



M 2016

# **ABATEMENT OF CHLORINATED PESTICIDES (HEXACHLOROCYCLOHEXANES) BY ZERO VALENT IRON MICROPARTICLES**

**JOANA MARIA PARCHÃO OLIVEIRA**  
DISSERTAÇÃO DE MESTRADO APRESENTADA  
À FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO EM  
ENGENHARIA QUÍMICA



**Integrated Masters in Chemical Engineering**

***Abatement of Chlorinated Pesticides  
(Hexachlorocyclohexanes) by Zero Valent Iron  
Microparticles***

**Master Thesis**

of

**Joana Maria Parchão Oliveira**

**Developed in the scope of the curricular unit Dissertation**

Accomplished in

**Universidad Complutense Madrid**



Orientation in UCM: **Dr. Aurora Santos López**

**Dr. Sergio Rodriguez Vega**



**Department of Chemical Engineering**

**July of 2016**







## Acknowledgments

The realization of this thesis was performed in the INPROQUIMA group directed by Dr. Arturo Romero Salvador whom I thank for accepting me and for giving me the opportunity to work in such an academically supporting environment leading to an exciting experience abroad.

I would like to express my sincere gratitude to my thesis coordinator Dr. Aurora Santos López who not only was also responsible for my acceptance at INPROQUIMA, but included me into the group and spared no means into all the material and support necessary. Thank you for all the support shown, concern, knowledge sharing and for providing guidance over this internship.

I would like to thank my thesis coordinator Dr. Sergio Rodriguez Vega who was always ready to answer any question and facilitate their time to me whenever I needed to discuss something or needed help.

I am particularly grateful for the assistance of Dr. Carmen Domínguez Torre for the tireless support she provided. I am very grateful for her partnership in the past few months and I would like to thank her for all the concern, good advice, patience and motivation.

To all members of INPROQUIMA group and to my colleague, Eva, a huge thank you for all the help and companionship provided, creating a great work environment inside the laboratory.

To all my professors and colleagues at FEUP who were responsible for bringing me to this point in my studies. I would like to particularly mention Prof. Luís Miguel Madeira who encourages students to seek an academic experience abroad. He was responsible for most of my mobility process, being always available to answer my questions and concerned with the evolution of the project.

To all my friends who accompanied me along the last years and were always present when I needed to exchange ideas or talk about frustrations related to work. Thank you so much for all the support in my personal and academic life.

Finally, for the unconditionally support emotionally and financially, thank you to my family, specially my mother who is always present in any decision I make and my grandparents, Irene and António Parchão, who have always guided me closely and motivated academically, regardless the barriers imposed by age. I can never repay you enough for everything you have done for me.



## Abstract

Nowadays, society is liable for the consequences associated with the excesses in the past. The treatment and management of contaminated sites arising from the uncontrolled and unregulated release of toxic waste is a matter of great global impact. Hexachlorocyclohexane was one of the mostly used pesticides since World War II until the 1990s. This compound, constituted by different isomers, is considered a persistent organic pollutant. Consequently, their treatment is now regulated upon detection in industrial waste and contaminated soil or water. Therefore, there are several research projects promoting its degradation, among which is highlighted the reductive dechlorination using zero valent iron microparticles.

This dissertation was carried out to study the  $\alpha$ ,  $\beta$ ,  $\delta$  and  $\gamma$  hexachlorocyclohexane isomers dechlorination reaction using zero valent iron microparticles. Their reactivity order was defined, as well as the possible interference of four isomers coexisting in the same solution on its degradation. A stability test was carried out in order to determine whether these microparticles keep stable throughout its use, using the same iron particles in three consecutive reaction cycles, for each isomer separately.

According to each isomer behaviour,  $\gamma$ -hexachlorocyclohexane was selected to study the influence of operating conditions in the dechlorination reaction. Thereby, it was elaborated an analysis of the initial pollutant concentration effect on the reaction (0.5, 3 and 6 mg/L), followed by the influence study of using different iron concentrations (1, 5 and 10 g/L). In addition, the temperature influence was analysed (10, 20 and 30 °C). Afterwards, it was determined a kinetic model based on the study of the operating conditions influence in order to better understand the  $\gamma$  - hexachlorocyclohexane degradation process.

In an attempt to simulate a more realistic situation, a small study was developed based on the possible effect of the addition of anions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) and cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ ) in the degradation of  $\gamma$ -hexachlorocyclohexane. As in reality this treatment implementation is performed in continuous mode, it was designed a column where reactions occurred, attaining a degradation degree of this compound similarly to when comparing with the results obtained in batch mode. In addition, the microparticles stability and the effect of coexistence of isomers were also tested.

In general, the experiments have yielded consistent results in both operating modes, resulting in the presentation of an estimated dechlorination reaction pathway for  $\gamma$ -hexachlorocyclohexane.

**Keywords:** Hexachlorocyclohexane, Dechlorination, Reduction, ZVI Microparticles

---

## Resumo

Atualmente, a sociedade está sujeita às consequências associadas a excessos de outrora. Uma questão de grande impacto global é o tratamento e gestão de zonas contaminadas oriundas da libertação descontrolada e não regulamentada de resíduos tóxicos. Um dos pesticidas maioritariamente usado desde a segunda guerra mundial até aos anos 1990 foi o hexaclorociclohexano. Este composto, constituído por diferentes isómeros, é considerado um poluente orgânico persistente, estando regulamentado o seu tratamento para a sua presença em resíduos de industriais e em solos ou águas contaminadas. Consequentemente existem vários estudos para promover a sua degradação, dos quais se destaca a descloração redutiva por ação de partículas de ferro com valência zero.

Nesta dissertação foi realizado um estudo sobre a reação de descloração em descontínuo de hexachlorociclohexanos por ação de micropartículas de ferro com valência zero para degradar os isómeros  $\alpha$ ,  $\beta$ ,  $\delta$  e  $\gamma$  deste composto. Definiu-se a ordem de reatividade dos diferentes isómeros, assim como a possível interferência na sua degradação da coexistência de quatro isómeros na mesma solução. Um ensaio de estabilidade no qual se reutilizaram as mesmas partículas de ferro em três ciclos reativos consecutivos foi realizado, separadamente para cada isómero.

