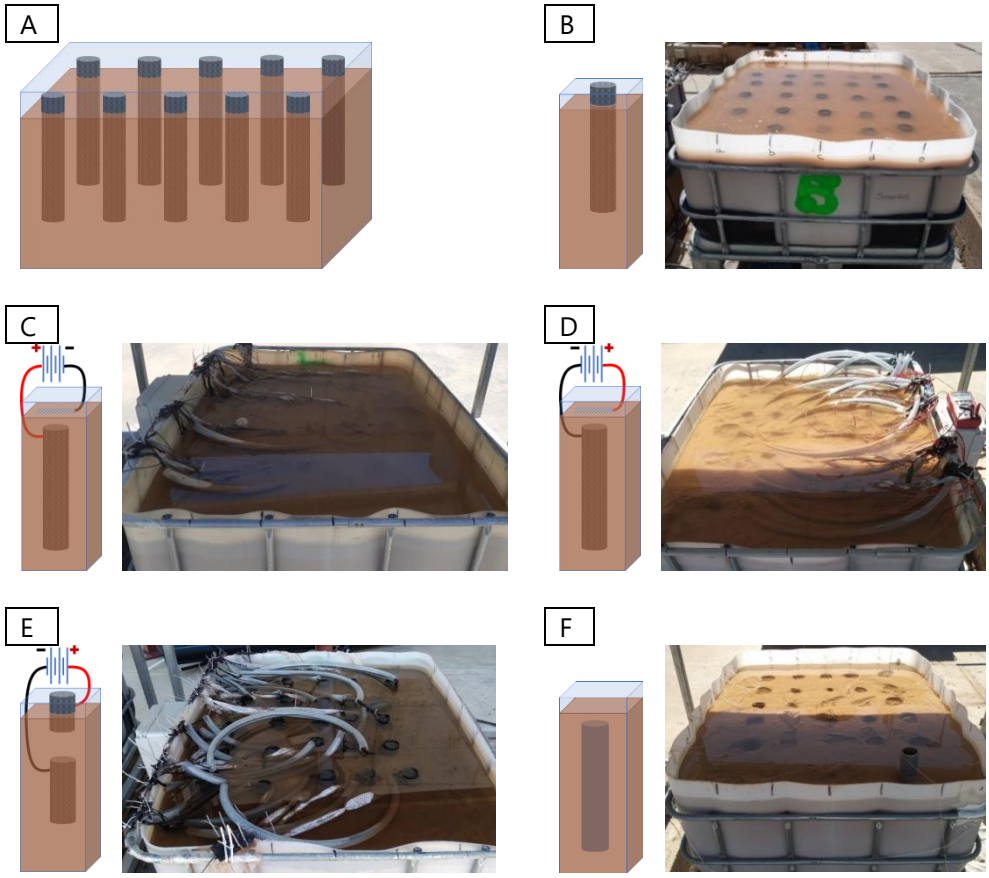


Figure 4.2: Schemes and images of electrobioremediation systems. A) System electrode general disposition; B) SNO; C) ANO; D) CAT; E) S-CAT; and F) PVC.

2.3. System sampling

Samples were taken at the beginning of the experiment (week 0), mid-term (week 10) and long term (week 20). Once the experimental period was finalized, the sediment inside the electrode was collected. The content of one device in every configuration was homogenized and air-dried at ambient temperature for further HCH analysis. The rest of the sediment was frozen for toxicity and microbial population analysis.

2.4. HCH concentration analysis

The homogenized air-dried sediment samples were analyzed by GC-MS in the SARGA laboratories (Sabiñanigo, Huesca). Initial HCH concentration was between 19.4 and 53.8 mg/kg, where the isomer range was: α-HCH, 4.8-40 mg/kg; β-HCH, 10.7-12.6 mg/kg; γ-HCH (lindane), 0.35-0.93 mg/kg; δ-HCH, 0.24-0.76 mg/kg; and ε-HCH, 0.65-1.24 mg/kg.

2.5. Phytoxicity analysis

In order to test the phytotoxicity of the treated sediment, *Sorghum saccharatum* seeds (Phytotoxkit test) were planted into the different treatment samples of 20th week. A cylindrical pot (height 10 cm, diameter 10 cm) was filled with sampled sediment and 14 seeds were germinated in the sediment. Three replicates of each system were tested. Pots were irrigated with tap water for a month and then germinated seeds were counted.

2.6. Analysis of microbial communities

The sediment in contact (1cm) with the working electrode was harvested and shipped to "Servei de Genòmica i Bioinformàtica" of Universidad Autónoma de Barcelona where DNA was extracted and sequenced by Illumina technology. The data were treated with the software "16S Metagenomics" version 1.0.1.0 (Illumina Inc.). R software was used for PCA and dendrogram calculation and plotting.

2.7. Monitoring of current intensity

Current intensity of the polarized electrodes (anode and cathode-based systems) where calculated using a data logger (Tinytag) and a resistor (1000 Ω).

2.8. Monitoring of electrode potential

The carbon-fiber electrode potentials were checked every four weeks. The electrodes were connected to a multimeter (AM-510-EUR, Beha-Amprobe) and the potentials were measured versus Ag/AgCl reference electrode (Hanna, 3.5 M KCl) submerged in the water covering the sediment. Three different electrodes were measured as replicates.

2.9. Cyclic voltammetry analysis

Cyclic voltammetry (CV) was assayed to characterize the electrochemical behavior of the electrodes in the soil at the beginning and at the end of treatments. The potentiostat NEV 4 (Nanoelectra S.L.) imposed two different scan rates (1 and 10 mV/s) in a range from -1 to 0.6 V. A Hanna reference electrode Ag/AgCl 3.5 M was used for these assays.

3. Results and Discussion

The potential of different electrobioremediation strategies to clean-up lindane-polluted sediment was tested under a number of configurations where the electrode, either as electron acceptor (SNO and ANO) or electron donor (CAT), was acting as sole stimulating agent or in presence of fertilizers and humic acids as redox mediators. Phytotoxicy analysis together with microbial community analysis contributes to understand the whole process.

3.1. Cathodic configurations outperform anodic ones for removing total HCH

The main parameter to evaluate the efficiency of our electrobioremediation strategies was to analyze the HCH concentration in the sediment before and after the treatment. Indeed, Total HCH concentration results from considering the whole content in HCH isomers (Fig 4.3-4.5).

Three different main strategies were evaluated, i) the use of a natural redox gradient exhibited by electroconductive material buried in the sediment, the so-called snorkel configuration (SNO), iii) the use of an electrode (anode) as electron acceptor (ANO) and, iii) the use of an electrode (cathode) as electron donor (CAT). Additionally, such configurations were tested in absence or presence of natural redox mediator like humic acids or/and agronomic fertilizer in order to enhanced the impact of the electrode. Lindane degradation has been reported to be favoured under reducing environments [Anu Prathap and Srivastava, 2013; Bashir et al., 2018; Elango et al., 2011; Li et al., 2011] due to the initial reductive attack to remove the chlorinated group.

Our results confirm this observation since the most efficient electrobioremediating configuration was precisely the cathodic one (Fig. 4.3) where the electrode is acting as electron donor. Indeed, 70% of total HCH was removed after 20 weeks in contrast with negligible variation observed in control sediment in presence of non-conductive material like PVC. Furthermore, humic acids enhanced the action of the cathode specially in the first 10 weeks (2-fold). A special cathode configuration with smaller dimension was located in the vicinity of the counter electrode to minimize resistance (S-CAT), and it was capable of removing 75% of total HCH in at least 10 weeks, half of the total treatment.

Table 4.1: Removal rate and removal efficiency of any system for HCH degradation

Electrobioremediation configuration	Degradation rate* (mg/(kg*day))
PVC	0.01 ± 0.04
SNO	0.06 ± 0.03
SNO-HA	0.08 ± 0.00
SNO-HA-F	0.02 ± 0.05
ANO	0.01 ± 0.02
ANO-HA	0.12 ± 0.06
CAT	0.16 ± 0.01
CAT-HA	0.18 ± 0.08
S-CAT	0.19 ± 0.10

*Degradation rate and uncertainty were calculated as first order slope.

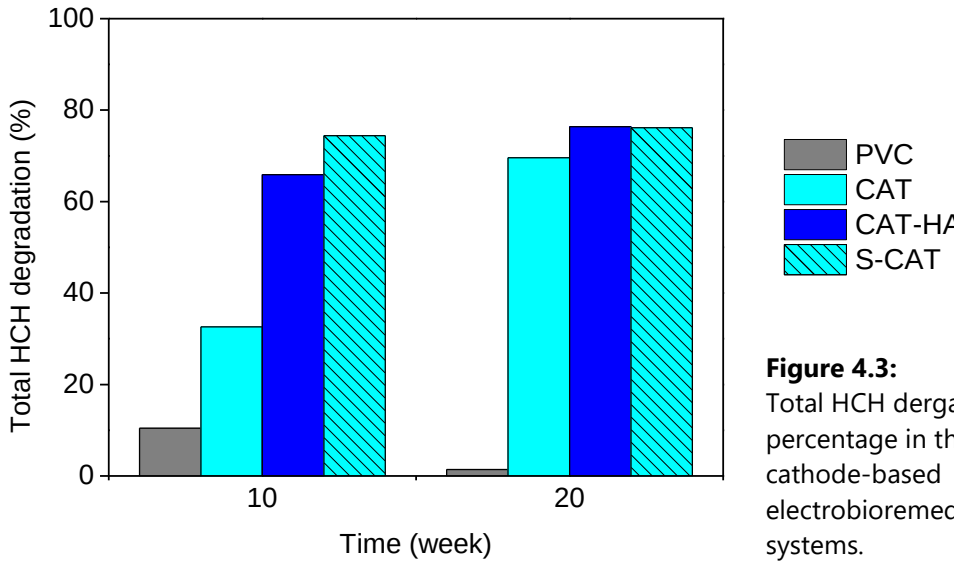


Figure 4.3: Total HCH dergadation percentage in the cathode-based electrobioremediation systems.