Tendo em conta o comportamento dos isómeros, foi selecionado o  $\gamma$ -hexaclorociclohexano para estudar a influência das condições de operação na reação de descloração. Procedeu-se então à análise do efeito relativo à concentração inicial de poluente (0.5, 3 e 6 mg/L), da influência do uso de diferentes concentrações de micropartículas de ferro (1, 5 e 10 g/L) e à da variação da temperatura (10, 20 e 30 °C). De forma a compreender melhor o processo de degradação do  $\gamma$ -hexaclorociclohexano, foi determinado um modelo cinético com base no estudo da variação de condições de operação.

Numa tentativa de aproximar o estudo de uma situação realista, foi elaborado um estudo superficial sobre o efeito da adição de aniões ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  e  $\text{Cl}^-$ ) e catiões ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  e  $\text{Na}^+$ ) na degradação do  $\gamma$ -hexaclorociclohexano. Uma vez que na realidade a aplicação deste tratamento é feita em modo contínuo, foi projetada uma coluna na qual se apurou a similaridade na eficácia de degradação deste composto relativamente ao testado em modo descontínuo. Foram também testados a estabilidade das micropartículas e o efeito da coexistência de isómeros.

As experiências realizadas permitiram obter resultados concordantes em ambos os modos de trabalho, resultando na apresentação da rota da reação de descloração de  $\gamma$ -hexaclorociclohexano estimada.

---

## Statement

I declare, under honour commitment, that the present work is original and all its non-original contributions are duly referenced with source identification.

*Jane Flávia Paes Oliveira*

*July 2016*

---



# Table of Contents

<b>1</b>	<b>Introduction.....</b>	<b>1</b>
1.1	Project’s motivation and relevance .....	1
1.2	Presentation of the Institucion.....	3
1.3	Labor Contributions .....	3
1.4	Thesis Layout .....	4
<b>2</b>	<b>State of the Art.....</b>	<b>5</b>
2.1	Water and Soil Treatments.....	5
2.2	Degradation of HCHs by Chemical Processes .....	6
2.3	Use of Zero Valent Iron Particles .....	8
2.4	Application on real situations .....	9
2.5	Previous work on Reduction of HCHs by mZVI .....	10
<b>3</b>	<b>Technical Description .....</b>	<b>11</b>
3.1	Reagents .....	11
3.2	Experimental Procedure.....	13
3.2.1	Batch Reactions .....	13
3.2.2	Fixed Bed Column Reactions .....	14
3.3	Analytical Methods.....	16
3.3.1	Gas Chromatography - Mass Spectrometry (GC-MS).....	16
3.3.2	Ion Chromatography (IC).....	16
3.3.3	High Performance Liquid Chromatography (HPLC).....	17
3.3.4	pH.....	17
<b>4</b>	<b>Results and Discussion .....</b>	<b>18</b>
4.1	HCH’s dechlorination reaction .....	18
4.1.1	Reactivity of HCH isomers .....	18
4.1.2	Iron Microparticles Stability .....	19
4.1.3	Influence of wastewater composition .....	20
4.2	Influence of Operation Conditions.....	21

4.2.1	Concentration of pollutant .....	21
4.2.2	Concentration of Iron Microparticles .....	22
4.2.3	Temperature .....	23
<b>4.3</b>	<b>Kinetic Model .....</b>	<b>24</b>
<b>4.4</b>	<b>Effects of different ions on lindane degradation .....</b>	<b>28</b>
4.4.1	Effects of anions presence .....	30
4.4.2	Effects of cations presence .....	32
<b>4.5</b>	<b>Application to Fixed Bed Reaction Column .....</b>	<b>33</b>
4.5.1	Comparison between Batch and Column: Lindane degradation .....	33
4.5.2	Long-term Stability Study .....	34
4.5.3	Mixture of $\gamma$ , $\alpha$ , $\beta$ , $\delta$ - HCH isomers in Column.....	35
<b>4.6</b>	<b>Reaction Pathway .....</b>	<b>36</b>
<b>5</b>	<b>Conclusions .....</b>	<b>39</b>
5.1	Main Conclusions .....	39
5.2	Limitations and Future Work .....	40
<b>Annex I.</b>	<b>Calibrations .....</b>	<b>46</b>
	HCHs.....	46
	Chloride.....	47
	Benzene .....	49
<b>Annex II.</b>	<b>Strategies to enhance <math>\beta</math>-HCH decay .....</b>	<b>51</b>
	Increase of Reaction Temperature .....	51
	Increase of Reaction Time .....	51

## List of Figures

Figure 1: Estimate of the quantity of HCH isomers deposited or stored as waste in different countries, based on a questionnaire process [6].	3
Figure 2: Representation of ZVI applications in real situations by a) direct injection [40] and b) PRB [42].	9
Figure 3: Theoretical dechlorination reaction of HCH using $Fe^0$ .	10
Figure 4: Scheme of the experimental procedure followed in batch experiments.	13
Figure 5: Scheme of the experimental procedure used in column experiments.	15
Figure 6: Reactivity order for HCHs isomers at 72 h reaction time ( $T=20^\circ C$ , $C_{Fe}=5\text{ g/L}$ , $C_{HCH0}=0.5\text{ mg/L}$ , $pH_0=7$ ; R1, R4, R7 and R10).	18
Figure 7: Degradation of HCH isomers in three successive runs ( $T=20^\circ$ , $C_{Fe}=5\text{ g/L}$ , $C_{HCH0}=0.5\text{ mg/L}$ , $pH_0=7$ ; R1-R12).	19
Figure 8: Degradation of isomers when in a mixture or isolated ( $T=20^\circ C$ , $C_{Fe}=5\text{ g/L}$ , $C_{HCH0}=0.5\text{ mg/L}$ , $pH_0=7$ ; R1, R4, R7, R10 and R13).	21
Figure 9 - Lindane concentration evolution (a) and $Cl^-$ balance (b) in the presence of mZVI ( $T=20^\circ C$ , $pH_0=7$ , $C_{Fe}=5\text{ g/L}$ ) at different initial concentrations of lindane (reactions R1, R14 and R15).	22
Figure 10: Lindane concentration evolution (a) and $Cl^-$ balance (b) in the presence of mZVI ( $T=20^\circ C$ , $pH_0=7$ , $C_{lindane0}=6\text{ mg/L}$ ) at different iron concentrations (reactions R15, R18 and R19).	23
Figure 11: Lindane concentration evolution in the presence of mZVI ( $C_{Fe}=5\text{ g/L}$ , $pH_0=7$ , $C_{lindane0}=6\text{ mg/L}$ ) at different temperatures (reactions R15-R17).	24
Figure 12: Apparent kinetic constants for different ZVI concentrations (R15, R18, R19).	25
Figure 13: Determination of constant $n$ by linear regression between $\ln(k_{app})$ and $\ln(C_{Fe})$ .	26
Figure 14: Apparent kinetic constants for different Temperatures with constant $C_{Fe}$ and $C_{lindane0}$ (reactions R15-R17).	27
Figure 16: Representation of Arrhenius Plot.	27
Figure 17: Comparison between the data predicted by the model and the measured data for lindane concentration at the different operation conditions tested.	28
Figure 18: Effect of ions presence on initial and final pH in the lindane dechlorination reaction at $T=20^\circ C$ , $C_{Fe}=5\text{ g/L}$ and $C_{lindane0}=6\text{ mg/L}$ (R15, R20-R38).	30
Figure 19: Effect of anions presence on the lindane dechlorination reaction in terms of $X_{\gamma\text{-HCH}}$ and $Cl^-/Cl_{max}$ at $T=20^\circ C$ , $C_{Fe}=5\text{ g/L}$ and $C_{lindane0}=6\text{ mg/L}$ (R15, R20-R29).	31