In contrast, anode-based configurations (Fig. 4.4) where electrode is acting as electron acceptor showed no significant removal after 20 weeks of incubation. In addition, the artificial addition of humic acids increased the impact of the anode so 50% of the initial total HCH was removed after the first 10 weeks. In the anode-based configuration, working electrodes accept electrons and compete with the HCH for those electrons, which minimizes chloride release from HCH.

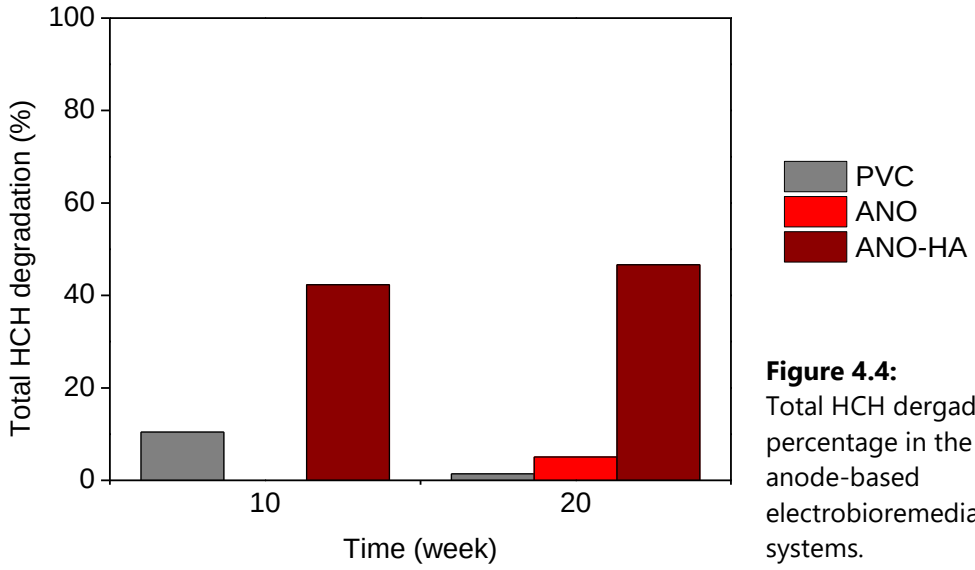


Figure 4.4: Total HCH dergadation percentage in the anode-based electrobioremediation systems.

Table 4.2: Porewater physicochemical parameters at the end of the experiment

Electrobioremediation configuration	pH	EC (µS/cm)	ORP (mV)	COD (mgO_2/L)	E4/E6
PVC	8.12	654	67.5	12.9	1.11
SNO	8.13	609	66.7	17.58	1.32
SNO-HA	8.61	1484	45.6	1569	2.55
SNO-HA-F	7.15	11120	70.2	744	1.80
ANO	8.38	442	73.2	12.8	1.27
ANO-HA	8.42	860	71.1	606	3.22
CAT	7.41	592	81.1	12	1.17
CAT-HA	7.82	648	77.9	433	1.66
S-CAT	7.66	508	75	7.75	1.18

E4/E6 is calculated through the ratio of the absorbances at 465 nm and at 665 nm and represent humification grade [Hong et al., 2010]. Abbreviations: EC, electrical conductivity; ORP, oxidation-reduction potential; COD, chemical oxygen demand.

3.2. Zero-energy configurations like snorkel also favour HCH removal

In snorkel systems (Fig. 4.5), SNO and SNO-HA reached 45 and 55 % of Total HCH degradation in 20 weeks respectively. Both systems were anaerobic and therefore, there was a reducing environment. In addition, organic matter from humic acids kept the system more reduced [Fiedler and Kalbitz, 2003; Gardiner et al., 2012]. SNO-HA-F hardly removed Total HCH in 20 weeks, probably because the fertilizer competes for accepting electrons [Kashima and Regan, 2015; Srinivasan and Butler, 2017], enhances the degradation of humic acids [Menšík et al., 2018] and generates algae growth that oxygenates [Glibert, 2020]. All this interferes with the degradation of Total HCH.

PVC configuration did not show impact in Total HCH removal, which underlines the recalcitrant nature of the compound.

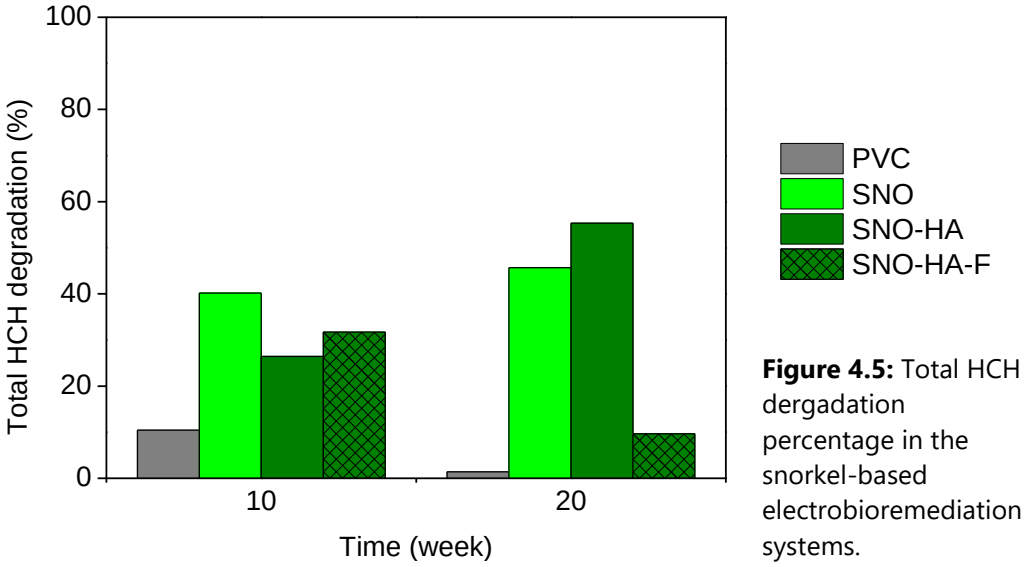


Figure 4.5: Total HCH dergadation percentage in the snorkel-based electrobioremediation systems.

3.3. Electrobioremediation impact on specific HCH isomers

α-HCH is the isomer with highest abundance so its degradation has an important impact in the removal of Total HCH. So thus, cathodic configurations (CAT, CAT-HA and S-CAT) removed 93-97% of α-HCH after 20 weeks resulting in a similar trend to the one observed in total HCH. In contrast, anodic configuration (ANO) or non-conductive PVC control showed no removal of α-HCH in the same period (Fig. 4.6).

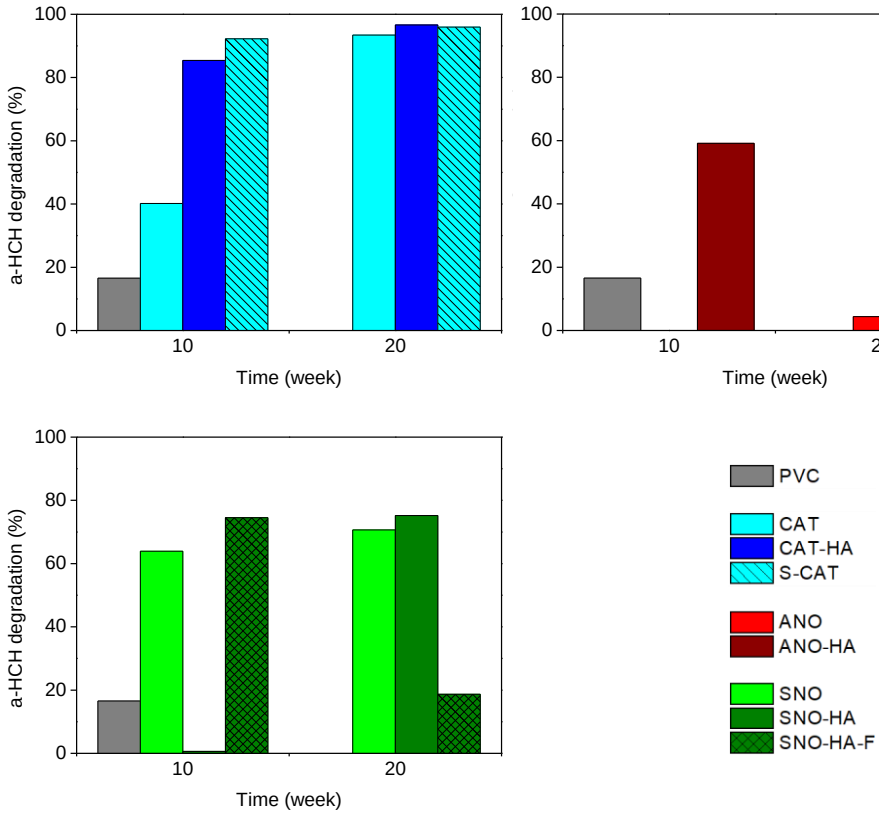


Figure 4.6: α-HCH dergadation percentage after different electrobioremediation treatments.

β-HCH is the most recalcitrant isomer from HCH [Bachmann et al., 1988; Nagata et al., 2005; Quintero et al., 2005; Usman et al., 2014], so it showed a different removal trend in comparison with Total HCH. However, cathodic configuration (S-CAT) were still the most favourable to remove it from sediment by enhancing dehalogenation reactions [Camacho-Pérez et al., 2012; Li et al., 2011] (Fig. 4.7).

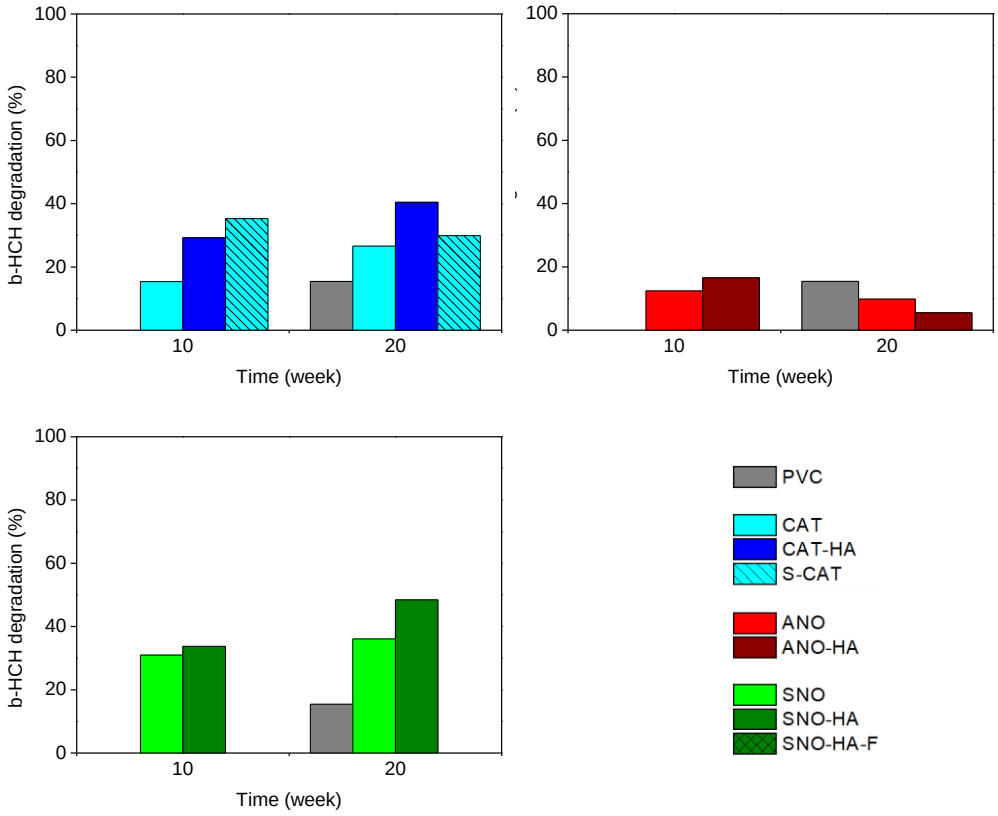


Figure 4.7: β-HCH dergadation percentage in the different electrobioremediation systems.

γ-HCH, commonly named as lindane, is the one exhibiting the insecticide action although it is also the most extensively studied regarding biodegradation pathways [Camacho-Pérez et al., 2012; Li et al., 2011]. The concentration of lindane in our polluted-sediment was 10-fold lower than α-HCH and β-HCH shown. Cathodic configuration outperforms the rest of designs, although all configuration tested shown some removal of lindane, including the control system in absence of electrode that did not show any effect in the rest of isomers (Fig. 4.8).

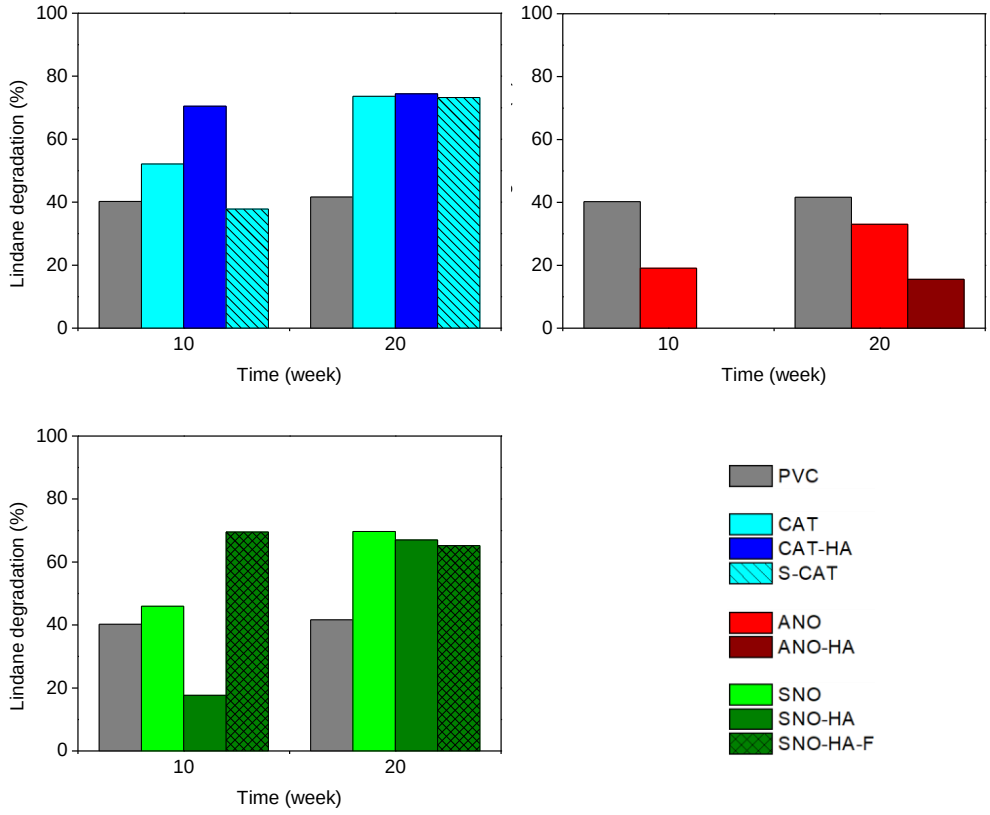


Figure 4.8: Lindane dergadation percentage in the different electrobioremediation systems.

Finally, the isomers δ-HCH and ε-HCH, present in minor concentration, were degraded just under cathode configurations, except snorkel one that stimulate some removal of ε-HCH (Fig. 4.9).

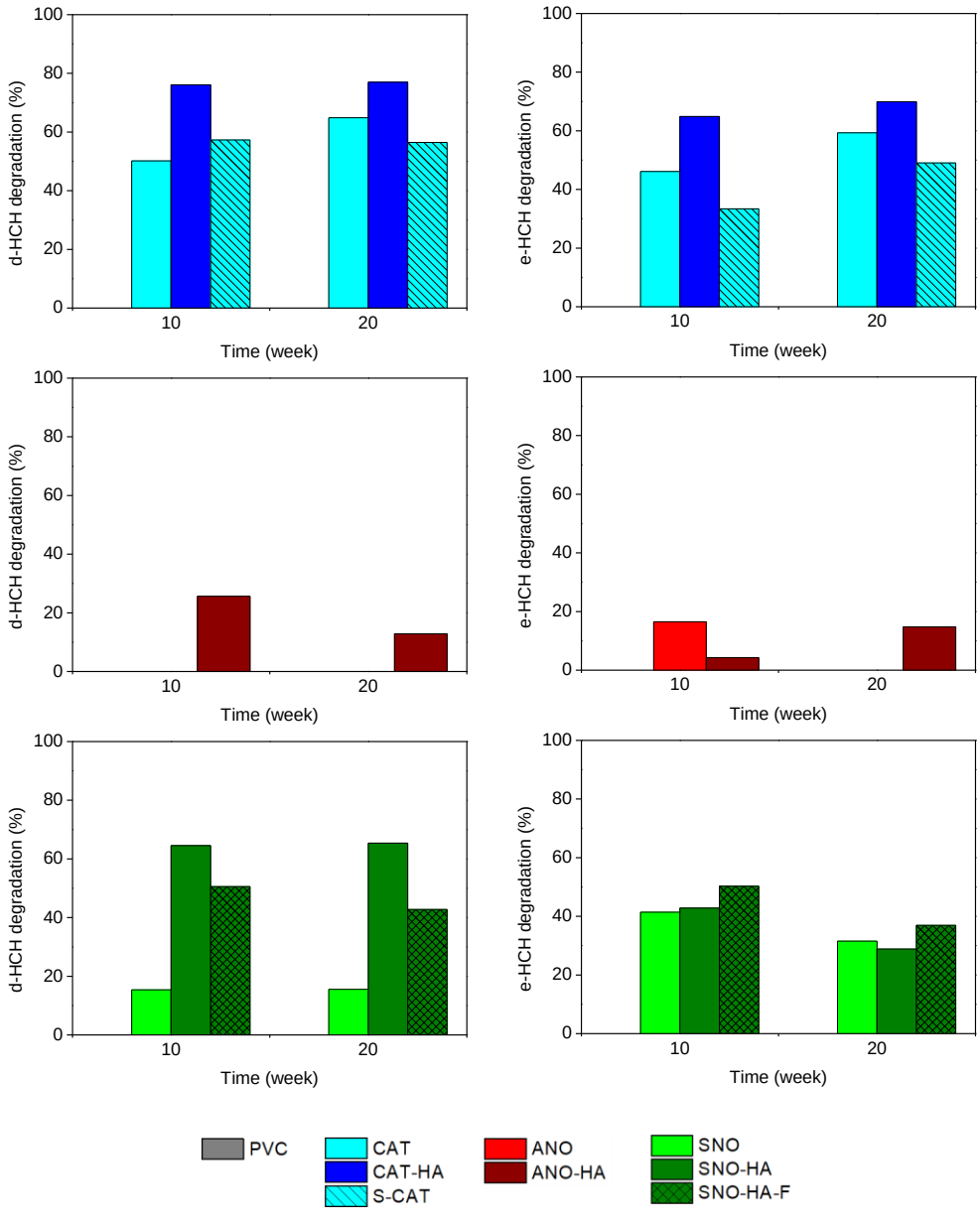


Figure 4.9: δ-HCH and ε-HCH dergadation percentage in the different electrobioremediation systems.