Figure 20: Effect of anions on the lindane dechlorination reaction in terms of  $X_{\gamma\text{-HCH}}$  and  $Cl^-/Cl_{\text{max}}$  at  $T=20^\circ\text{C}$ ,  $C_{\text{Fe}}=5\text{ g/L}$  and  $C_{\text{lindane0}} = 6\text{ mg/L}$  (R15, R24-R26 and R30-R35). ..... 32

Figure 21: Lindane concentration evaluation in terms of  $1-X$  and  $Cl^-/Cl_{\text{max}}$  ( $T=20^\circ\text{C}$ ,  $C_{\text{lindane0}} = 6\text{ mg/L}$  and  $\text{pH}_0=7$ ) for Batch and Column (R15 and RC1). ..... 34

Figure 22: Lindane degradation reaction in column ( $T=20^\circ\text{C}$ ,  $C_{\text{lindane0}} = 6\text{ mg/L}$  and  $\text{pH}_0=7$ ) for different  $W/Q_i$  values during 10 days (RC2). ..... 35

Figure 23: Degradation of different concentrations of HCH isomers in Batch and Column in terms of  $Cl^-/Cl_{\text{max}}$  at  $20^\circ\text{C}$  (R13, RC3 and RC4). ..... 36

Figure 24: Concentration evolution for different compounds involved in the dechlorination of lindane ( $T = 20^\circ\text{C}$ ,  $C_{\text{lindane0}} = 6\text{ mg/L}$ ,  $C_{\text{Fe}} = 5\text{ g/L}$  and  $\text{pH}_0 = 7$ ) in column (RC1). ..... 37

Figure 25: Evolution for different compounds involved in the dechlorination of lindane ( $T = 20^\circ\text{C}$ ,  $C_{\text{lindane0}} = 6\text{ mg/L}$ ,  $C_{\text{Fe}} = 5\text{ g/L}$  and  $\text{pH}_0 = 7$ ) in terms of  $X$ ,  $Cl^-/Cl_{\text{max}}$ ,  $B/B_{\text{max}}$  (RC1). ..... 37

Figure 26: Proposed reaction pathway for degradation of lindane in the presence of zero valent iron microparticles. .... 38

## List of Figures - Annex I

Figure A I 1: Chromatogram obtained by GC -MS for all HCH isomers and calibration curves. .... 47

Figure A I 2: Chlorides calibration curve. .... 48

Figure A I 3: Calibration curve for low concentration of chlorides. .... 48

Figure A I 4: Calibration curve for high concentration of chlorides. .... 49

Figure A I 5: Benzene calibration curve. .... 49

Figure A I 6: Calibration curve for low concentration of benzene. .... 50

## List of Figures - Annex II

Figure A II 1: Degradation of  $0.5\text{ mg/L}$  of  $\beta\text{-HCH}$  in terms of  $1-X$  at different temperatures. .... 51

Figure A II 2: Degradation of  $0.5\text{ mg/L}$  of  $\beta\text{-HCH}$  in terms of  $1-X$  for longer reaction time. .... 52

## List of Tables

<i>Table 1: Isomeric conformation and average composition of technical HCH. ....</i>	<i>2</i>
<i>Table 2: Comparison between mZVI and nZVI. ....</i>	<i>8</i>
<i>Table 3: Properties of Zero Valent Iron microparticles used in the project. ....</i>	<i>10</i>
<i>Table 4: Chemicals used during experimentation. ....</i>	<i>12</i>
<i>Table 5: Objective and experimental conditions of reaction runs carried out in batch mode. ....</i>	<i>14</i>
<i>Table 6: Objective and experimental conditions of the reaction runs carried out in continuous mode</i>	<i>15</i>
<i>Table 7: Experimental conditions of reaction runs carried out in Batch in order to study the presence of different ions. ....</i>	<i>29</i>

## Notation and Glossary

B	Benzene	
C	Concentration	mg/L
Eq	Equation	
k	Rate Constant	$h^{-1}$
nd	Not Defined	
T	Temperature	$^{\circ}C$
t	Time	h
w	Rotation per minute	rpm
r	Radius	
S	Superficial Area	
X	Conversion	

### *Greek Letters*

$\alpha$	alpha HCH isomer
$\beta$	beta HCH isomer
$\emptyset$	Diameter
$\varepsilon$	Porosity
$\delta$	delta HCH isomer
$\gamma$	gamma HCH isomer
$\rho$	Density

### *Indexes*

0	Initial value
app	Apparent
f	Final value
max	Maximum value possible to obtain
p	Pore

### *Listo of Acronyms*

AOP	Advanced Oxidation Process
ARP	Advanced Reduction Process
ATSDR	Agency for Toxic Substances and Disease Registry
DNAPL	Dense Non-Aqueous Phase Liquids
EFSA	European Food Safety Authority

EPA	US Environmental Protection Agency
FAO	Food and Agriculture Organization
GC-MS	Gas Chromatography - Mass Spectrometry
HCH	Hexachlorocyclohexane
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ISCO	<i>In Situ</i> Chemical Oxidation
ISCR	<i>In Situ</i> Chemical Reduction
ITRC	<i>Interstate Technology &amp; Regulatory Council</i>
mZVI	Micro-scale Zero Valent Iron particles
MW	Molecular Weight
nZVI	Nano-scale Zero Valent Iron Particles
POP	Persistent Organic Pollutant
PRB	Permeable Reactive Barrier
SPME	Solid Phase Micro Extraction
TOS	Time on Stream
UV	Ultraviolet Radiation
UNEP	United Nations Environment Programme
WHO	World Health Organization
ZVI	Zero Valent Iron



# 1 Introduction

## 1.1 Project's motivation and relevance

In our society, for a long time, it has been normal to resort to the use of pesticides to control insect pests. Ever since society began to develop industrially and scientifically this use has become a global environmental and human health concern, leading to the need for regulatory agencies to control the overuse of pesticides [1].

The Food and Agriculture Organization (FAO) defined pesticide as a substance or mixture of substances meant for preventing, destroying or controlling any pest [2]. It can be a chemical or biological agent and despite their benefits, there are a few drawbacks such as potential toxicity to humans and other species. The risk of a pesticide depends on two things: exposure and toxicity. The exposure relates to the amount that gets on the human/animal body, or the amount that is released into the environment and the toxicity is a measure of how poisonous it is [3].

In 2006 and 2007, the world used approximately 2.4 megatons of pesticides, with herbicides constituting the biggest part of the world pesticide use at 40%, followed by insecticides (17%) and fungicides (10%) [4].

Of all types of pesticides, insecticides are the ones with the largest potential to change the environment where they are introduced in. These are classified based on their structure and mode of action, being one of the most well-known types the organochlorines. These, as is implicit, consist in chlorinated hydrocarbons [5].

Hexachlorocyclohexanes (HCH) were one of the most extensively used organochlorine pesticides worldwide, produced mostly after the Second World War until the 1990s. This pesticide, has been used both as technical HCH (a mixture of all its isomers) or as Lindane (isomer  $\gamma$ -HCH) [6]. HCHs were first prepared by Michael Faraday in 1825 by adding chlorine to benzene in the presence of UV resulting in an isomeric mixture consisting of five major stable isomers [7].

Depending on the orientation of the chlorine atoms, whether being axial (a) or equatorial (e), these isomers are named  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ - and  $\epsilon$ -HCH. The average composition of technical HCH along with the conformation of the different isomers is presented in Table 1 [8]. Due to its different conformations, each isomer has slightly different physical and chemical properties, excluding solubility that is very low for all of them in water [9].

*Table 1: Isomeric conformation and average composition of technical HCH.*

Isomer	Conformation	Percentage
$\alpha$ -HCH	aaeeee	65 - 70
$\beta$ -HCH	eeeeee	7 - 10
$\delta$ -HCH	aeeeee	6 - 10
$\varepsilon$ -HCH	aeaeae	1 - 2
$\gamma$ -HCH	aaaeae	14 - 15

Of all the HCHs isomers,  $\gamma$ -HCH presents the highest insecticidal properties. Therefore, in the 1950s some companies began to isolate this active ingredient until they achieved a purity of 99% for commercial purposes, identifying it as Lindane [10]. The purification process of this isomer from the technical mixture evolves multiple steps thereby increasing its production cost. Either companies choose to use the concentrated  $\gamma$ -HCH or the technical HCH mixture, about 85% of the product obtained throughout the process represents other isomers without insecticide activity that can be considered as by-products of Lindane production [11]. Normally these by-products became hazardous waste, which is very concerning since for each tonne of Lindane produced it is generated about 8 - 12 tonnes of other isomers [6].

Is estimated that between 4 and 7 million tonnes of wastes of toxic, persistent and bioaccumulative residues (largely consisting of  $\alpha$  and  $\beta$ -HCH) have been produced and discarded around the globe during the 60 years of Lindane production. These residues tend to accumulate in both soils, contaminating plants and consequently entering the animal feed chain, and water. They also contaminate the air, which is a concerning aspect as it serves as means of transport for the contaminants from stockpiles of waste to other places [10].

The peak production of Lindane occurred in the 1960s and the early 1970s and, although its use had stopped in several European countries by the 1970s, the largest share of its use and production was within Europe (representing approximately 63% of the total global, Figure 1) [6]. Most nations have banned the use of this pesticide over the years, except India that continued producing it until 2010 under the pretext of using Lindane for pharmaceutical purposes to control malaria [11].

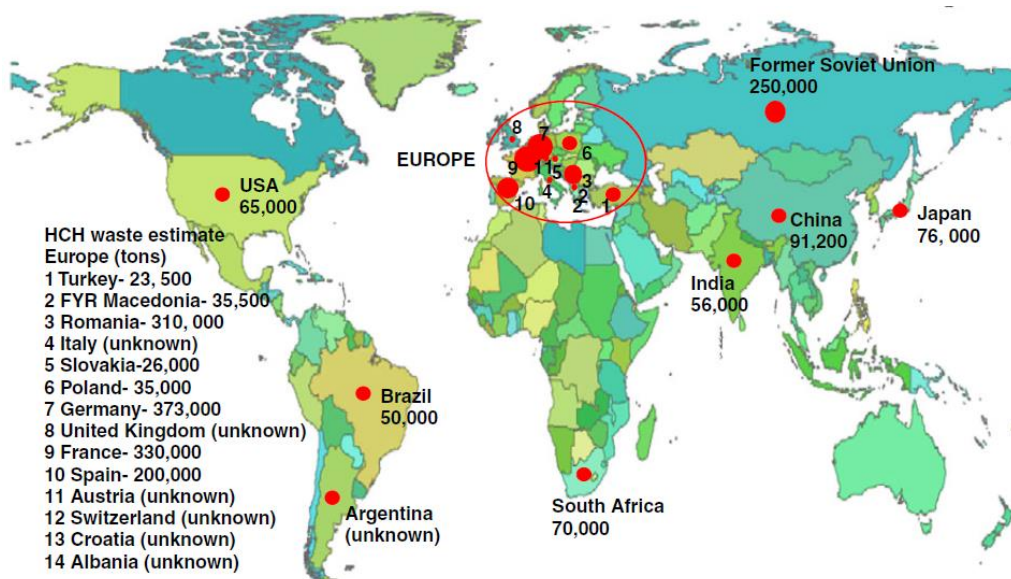


Figure 1: Estimate of the quantity of HCH isomers deposited or stored as waste in different countries, based on a questionnaire process [6].