3.4. Phytotoxicity assay demonstrates true bioremediation of lindane polluted sediment

In order to test, not only HCH removal, but also sediment detoxification, a phytotoxicity test using *Sorghum saccharatum* seeds was performed on samples collected at the end of the assay (Fig. 4.10) [Baczyński et al., 2018; Giannis et al., 2008; OECD, 2006]. Thus, electrode-free sediment hosting a PVC cylinder as control, kept enough pollutant to reduce germination to just 19% of the total number of seeds. In contrast, sediment hosting a cathodic configuration (S-CAT) allowed 81% of the seed being germinated. This evidence of toxicity-free sediment is consistent with the lowest concentration of Total HCH detected precisely under S-CAT configuration. The rest of the configuration showed a profile where germination was allowed between 40 and 60% of the total number of seeds. The addition to humic acids (HA) reduced the % of germination in comparison with those HA-free configurations, maybe by the generating free radicals in organic molecules in presence of polarized electrodes [Dykstra and Pavlostathis, 2020; Fridovich, 1998; Son et al., 2019]. In contrast, germination was 60% when HA were applied in presence of non-polarized electrodes like snorkel configuration [Ali et al., 2020; Rodrigues et al., 2017].

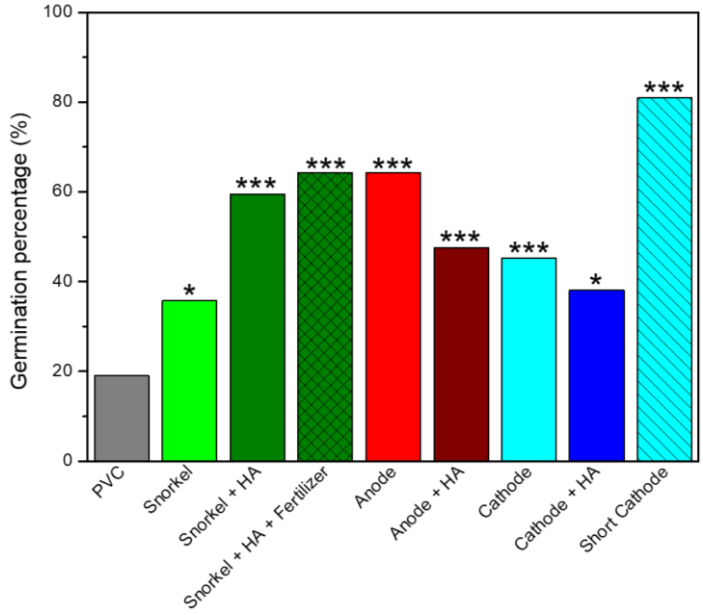


Figure 4.10: Seed germination in sediments after different electrobioremediation treatment during 20 weeks. Germination was shown as percentage of total number of seeds. Asterisks show chi-squared test between PVC configuration and the other configurations: * idicate p-value<0.01 and *** indicate p-value<0.001.

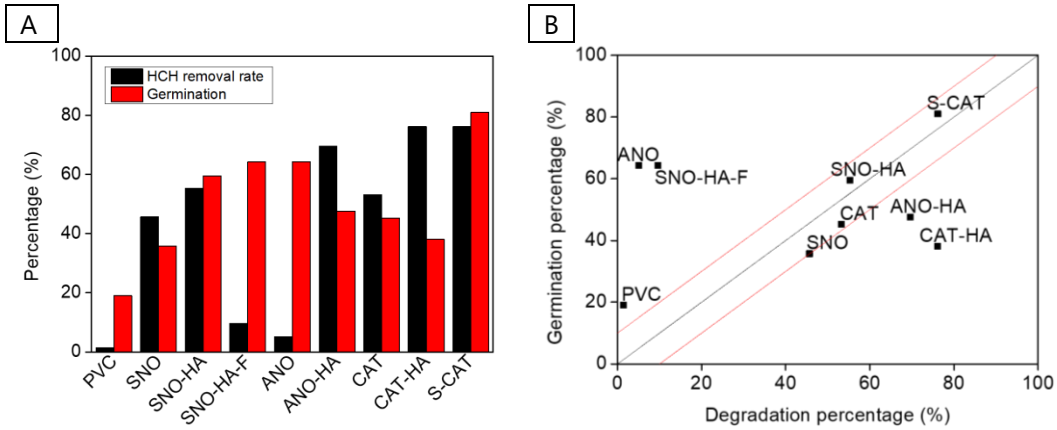


Figure 4.11: Seed germination correlated with Total HCH removal A) for the different configurations and B) as a dependent variable.

3.5. Analysis of microbial communities after electrobioremediation treatments

Different electrobioremediation configurations showed very different patterns of HCH removal and, eventually, also different phytoxicity. Assuming electrodes, either cathodes or anodes, are thought to stimulate microbial activity it is reasonable to expect significant shifts in the microbial community in the vicinity (1cm) of the electrodes. Thus, the Illumina analysis of 16S gene sequences revealed significant differences and similarities shown in a dendrogram (Fig 4.12).

The electrode-free sediment hosting a PVC cylinder was used as a control population after 20 weeks of incubation. Indeed the snorkel configuration following a natural redox gradient in absence of external polarization showed a microbial community profile very similar to the control population. In contrast, cathode-based configuration was the system showing less similarity with the control population. It is remarkable that the configuration selecting the most unique microbial profile correspond with the highest removal of HCH isomers including lindane. Regarding the Principal Component Analysis (PCA) (Fig. 4.12), several groups can be distinguished. Those microbial populations selected under cathode-based configurations (in blue) are shown at the top. A large group including control population (PVC, purple) together with anodic (red) and with snorkel configuration (green) was identified. Near the coordinate (0, 0) those population around snorkel supplied with humic acids and fertilizers can be identified. These clusters

are strongly marked by electrophilic bacteria (bacteria that proliferate in presence of electrodes) such as *Geobacter*, *Desulfosporosinus* and *Dethiobacter*, but also by other, a priori, non-electrophilic bacteria such as *Parcubacteria* (intertae sedis), *Anaerorhabdus*, *Olsenella* and *Howardella*.

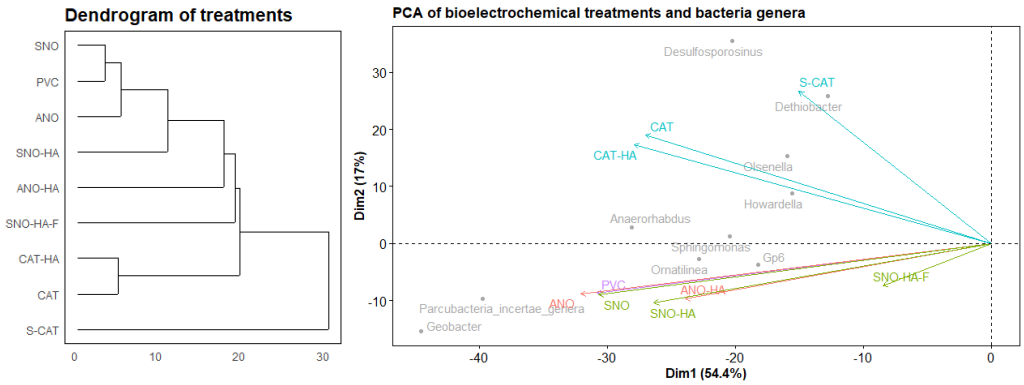


Figure 4.12: Dendrogram and Principal Component Analysis (PCA) of microbial population from different electrobioremediation configurations.

The abundance of electrophilic bacteria showed differences between treatments (Fig. 4.13). Electrode-free sediment (19%) and snorkel-based (15-18%) configuration selected for the lowest presence of electrophilic bacteria. The artificial addition of fertilizer including nitrate in the sediment and could decrease the competitiveness of electrophilic bacteria and increase the proliferation of the non-electrophilic [Kashima and Regan, 2015; Srinivasan and Butler, 2017]. Besides, snorkel configuration is the system with the most similar population to PVC (Fig. 4.12) and indeed it did not show a robust enhancement in the removal of total HCH.

Configuration selecting for anodophilic bacteria (bacteria that proliferate in presence of electrodes acting as electron acceptor) correspond to anode-based configuration or snorkels supplemented with humic acids. The high abundance of bacteria from genus *Geobacter* (4-12%) is not surprising considering that its presence in anodic biofilms [Logan et al., 2019; Pant et al., 2010] and its capacity for respiring humic acid [Lovley et al., 1991] is well reported.

Regarding those cathode-based configurations, they selected for a cathodophilic bacteria (those proliferate in presence of cathodes) like *Desulfosporosinus* (16%) and *Dethiobacter* (12%) that reached high percentages while showing the highest removal of total HCH including lindane isomer.