Lindane and other isomers, especially the  $\alpha$ - and  $\beta$ -HCH, have carcinogenic, persistent, bioaccumulative and endocrine disrupting properties [12, 13]. Due to this and to its excessive use over several years, Lindane has become a heavily studied substance and has been highlighted for regulatory intervention in the early 2000s, leading to a proposal to frame it and its major isomers in the Stockholm Convention Persistent Organic Pollutant (POPs) list [13]. In 2009 Lindane,  $\alpha$ - and  $\beta$ -HCH were accepted in the 4th meeting of the Conference for inclusion in the Stockholm Convention POPs list [14, 15], creating a global obligation to find ways to control and eliminate these contaminants.

## 1.2 Presentation of the Institution

INPROQUIMA group is integrated in the Chemical Engineering Department of Universidad Complutense of Madrid and focuses its activities towards sustainable development research. The researching lines addressed by this group are related to industrial and environmental processes, in order to improve the quality of products, the energy balance, the process safety and environmental concerns.

## 1.3 Labor Contributions

One of the group's researching line is the treatment of waters containing organic contaminants, and currently new strategies are being developed for the treatment of water contaminated by HCHs. The work in this thesis was inserted in the ongoing investigation,

helped in its progress and in the preparation of a scientific paper. The behaviour of the different isomers of this contaminant had been studied, as well as the stability of the iron particles preselected for the reaction. In addition, the experiments were updated from batch to column bringing the study to more realistic situations. It was also developed a kinetic model and estimated the reaction route.

## 1.4 Thesis Layout

This thesis is divided into five distinct chapters beginning with this introductory chapter, where a general perspective of the motivation and research questions underlying this work are presented. It is presented the pesticide in study and is explained the importance of finding an effective procedure to eradicate it.

The following chapter presents the state of the art, containing the fundamentals required to understand the methods most commonly used to treat this type of contaminant as well as its applications to real situations. The developed project is contextualized in the work carried out by the research group and the assumptions made that led to choosing the techniques and materials used are explained.

The third part of this document presents the technical description in which the used reagents and materials are discriminated. All the procedures performed throughout the project and analytical methods applied are described.

In Chapter 4 all results obtained, by applying the methods described in the previous chapter, are presented and discussed. Initially is approached the study of the dechlorination reaction of HCHs, followed by an analysis of the effect of changing some operating parameters. It is determined the kinetic model for the study conducted previously and then examined the effect of the presence of salts in solution. The conducted study is also applied to a fixed bed reaction column to approximate the existing conditions to real environments. Finally, based on the elaborated work it is estimated the route of HCHs degradation reaction.

In the final chapter, the main conclusions, along with comments on the limitations of this work and suggestions for future work are presented.

## 2 State of the Art

### 2.1 Water and Soil Treatments

The composition of HCH isomers around the world is variable, however its higher concentrations were detected in the northern hemisphere as expected since the major producers of HCH are located there [16]. Although HCHs have been deposited in stockpiles, their relatively high volatility has led to global transport even into outlying locations such as the Arctic. This explains why HCHs can be detected in all environmental compartments such as water, soil, air or animals, and why it is important to study ways to eradicate these contaminants from both water and soil (where they mostly tend to deposit) [10].

Wastewaters can be composed of a very diverse mixture of compounds, largely dependent on what type of industry is creating the waste stream. Its treatment should begin at the source, keeping the contaminant's level to its minimum and avoiding the discharge of harsh chemicals to the environment. Regardless whatever treatment steps a wastewater undertakes, a significant amount of wastewater treatment systems will have as a final step the discharge of effluent to a soil absorption system [17]. This is the reason why is important to comprehend how both soil and water treatments work, since these contaminants used to be released without any treatment [6]. Generally, both soil and water treatment methods include technologies associated with physical, chemical, biological and thermal processes [18, 19].

Soil remediation is necessary to clean and preserve high quality standards of soil and water and embraces various processes intended to remove contaminants such as hydrocarbons, pesticides and volatiles of soil. This processes can be divided in four main types of techniques: i) bioremediation that uses aerobic or anaerobic bacteria to consume or abolish the contaminants [7, 11]; ii) thermal remediation that intends to evaporate impurities; iii) air injections projected to force organic vapours outwards the soil; iv) encapsulation of contaminants [19].

The purpose of wastewater treatments is to allow the release of human and industrial effluents on the natural environment without polluting it. Commonly these consist of a combination of processes, each one with different purposes. Firstly, the effluent goes through a preliminary treatment to separate the largest materials often found in raw wastewaters and then is exposed to a primary treatment, intended for the removal of other solid particles by sedimentation. Then the effluent goes to a secondary treatment where suspended solids and residual organics are removed by processes like activated sludge, biofilters, oxidation

reactions or even a combination of these. If the effluent has some constituents which cannot be removed by these treatments, for instance nitrogen, refractory organics (like HCH isomers) or heavy metals, an additional advanced process is used. This can be referred to as tertiary treatment when added after the secondary treatment or be combined with primary or secondary treatment, depending on what is desired [20, 21].

## 2.2 Degradation of HCHs by Chemical Processes

There are several remediation techniques to degrade HCHs such as biodegradation [22-24], photo-degradation processes [25], treatments involving the use of ferrous sulphide [26] and use of zero valent iron [27-29]. There are also a few studies focusing on the use of redox reactions (oxidation and reduction) to degrade Persistent Organic Pollutants (POPs) showing a promising efficiency [28, 30-34].

In the category involving redox reactions exist both advanced or simple oxidation and reduction processes. These are based in the transfer from an electron donor to an electron receptor, depending on their redox potential. The chemical substance with the lower redox potential acts as an electron donor and is referred to as a reducer. In contrast, the substance with the higher redox potential is called oxidant and acts like a receptor of electrons [35].

Advanced Oxidation Processes (AOP), although making use of different reacting systems, are all characterized by the same chemical features based on the production of OH radicals. Additionally, similarly to what occurs in a normal oxidation process, these radicals are used to attack the majority of organic molecules. Both this processes, AOP and chemical oxidation, are characterised by little selectivity of attack, which is a useful attribute when using in wastewater treatment. However, it carries a few consequences when applied to soil treatment, as it destroys compounds that are part of the environment. Therefore, for an appropriate application of oxidation processes should be selected an appropriate reagent, given the contaminant that is intended to attack. The best reactants tend to be rather expensive and sometimes is required its use in excess increasing the process costs. [36].

Regarding reducing processes, Advanced Reduction Processes (ARP) or chemical reduction, they require an operation mode similar to the one employed by the oxidation ones. However, reducing agents are used instead of oxidant ones. Much research has been conducted on reactions involving this but there is a shortage in the study of its application on wastewater degradation [36].

The application of these processes in real situations can be implemented by two main methods: *ex situ* or *in situ* treatments. *Ex situ* treatment technologies remove the original water/soil from its original location to a controlled environment where the treatment takes

place. This presents the main advantage of the method once allows sufficient time and conditions to apply any treatment, however is not easy to execute when working with a large quantity of water/soil [37]. The application of *in situ* treatment technologies is performed mainly where excavation of soil is undesirable or where permeable soils are present, enabling the treatment of contaminations at depths which would be unaffordable or prohibited to excavation [38].

Since HCHs can be found in large quantities and due to its toxicity, the most cautious approach is applying an *in situ* treatment to prevent the spread of this pollutant to uncontaminated sites. Among the existing methods with good efficiency to degrade these compounds underlines the oxidation and reduction processes. Each of these processes has its advantages and disadvantages that should be taken into account, depending on several factors.

In *In situ* Chemical Oxidation (ISCO) processes a reagent is injected into the soil/groundwater and the chemical reaction takes place underground. These reagents are selected based on its redox potential and normally fluorine, hydroxyl radical and persulfate radical are the ones most often used, all with relatively inexpensive associated cost. This process can treat Dense Non-Aqueous Phase Liquids (DNAPL) or dissolved contaminants with acceptable efficacy but its strong oxidants can also damage naturally occurring species without selectivity. Besides that, it works properly when the pollutant is concentrated but if it is dispersed the process would become much more expensive. These drawbacks along with the handling hazard associated to some reagents leads to ponder that this may not be the most appropriate technique [30, 39, 40].

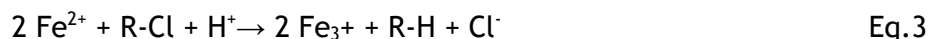
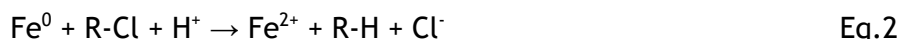
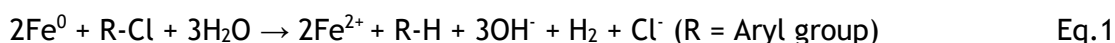
An *In Situ* Chemical Reduction (ISCR) process can treat several types of contaminants including DNAPLs, destroying most of the contamination without having to pump groundwater for treatment. The reducing agents used in the chemical reaction are zero valent metals with an inexpensive cost associated, such as iron, magnesium, aluminium and zinc [41] or bimetallic materials, such as iron coated with a thin layer of palladium or silver [42]. This process has two major ways of adding these agents to the contaminated soil or groundwater: i) direct injection which consists in mixing the reducing agent with water, creating a slurry that is pumped down into the soil until it reaches the contaminated area; ii) creating a Permeable Reactive Barrier (PRB) that acts like a permeable wall through which the groundwater flows, reacting with the reducing agent [40]. Therefore, ISCR presents little risk for the surrounding community and workers because the reaction takes place underground not exposing the contaminants. Additionally, another advantage is that it only attacks the pollutants [42].

Examining all the possibilities it appears that ISCR is a method with several advantages that can be implemented in several situations. Therefore, it is interesting to investigate ways to improve it.

## 2.3 Use of Zero Valent Iron Particles

Zero valent iron (ZVI),  $\text{Fe}^0$ , is the iron metal in its pure form and has been used for a long time in environmental remediation processes. ZVI is characterized by a good reactivity, small particle sizes - that can be used in diverse techniques - and a low associated cost [35]. It has been tested on the remediation of an extensive range of contaminants and has proved to be a good reducing agent for dechlorination reactions, including the degradation of HCHs [27-29, 43, 44].

The mechanism behind the reducing effect of ZVIs is based on the general reaction presented on Equation 1. On Equation 2 is demonstrated the reduction on the metal surface when in the presence of a proton donor. Additionally, on Equation 3 is represented its prolongation by further oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  [35, 42].



ZVI particles can be divided into categories based on its size, being largely used to dechlorinate HCHs the ones with dimensions lower than  $1 \mu\text{m}$ , also known as zero valent iron nanoparticles (nZVI) [45-47]. However, the slightly bigger ones, zero valent iron microparticles (mZVI), show similar results as nanoparticles in terms of dechlorination with a few advantages more. In Table 2 some features relative to both sizes of particles are presented and is notable that further research is necessary to comprehend its behaviour [29].

Table 2: Comparison between mZVI and nZVI.

Size	Price (€/kg)	Availability	Dechlorination rate	Stability
nZVI	High	Low	High	Low
mZVI	Low	High	Moderate	nd

Remediation techniques using ZVI are based on direct contact between iron particles surface and the dissolved contaminant, so it is extremely important that these particles are well dispersed [35]. Thus, it is expected that nZVI present faster reaction rates due to its higher contact superficial area that lead to high efficiency of dechlorination. However, mZVI

can also achieve the same efficiencies as nZVI with slightly lower rates that end up not being significant.

Since microparticles show quality features for dechlorination processes, they are a promising reducing agent that could replace nZVI which are more expensive. Therefore, mZVI behaviour should be completely comprehended and more research should be undertaken in order to optimize reduction processes.