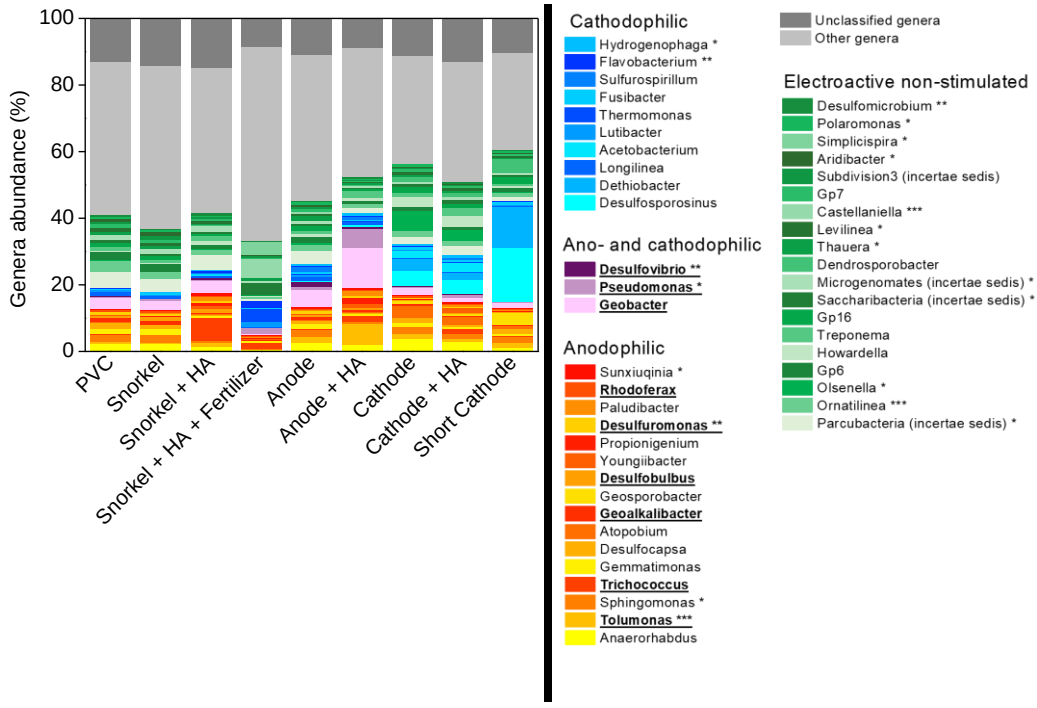


Figure 4.13: Taxonomic distribution of the electrobioremediation systems at genus level. Bold and underlying genera include bacteria with confirmed electroactive activity. * indicate aromatic pollutant-degrading bacteria, ** indicate lindane-degrading bacteria, and *** indicated humic acid-degrading bacteria

All anode-based and snorkel configurations enhanced the selection of bacteria previously reported as lindane-degrading bacteria (ca. 2-2.5% abundance). However such configurations resulted in a low removal of HCH in comparison with cathode-based configurations. Furthermore, the artificial addition of humic acids and fertilizers under snorkel configurations also selected for lindane-degrading bacteria selection [Dadhwal et al., 2009].

All cathode-based configurations (CAT, CAT-HA and S-CAT) showed a lower abundance of bacteria previously reported as lindane-degrader (ca 0.7-1.3%) in spite of removing HCH at higher rates. We hypothesized two possibilities for explaining such finding: i) the low presence of HCH after 20 weeks of treatment justify a low abundance in lindane-degrading bacteria, or ii) cathode-based configurations select for lindane-degrading bacteria not previously reported.

3.6. Anode-based configurations select for aromatic compounds degrading bacteria.

Electrobioremediation strategies using bioanodes have been shown to promote microbial communities involved in the degradation of aromatic compounds [Daghio et al., 2016; Hamdan et al., 2017; Tucci et al., 2021b; B. Yu et al., 2017]. This was also the case in the current study regarding anode-based configurations using a lindane-polluted sediment (marked with * in Fig 4.13).

The abundance of bacteria degrading aromatic compounds was increased from 17 % in the electrode-free control community to ca. 22 % when the anode-based configuration was supplemented with humic acids (Fig. 4.14). The use of such redox amendment to enhance aromatic hydrocarbon biodegradations has been previously reported [Lovley et al., 1996].

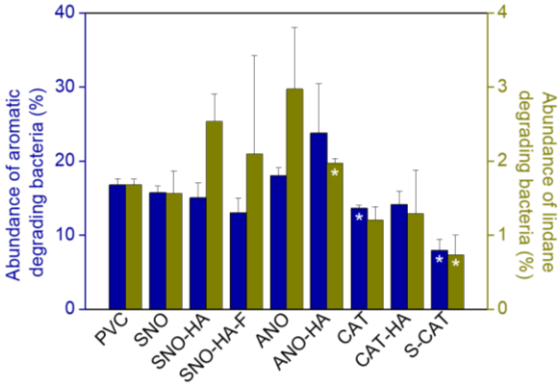


Figure 4.14:
Abundance of bacteria reported as aromatic pollutant- and lindane-degrading bacteria among different electrobioremediation configurations. Asterisks show chi-squared test between PVC configuration and the other configurations: * indicate p-value<0.01.

3.7. Current confirm electrobioremediation activity

To confirm the role of electroactive microorganisms, their activity should be confirmed. The current intensity flowing in every system is dependent on the reactions occurring at the electrodes. In turn, the reactions occurring in the working electrode are dependent on the microorganism-electrode reactions, since the electroactive microorganisms act as catalysts in the reactions involved through electroactive metabolism. Hence, current intensity is a direct evidence of electroactive metabolism. Therefore, once mature biofilm is ensured in all systems (week 10), the current intensity obtained in the polarized systems are a reflection of the activity catalyzed by the bacteria.

Anode-based systems showed a substantially decreasing activity from less than 1 mA to minimum values. On the other hand, cathode-based systems show much higher currents in a constant manner (2.5-5 mA), indicating activity that is maintained during this period (Fig 4.15). This is consistent with the variations of the contaminant concentration, since cathode-based systems show a higher HCH removal due to the electroactive microorganism activity.

Snorkel-based systems have no current recording, as they are non-polarized systems, but their degradation may be due to the fact that they act as anode and cathode simultaneously through spontaneous reactions, driven by natural redox gradient in the soil. This is why snorkel-based systems are able to improve degradation compared to anode-based systems but it is still worse than cathode-based systems, due to electron donor limitations in natural system.

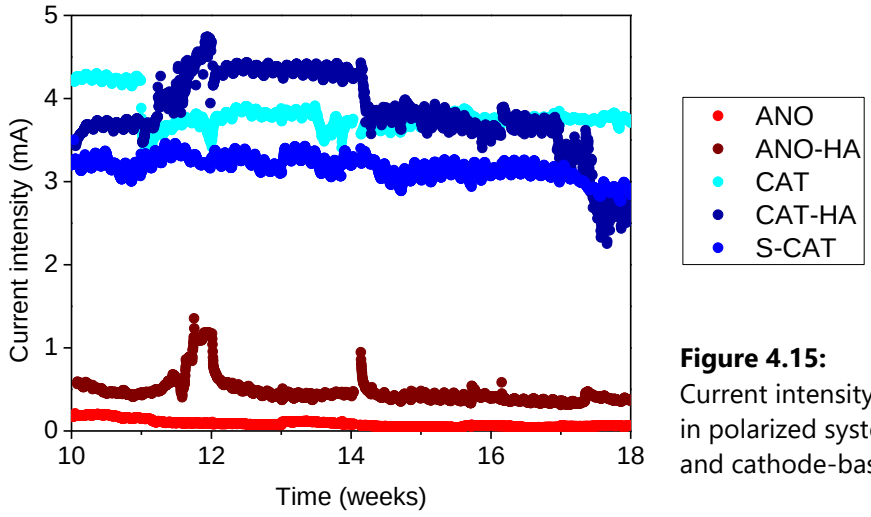


Figure 4.15: Current intensity production in polarized systems (anode and cathode-based systems).

3.8. Evolution of electrode potential during electrobioremediation treatments.

The electrobioremediation task was performed at the polluted site in a remote area so the electrode potential from different configurations was monitored monthly during the course of the assay. All cathode-based configurations (CAT, CAT-HA and S-CAT) kept an electrode potential of ca. -1.5 V vs. Ag/AgCl throughout the whole treatment period (Fig. 4.16). The reducing potential in the cathode systems, directly or catalyzed by bacteria, could i) remove chlorine atoms from the organic molecules as lindane, ii) generate hydrogen gas and iii) facilitate the precipitation of carbonate and other insoluble salts that may create a functionalizing crust on the electrodes [Chen et al., 2009; Komaba et al., 2008]. In contrast, electrode potential in anode-based configurations showed values of ca. 4 V. Such high oxidative value was recorded probably due to the reference location (water overlaying the sediment) a few cm from working electrode. The true value of the anodic potential should be certainly lower if reference electrode would be in the vicinity of buried working electrode.

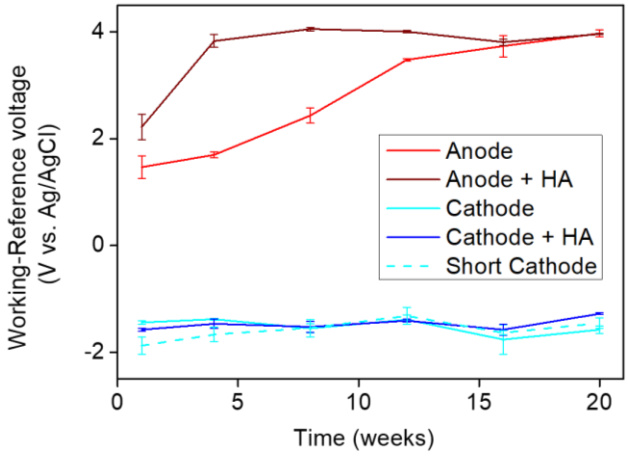


Figure 4.16: Working electrode potential for different electrochemical configuration.

3.9. Cyclic voltammetry reveals microorganisms interaction

The different evolutions of the electrodes and their relationship with the sediment were revealed through cyclic voltammetry (CVs) analysis (Fig. 4.17). Cathode-based configurations generated wide voltammograms, all with a similar shape. However, the presence of humic acids triggered the production of current. The width of the voltammograms in cathode-based configurations may correspond to an increase of microbial electroactivity. Previous studies have also demonstrated a cathodic capacity increase in interaction with electroactive microorganism biomass [Annie Modestra and Venkata Mohan, 2019]. This interaction coincides with their higher current production and subsequent HCH remediation.

On the contrary, anode-based configurations showed the voltammograms more similar to the initial sediment, indicating lower microorganisms proliferation and highlighting the possibility of a noticeable ohmic loss. That the reason because the anode-based systems flowed lower intensity current and, consequently, degraded less HCH.

Finally, snorkel-based configuration showed more electrochemical interaction than the previous ones, appearing an oxidation peak (-0.1 at 1 mV/s and 0.2 at 10 mV/s). These interactions could be caused by biomass apparition [Smith et al., 2015; Vidic and Manzano, 2021]. Snorkel could have promoted more microorganism biomass proliferation than anode and cathode, while cathode promoted more abundance of electroactive microorganisms, but less biomass generation. These results are consistent with the microbial population analysis, where polarized systems (anode and cathode-based) showed electroactive microorganisms abundance higher than snorkel.

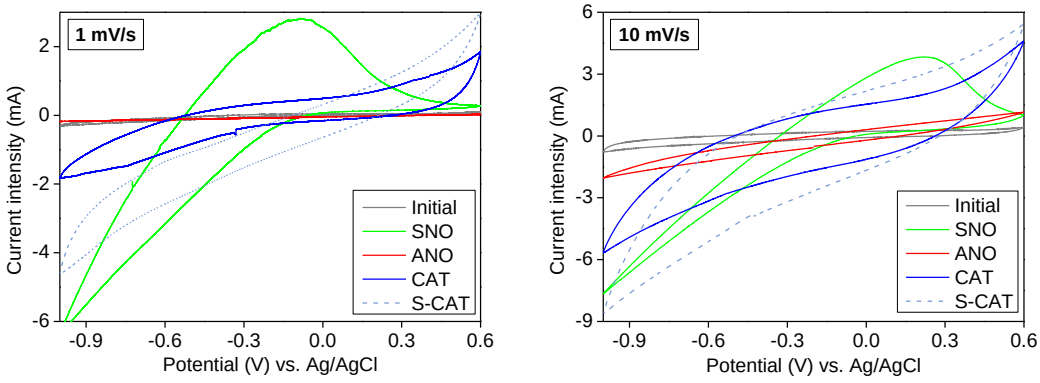


Figure 4.17: Working electrode voltammograms at 1 and 10 mV/s. Scan rate from -1 to 0.6 V.

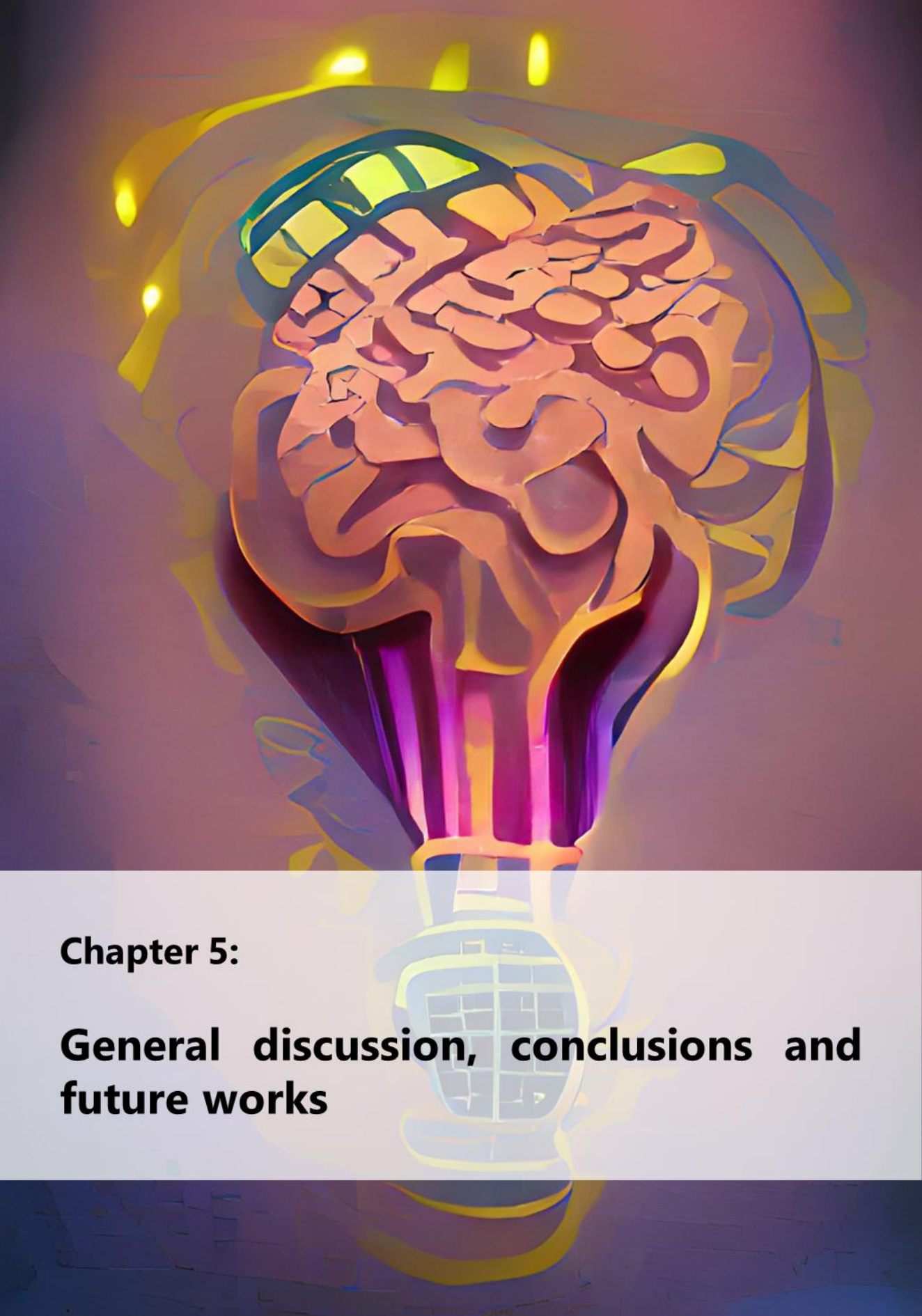
4. Conclusions

Different electrobioremediation strategies for cleaning up a real sediment polluted with lindane were tested. The results demonstrate that HCH degradation is certainly feasible under cathode-based configurations capable of removing 75% of Total HCH in just 10 weeks. In addition, performance on such configuration was slightly enhanced to 75% in presence of humic acids. On the other hand, anode systems only showed some degradation of Total HCH when humic acids were added, but not in the unamended system.

Removal of independent HCH isomers differs slightly from Total HCH. The cathode-based systems degrade up to 97% of α-HCH while β-HCH, the most recalcitrant isomer, was only partially removed. The concentration of γ-HCH isomer, pure lindane, decreased in all systems, including the electrode-free control sediment. Finally, the δ- and ε-HCH isomers, minority isomers, were degraded mainly by cathode-based configurations.

Nevertheless, phytoxicity analysis revealed a true remediation task since 81% of *Sorghum saccharatum* seed were germinated in comparison with 17% from polluted sediment.

Electrodes also revealed an impact for selecting specific microbial communities like *Desulfosporosinus* and *Dethiobacter* genera under cathode-based configurations. *Geobacter* was also detected in anode-based and humic acid supplemented configurations although no correlation was found with lindane removal configurations. The electroactivity of these microorganisms were confirmed by the current intensity and the voltammograms and is finally subsequent of the HCH degradation.



Chapter 5:

General discussion, conclusions and future works

Chapter 5: General discussion, conclusions and future works.

1. General discussion and conclusions

The main objective of this thesis was to evaluate electrobioremediation as main strategy to clean-up polluted soils but also to monitor contamination in groundwater. Electrons interchange associated to microbial remediation, through oxidations and reductions reactions, can be interpreted as a signal for the presence of certain pollutants so biosensing actions can be designed. Electrobioremediation, as tool for removing organic pollutants from soil, can be properly enhanced using the electrodes as electron donor or acceptors according to the nature of the contaminant. This work explores systems alternative to conventional ones to precisely detect and remediate environments polluted by aromatic hydrocarbon like BTEX or agrochemicals like lindane. We have presented the final considerations of this thesis in question-answer mode.

1.1. How to detect contaminants in groundwater by means of electroactive bacteria?

Electroactive microorganisms or microorganisms directly associated with them (Direct Interspecies Electron Tranfer, DIET) degrade pollutants generating or consuming electrons that can be harvested. [Prévoteau and Rabaey, 2017]. In fact, the electric current is a kinetic measurement related to the concentration of the contaminant, so microbial electrochemical cells can be designed to be in fact microbial electrochemical sensors. Typically, such microbial electrochemical sensors have been widely developed either under i) microbial fuel-cell (MFC) configuration [Chouler et al., 2018; Cui et al., 2019; Di Lorenzo et al., 2014; Jiang et al., 2018b; W. Liu et al., 2019; Nandimandalam and Gude, 2019b], or ii) under microbial electrolysis-cell (MEC) [Adekunle et al., 2019; Hua et al., 2019]. Moreover, the use of genetic engineered strain of *Geobacter* to condition the production of electricity to a regulatory circuit is certainly a possibility [Ueki and Lovley, 2010] and, more recently, *E. coli* was used as chassis to detect thiosulfate using an abiotic electrochemical reaction [Atkinson et al., 2022].