## 2.4 Application on real situations

As mentioned on Section 2.2, there are two major techniques for applying the reducing effect of mZVI in real situations. Both of them are schemed in Figure 2.

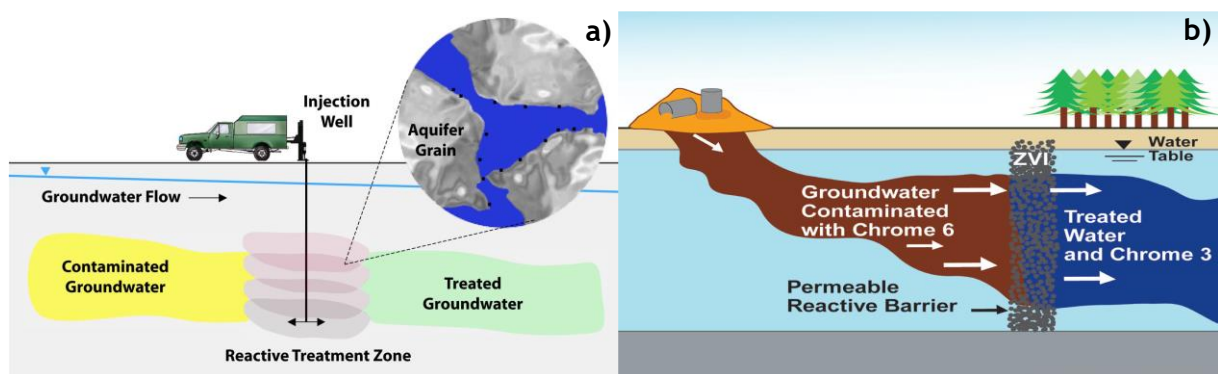


Figure 2: Representation of ZVI applications in real situations by a) direct injection [40] and b) PRB [42].

Soil and groundwater remediation by iron injections is mainly based on the stability and mobility of the particles. The injection can be performed by different procedures, such as: i) direct push, a mainly used technique that allows a higher pressure injection attaining specific depths; ii) direct push with pneumatic or hydraulic help; iii) gravitational infiltration, applied on permeable soils and iv) injection wells implemented by multiple thin injections easy to monitor [35, 40, 48]. These injection methods are associated with high remediation costs, as these techniques involve a dense system of injection points associated with elevated energy costs.

PRBs are designed to be more permeable than the surrounding environment so that groundwater can easily flow through the structure without significantly altering groundwater hydrology. This factor represents one of the best advantages of this technique, since it uses the natural flow of existent water. Subsequently there is no need for a pumping system and its associated cost tends to be smaller, comparing with other similar technologies. They can be installed anywhere along the groundwater plume and are designed to address different site-specific objectives. Furthermore, due to redox reactions some precipitates can be formed over time and sediment on these barriers, possibly reducing its activity. Although this

is estimated to occur just several years after the implementation of the barrier. Therefore, it might be necessary the rejuvenation of the ZVI in the PRB by that time [40, 49].

Both described techniques have a limiting factor in common concerning to the aggregate formation and consequent sedimentation of the mZVI particles. Moreover, microparticles tend to aggregate and when that happens there is a limited spread along the effluent or soil. Hence, reducing the specific surface area between these and decreasing the reactivity. Additionally, is extremely important to ensure that mZVI particles are well dispersed by monitoring the area where the treatment is being applied [35].

## 2.5 Previous work on Reduction of HCHs by mZVI

The degradation of HCHs by a dechlorination reaction using ZVI particles as a reducing agent has been studied. In Figure 3 is presented the shortened reaction expected for dechlorinate this compound by the mass balance of the reactants (Figure 3).

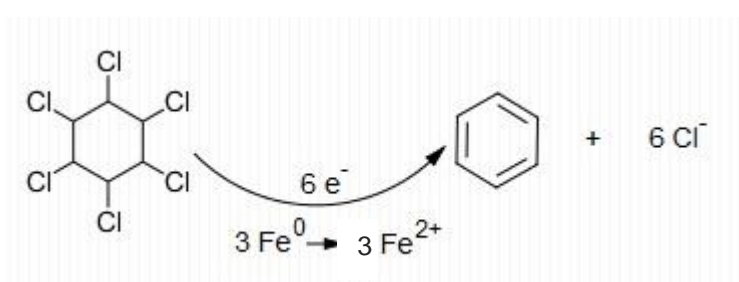


Figure 3: Theoretical dechlorination reaction of HCH using  $Fe^0$ .

There have been several studies that support the idea that the dechlorination reaction of HCHs occurs by dichloroelimination or dehydrohalogenation [29, 43].

This project was elaborated as a continuation of an already in development project from INPROQUIMA group. Due to the existing landfills of lindane in some locations in Spain and its mismanagement consequences, some incentives have been given in order to improve the research and develop new techniques [50-52].

From previous work it [53] had been selected the type of mZVI used in this project, from the several types tested. This mZVI properties are collected in Table 3.

Table 3: Properties of Zero Valent Iron microparticles used in the project.

$\varnothing_{ZVI}$ ( $\mu\text{m}$ )	$\rho_{app}$ ( $\text{g}/\text{cm}^3$ )	$S_{BET}$ ( $\text{m}^2/\text{kg}$ )	$\varepsilon$	$r_p$ ( $\mu\text{m}$ )	$Fe^0$ (%)
70	2.99	35	0.37	4.20	99.00

## 3 Technical Description

### 3.1 Reagents

The synthetic wastewaters used for the project analysis were prepared differently according to what was intended to study. The first step consists in dissolving the  $\alpha$ -,  $\beta$ -,  $\delta$ - and  $\gamma$ - HCHs isomers which are in powder form. So as to do this, each isomer was initially dissolved in acetone due to their low solubility in water, in order to attain a 10 g/L concentration. Afterwards, these solutions were dissolved by adding a designated volume of ultrapure water (purified on a deionization system) until the intended concentration was achieved.

All studies were performed based on this procedure to obtain the synthetic waters, using all isomers in an isolated way or in a mixture. Also, all chemicals used during the laboratory work are collected in Table 4 and all the dilutions accomplished were performed using ultrapure water.