1.1.1. How can we detect BTEX and other petroleum-derived compounds?

The degradation pathways of petroleum-derived compounds follow a similar pattern: most of the pathways described are oxidative. Therefore, in Chapter 1, oxidizing bioelectrochemical reactions are enhanced to promote the degradation of BTEX, ETBE and kerosene and the subsequent increase in current intensity. That is, these compounds are bioelectrochemically oxidized to achieve an amperometric signal. Additionally, some of these compounds could be expected to generate amperometric signal through reduction reactions, as in the case of 1,4-benzoquinone, a BTEX degradation by-product, for which reductive pathway has been tested [Cesarino et al., 2012]. These techniques can be combined to design more accurate sensors in the future.

In contrast, in the case of vinylcyclohexene no current was detected. This compound has no known degradation pathway; therefore, two options can be evaluated: either it cannot be biologically degraded and therefore cannot generate a bioelectrochemical signal, or the microorganisms that are potentially capable of performing this bioelectrochemical degradation are not found in our microbial electrochemical sensors. To further study detection of this compound by this method, it would be necessary to find the microorganism capable of degrading it and attaching it to our device.

1.1.2. How can we detect lindane?

The degradation of halogenated compounds, in contrast to petroleum-derived compounds, usually occurs via reductive pathways. Therefore, we tested whether the bioelectrochemical reduction of lindane generates an amperometric signal (in chapter 1) and we actually confirmed that this degradation pathway was the optimal one in our electrobioremediation strategies (chapters 2 and 3). In order to have a proper correlation between current consumption and lindane reduction it is mandatory to have accurate knowledge of the groundwater composition to discard reduction of alternative electron acceptors like oxygen, nitrate, etc.

In addition to amperometric techniques, microbial electrochemical sensors have proven to be useful through other electrochemical techniques such as voltammetry, potentiometry or conductimetry that could improve or refine the sensors designed in this thesis.

1.2. Which polarization configurations in electrobioremediation allow degradation of lindane and isomers?

Degradation of halogenated compounds usually occurs via reductive pathways [Smidt and de Vos, 2004]. However, the aerobic route of lindane degradation, which contains oxidations but no reductions among the first steps, has been extensively studied in comparison with the anaerobic ones [Kumar and Pannu, 2018; W. Zhang et al., 2020]. This led to the following question: what pathway should be activated to degrade lindane?

Comparative experiments between reductions and oxidations of lindane-contaminated soils and sediments have shown in all cases that lindane degradation is improved under reductive conditions (Chapters 3 and 4).

However, the ring cleavage and subsequent reactions, requires from oxidative reaction. Therefore, it is worthwhile to explore combined degradations in which the cathode-anode is reversed or the cathode is switched on-off with a known frequency. Although the test performed in Chapter 3 did not achieve an increase in degradation after following such strategy other studies reporting alternative use of anode-cathode indicate that different frequencies in polarity could optimize lindane removal [Hou et al., 2022].

On the other hand, some of the lindane isomers appear to be degraded under different redox conditions. β-HCH (the most recalcitrant isomer) in Chapter 3, needed oxidation conditions (chapter 3) while in those *in-situ* electrobioremediation assays (Chapter 4) was degraded under reduction conditions. So in the case of specific isomers, more tests comparing oxidative and reductive pathways should be performed to confirm how their electrobioremediation can be eventually enhanced.

Therefore, lindane electrobioremediation efforts should be driven to cathode direction. Other strategies as combination cathode-anode could improve lindane and HCH isomers removal.

1.3. Does the addition of amendments enhance the electrobioremediation of lindane?

In many cases, bioremediation is enhanced or stimulated by increasing the amount of nutrients [Villalba Primitz et al., 2021], modifying the pH [J. Zhang et al., 2020], or adding co-substrates [Bianco et al., 2020] to increase the degradation of the target compound [Cao et al., 2016]. In the case of electrobioremediation, electroactive microorganisms can be additionally stimulated by adding redox mediators [M. Chen et al., 2020; Lovley, 2000; Mazarji et al., 2020; Y. Zhang et al., 2020]. AQDS, a humic acid analogue, has been successfully used in electrobioremediation systems for organochlorine compounds [Aulenta et al., 2010]. The addition of humic acids increased the degradation of lindane and isomers, especially in the reductive treatment with cathodes (the most effective treatment in chapter 4).

We also tested the addition of fertilizer as multi-nutrient amendment to increase overall microbiological activity. However, this amendment did not show a favorable effect on lindane degradation.

Therefore, other redox-mediator amendments, such as flavins or sulfur, should be considered to promote reductive lindane degradation. Moreover, different strategies such as co-substrate or surfactant additions could be further tested.

1.4. What is the optimal design of an electrobioremediation system?

Advances in electrobioremediation designs are mainly based on increasing the number of anodes or implementing cylindrical electrodes to increase the volume of soil affected (the cylinder is the geometric figure with an optima volume/surface ratio). In Chapter 3, conventional flat electrodes typically used by other authors, were replaced by cylindrical shaped elements to maximize the volume/surface ratio. The use of such elements enhanced lindane degradation. Meanwhile, in Chapter 4, we explored the surface ratio for anode/cathode. Actually, electrobioremediation resulted more effective when anode and cathode were implemented with the same surface (S-CAT in chapter 4). Total HCH removal obtained were >75% in cathodic configurations while electrode-free control stayed in the same concentration. This means that cylindrical devices and the relation between electrodes should be further studied.

In addition, devices were optimized depending on the contaminated matrix. In the case of a flooded soil or sediment, it was confirmed that a cylindrical electrode would work.

However, when dealing with a non-flooded soil, the optimization would start by maintaining minimum and constant moisture. Based on previous studies in Bioe group ([Domínguez-Garay and Esteve-Núñez, 2018), a system with an out-of-soil electrode separated from the soil by a conical ceramic barrier allows to operate bioelectrochemcial systems in non-flooded soils. This system was reported to be efficient for atrazine removal [Domínguez-Garay and Esteve-Núñez, 2018]. In the current thesis we confirmed its impact for remediating lindane polluted sites. Thus, it was demonstrated that minimum moisture (<16% in all systems) was sufficient to perform electrobioremediation treatments. This moisture was enough for ions mobility from treated soil and through ceramic barrier. The ceramic barrier allowed indeed the ions transfer between anolyte and catholyte.

On the other hand, our non-flooded system was evaluated far-away from electrodes (until 50 mm). Previous studies analyze area of influence of electrodes [Tucci et al., 2021b] because of its importance on scaling-up, and this study have revealed how the electrode impact in our system reached more than 50 mm.

1.5. How does the electrode evolve during electrobioremediation?

The electrodes can drive different reactions depending on the chemical nature of the electrolyte. If the conductivity is high, the charge transfer between electrodes will be faster. On the contrary, in presence of a low conductivity medium, the resistance will limit the process. This difference was observed in chapter 3, where a medium without dissolved salts decreased the potential difference. In addition, reactions can vary over time as the reagent is depleted. In both Chapter 3 and Chapter 4 we observed how the electrode potentials vary until equilibrium was reached. In soil, anode potential stayed near to 2.5 V while cathode near to -2 V. In sediment, cathode potential stayed near to -2 V while anode differed in the system (2 V in lab system, in Chapter 3; 4 V in outdoor configurations, shown in Chapter 4).

In Chapter 4 our results revealed that the surface of the electrodes reacts differently depending on the polarization they have maintained (anode, cathode or null). At the cathodes the capacitance increases enormously, while the anodes became a pure resistor and the snorkels (null polarization) show some faradaic reactions.

1.6. What is the final redox state of the soil matrix after electrobioremediation?

The effect of the electrodes spreads beyond their own surface. In flooded soils or sediments, changes in the porewater (which is mobile) can be observed to analyze long-distance effects. In the polarized cases in Chapter 3, the pH and conductivity of the porewater increased. Such rise could be due to carbonate deposition by the cathode, which was confirmed by the increase in capacitance of cathode voltammetries in Chapter 4.

To study in more detail the effect of electrobioremediation on the soil or sediment, other porewater parameters such as organic matter, inorganic carbon or dissolved oxygen could be analyzed.

1.7. Did we really clean-up our lindane-polluted soil?

The vast majority of experiments devoted to remediate contaminated environments focus on the elimination (or just transformation) of the main pollutant. However, the by-products of the degradation reactions are sometimes equally or even more harmful [Götz et al., 2012]. To estimate the accuracy of the bioremediation task, some studies test the treated matrix through ecotoxicological analysis. In Chapter 4, we showed that the best ecotoxicity results for lindane-polluted soil electrobioremediated through a cathode design. The best result was obtained in the system with cathode surface was so extended as counter surface (81% germination vs. 19% in the control). This electrochemical strategy can be related to the chemical structure of lindane, and the need of reductive reactions for the cleavage of Cl-C bond [Quintero et al., 2005]. Thus, it seems reasonable to keep exploring biocathode-based strategies for remediating lindane polluted soils.

1.8. What is the effect of our electrobioremediation task on the natural bacterial community?

Electrobioremediation was reported to change the bacterial population in several studies [Holmes et al., 2004; Lu et al., 2014a]. In chapter 4 we reported a microbial community shift during the electrobioremediation process where, eventually, electroactive bacteria outcompete then natural system. Such electroactive populations were more abundant when redox mediator, as humic acids, was added as amendment. These populations were promoted depending on the polarization; anodophilic bacteria

such as *Geobacter* appeared on anodes and cathodophilic bacteria such as *Desulfosporosinus* and *Dethiobacter* on cathodes. We also observed how the microbial population of lindane degrading bacteria, such as *Desulfovibrio*, *Desulfuromonas* and *Flavobacterium* and aromatic-compound degrading bacteria, such as *Pseudomonas*, *Sphingomonas*, *Parcubacteria* or *Hydrogenophaga* were less abundant in the systems with low presence of lindane. Thus, certain bacterial abundance could be used as indicators of contamination, although this hypothesis should be further investigated.

The data collected here could be used in remediation through bioaugmentation by releasing specific bacteria or through combination of electrobioremediation and bioaugmentation by releasing electroactive bacteria. Knowing the bacterial population responsible of lindane biodegradation in a specific soil, we could isolate such microorganisms and eventually add them to the polluted soil as part of a bioaugmentation action.

2. General conclusions

- The microbial electrochemical sensor designed in this thesis allowed the detection of dissolved contaminants in groundwater by means of a 3-electrode system.
- BTEX, ETBE and complex mixtures such as kerosene were detected by developing an anodic electroactive biofilm.
- Electrobioremediation of lindane-contaminated soils and sediments was enhanced by electrodes. It was especially enhanced when the cathode acted as *in-situ* electron donor.
- HCH isomers were degraded under different conditions than lindane. α-HCH by cathodic, β-HCH by anodic, and δ-HCH and ε-HCH by cathodic and anodic configurations.
- Energy savings in the electrobioremediation systems slowed the treatment rate and polarity reversal did not improve the degradation efficiency of lindane.
- Our electrobioremediation system designed for non-flooded conditions were validated for lindane degradation. 98% of lindane removal was reached even at 50 mm from the electrode
- Humic acid amendment as a redox mediator improved the treatment and accelerated the bioelectrochemical processes.
- Soil toxicity for sorghum germination decreased in all the electrobioremediation treatments. Control system germinated 19% of planted seeds while the most efficient system (cathode and anode with equal surface area) achieved 81% germination.
- The bacterial community present at the end of the experiment confirmed the effect of electrobioremediation. Andophilic bacteria (*Geobacter*) appeared on the anodes, and on the cathodes, catodophilic bacteria (*Desulfosporosinus* and *Dethiobacter*).
- Lindane degrading bacteria (*Desulfovibrio*, *Desulfuromonas* and *Flavobacterium*) decreased in abundance in the cathode systems, probably because contaminant was already degraded.
- Aromatic degrading bacteria (*Pseudomonas*, *Sphingomonas*, *Parcubacteria* or *Hydrogenophaga*) increased their abundance in anodes.

3. Future works and recommendations

Results generated in this thesis allow us to recommend a number of future experiments. Microbial electrochemical sensors and electrobioremediation systems are non-optimized processes with opportunities for improvement. These opportunities require researching efforts in multiple disciplines such as biotechnology, geochemistry or electrochemistry.

3.1. To improve microbial electrochemical sensors

Results of microbial electrochemical sensors show that bioanodes are the most common way of degrading compounds [Yang et al., 2020]. However, understanding the potentials could be further explored. In the case of mixed cultures, different potentials could promote different metabolism bacteria activation; therefore, specific anode potentials used for each compound may allow developing high-specificity sensors.

Promoting not just oxidative potential but reductive ones by means of biocathodes could be useful in the case of a few targeted compounds [X. Wang et al., 2020a] as lindane.

Other techniques not tested in this thesis could also improve these processes. Different electrochemical techniques should be explored to improve the performance of microbial electrochemical sensors. Potentiometries [Liu et al., 2014], voltammetries [Timur et al., 2007b], conductimetries [Tekaya et al., 2014] and impedometries [López Rodriguez et al., 2015] have been successfully tested in other studies.

The biological component of the sensor also has great scope for improvement. Genetic modification of microorganisms enables the combination of actions present in different wild microorganisms occur in a sole modified organism. It can be used to combine pollutant degradation and current generation in the same organism. This technique directed at microbial electrochemical sensors may be used to design microorganisms that generate electricity (generate an electrical signal) while degrading the target compound [Awate et al., 2017]. Alternatively, the target compound could function as an activator of a process that enhances the electrical signal [Ueki et al., 2016]; in this case, biodegradation of target analyte is not necessary.

In addition, biofilm encapsulation can allow microorganisms to tolerate unfavorable conditions for long time [Estevez-Canales et al., 2018]. This technique allows an *ex-situ*

preparation of the sensor that could accelerate the start-up and increase the accuracy of the detection [Rawson et al., 1989]. Biofilm encapsulation, together with the process known as DIET, permits the design of encapsulation gels with microorganisms chosen *a la carte*. In this encapsulation, some microorganisms degrade the compound to simpler organic molecules and these molecules are used by electroactive microorganisms [Tucci et al., 2022].

3.2. To improve electrobioremediation systems

The strategies implemented during the thesis to increase the efficiency of electrobioremediation have been based on geometry modification, amendment additions and design developments for specific conditions. Electrode geometry was improved by the use of cylinders (the shape that optimizes the surface-electrode/volume-treated ratio). However, it would be worthwhile to study the second most studied modification, the increase of the bioelectrode surface area [Tucci et al., 2021b]. Several studies have proposed systems with increased anodic surface area to increase the remediation capacity of petroleum-derived compounds [Li et al., 2015; Zhang et al., 2015]. Increasing the bioelectrode surface area should be tested to increase the electrobioremediation of lindane.

Concerning the electrodes, the results of chapter 4 also showed that the anode/cathode surface ratio is important. Further experiments should be carried out to find the optimum ratio. Linked to this point, the distance between electrodes is also an important issue that could be studied.

In non-flooded soils, a system was configured in based of previous experiments of our group [Domínguez-Garay and Esteve-Núñez, 2018]. More investigations on the minimum moisture and the optimum moisture would be necessary. In addition, this system could be improved by testing new materials with higher permeability to increase the moisture. Another option to facilitate the degradation of the contaminant would be the insertion of ceramic barriers full of water surrounding the electrode to achieve more homogeneous moisture.

Polarization variations were studied in chapter 3 without favorable results. However, considering previous reports regarding lindane treatment [Hou et al., 2022], this strategy should be taken into account for future systems. Modifications in the frequency of changes would be desirable.

Distance at which the electrode exerts its effect is a parameter calculated in other studies [Tucci et al., 2021b]. It has been measured in the non-flooded system of chapter 3. In a scaling process, radius of influence could be relevant; therefore, it would be important to study over longer distances to find out the maximum remediation distance.

Of the two amendments tested in chapter 4, the fertilizer did not show positive results, while the humic acids increased the degradation capacity. This highlights the use of redox mediators to improve electrobioremediation systems. There are several redox mediators that could be studied to improve the system, such as flavins or sulfur. The concentration of these mediators is another point to be studied.

In addition, a detailed study of the by-products related lindane degradation would increase the knowledge of the degradation pathways.

Finally, it is important to remember that electrobioremediation is a bioremediation strategy, and as such, could be combined with other strategies such as nanoremediation or bioaugmentation. Electroactive biofilms could be encapsulated together with nanoparticles [Y. Liu et al., 2021] and used into a electrobioremedaition system.

3.3. To assess the electrobioremediation impact

Electrobioremediation affects more chemical, biological and physical parameters than just contaminant removal. To understand how and how much it affects we have studied the parameters separately.

In chapters 3 and 4 the electrode potential and current were monitored and voltammetric tests were performed. Voltammetry and monitoring could be performed more frequently to have a better follow-up of the electrode evolution. Moreover, other electrochemical tests could provide more detailed data. Impedometric tests allow further study of the electrical behavior of each component of the system. This allows us to detect process limiting points such as high electrode resistances or excessive anode-cathode distances.

Chapter 4 included an analysis of the bacterial population to elucidate the processes involved. However, an important part of the microbiome is the fungi. Degradation of

lindane has been demonstrated in fungi and yeasts [J. M. Saez et al., 2017]; therefore, to study the biodiversity of fungal population during treatment would be of interest.

On top of that macroscopic organisms are also important. Some macroscopic fungi can degrade lindane [Guillén-Jiménez et al., 2012], so it would be worthwhile to study their evolution during electrobioremediation. On the other hand, there are other organisms that do not degrade lindane but serve as indicators of soil health. Shorgum germination was studied in Chapter 4 to quantify soil health, but there are organisms that can act as bioreporters such as earthworms or insects. Counting these species would be another way to quantify soil health.

Modifications in the porewater were also studied in chapter 3. Further knowledge on the soil matrix or porewater would provide more information on the processes occurring. In future studies it would be advisable to analyze parameters such as nutrients (N, P, K), other ions relevant to lindane (Cl ions), changes in pH and salinity, organic matter in general and concrete forms (humic and fulvic extraction).

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Acknowledgement and foundations

We would like to express our heartfelt gratitude to the Governments of Madrid and Aragon from Spain, IMDEA Agua (IMDEA Water Institute) and the companies Talantia,S.L., Repsol, S.A. and Sociedad Aragonesa De Gestion Agroambiental S.L. (SARGA) for all the support received at different stages of the thesis.

This thesis has been directly founded by:

Program: "LAS AYUDAS PARA LA REALIZACIÓN DE DOCTORADOS INDUSTRIALES EN LA COMUNIDAD DE MADRID"
Title: Estrategias 3D de "cableado" redox en bacterias electroactivas para recuperar ambientes contaminados
ID: IND2017/AMB7703
Responsible Investigator: Esteve Núñez, Abraham
PhD Student: De Deus Villagra, Andrés
Organization: Universidad de Alcalá
Company: Nanoelectra, S.L.
Foundation: 130 700 €

Program: CONTRATOS DE INVESTIGACIÓN CON UNIVERSIDAD DE ALCALÁ (ART. 83)
Title: Viabilidad de la estimulación electroquímica de bacterias para la degradación de compuestos organoclorados en el subsuelo
ID: 2017/00365/001
Principal Investigator: BOLTES ESPÍNOLA, Ana Karina
Other Investigators: ESTEVE NÚÑEZ, Abraham
Start date: 01/11/2017
Finish date: 31/12/2017
Foundational Company: Talantia S.L.
Foundation: 16.637,50 €

Universidad de Alcalá

DEPARTAMENTO DE QUÍMICA ANALÍTICA, QUÍMICA FÍSICA E INGENIERÍA QUÍMICA