Table 4: Chemicals used during experimentation.

Substance	Chemical Formula	MW (g/mol)	Purity (%)	Supply Company	Application
Acetone	C <sub>3</sub> H <sub>6</sub> O	58.1	99.8	Sigma-Aldrich	HCHs' solvent
Acetonitrile	CH <sub>3</sub> CN	41.1	99.9	Scharlau	HPLC mobile phase
Benzene	C <sub>6</sub> H <sub>6</sub>	78.1	99.9	Sigma-Aldrich	HPLC identification and calibration
Calcium Sulfate	CaSO <sub>4</sub>	136.1	>99.0	Riser	Ions effect
Cyclohexanone	C <sub>6</sub> H <sub>10</sub> O	98.1	>99.0	Sigma-Aldrich	Internal Standard
γ - HCH	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	291	99.9	Fluka	Pollutant
α - HCH	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	291	99.8	Fluka	Pollutant
β - HCH	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	291	98.5	Fluka	Pollutant
δ - HCH	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	291	99.4	Fluka	Pollutant
mZVI	Fe <sup>0</sup>	55.8	99.0	Höganäs	Reducing Agent
Magnesium Sulfate	MgSO <sub>4</sub> ·7H <sub>2</sub> O	246.5	>99.0	Probus	Ions effect
Sodium Bicarbonate	NaHCO <sub>3</sub>	84.0	99.7	Panreac	IC analysis, Ions effect
Sodium Carbonate	Na <sub>2</sub> CO <sub>3</sub>	106.0	99.8	Panreac	IC analysis
Sodium Chloride	NaCl	58.4	99.0	Sigma-Aldrich	IC analysis, Ions effect
Sodium Sulfate	Na <sub>2</sub> SO <sub>4</sub>	142.0	99.0	Sigma-Aldrich	Ions effect
Sulfuric Acid	H <sub>2</sub> SO <sub>4</sub>	98.1	95.0	Fisher Chemical	HPLC mobile phase

## 3.2 Experimental Procedure

The experiments carried out during the project can be separated into two parts: reactions in discontinuous (batch) and continuous (column).

### 3.2.1 Batch Reactions

The dechlorination experiments were performed following the experimental procedure described in Figure 4. For each reaction, several glass bottles (26 mL) containing 20 mL of synthetic wastewater were placed simultaneously on an orbital thermostatic bath at an equivalent stirring velocity of 100 rpm. In order to analyze the evolution of reaction, reactors were removed from the bath at specific times. The liquid phase extracted was separated from mZVI using a magnet - to attract the majority of the iron - and a syringe with a 0.45  $\mu\text{m}$  Nylon filter to ensure that there's no iron in the water to be examined. Then samples were immediately analyzed in High Performance Liquid Chromatography (HPLC), Gas Chromatography - Mass Spectrometry (GC-MS) and Ion Chromatography (IC).

Regarding the experiments involving the study of iron stability, iron microparticles were recovered by filtration using a conical flask with vacuum assistance and a cellulose nitrate membrane ( $\phi_p = 1.20 \mu\text{m}$ ). These microparticles were dried at 60 °C for approximately 24 h and then used again in a new reaction cycle.

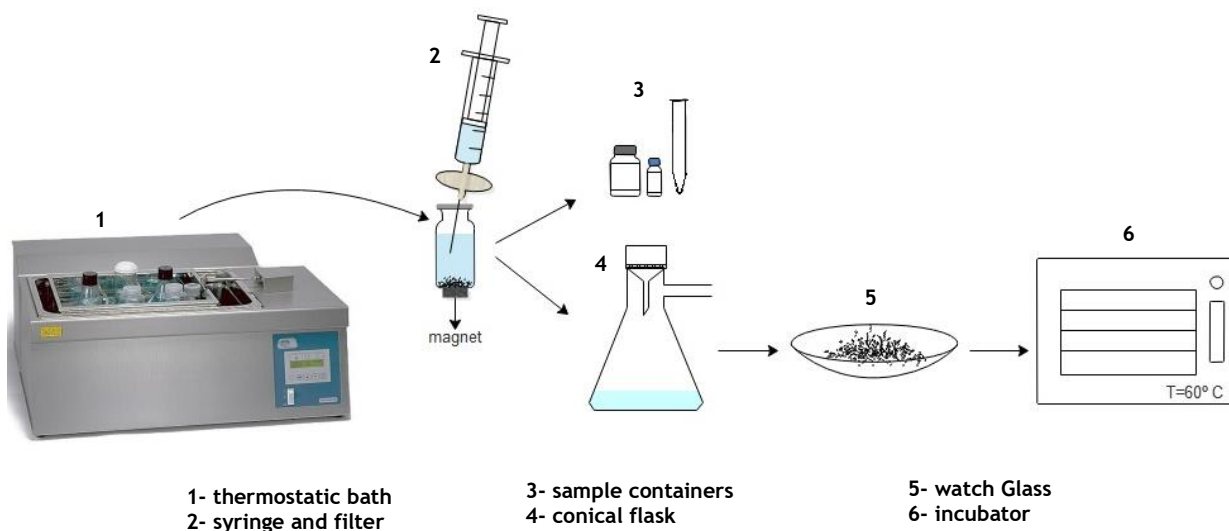


Figure 4: Scheme of the experimental procedure followed in batch experiments.

In Table 5 are summarized the dechlorination reaction runs carried in batch experiments, as well as the operating conditions studied.

Table 5: Objective and experimental conditions of reaction runs carried out in batch mode.

Objective	Reaction	C <sub>γ</sub> (mg/L)	C <sub>α</sub> (mg/L)	C <sub>β</sub> (mg/L)	C <sub>δ</sub> (mg/L)	C <sub>Fe</sub> (mg/L)	Use of Fe	T (°C)
HCH's dechlorination reaction	R1	0.5	-	-	-		1°	
	R2	0.5	-	-	-	5	2°	20
	R3	0.5	-	-	-		3°	
	R4	-	0.5	-	-		1°	
	R5	-	0.5	-	-	5	2°	20
	R6	-	0.5	-	-		3°	
	R7	-	-	0.5	-		1°	
	R8	-	-	0.5	-	5	2°	20
	R9	-	-	0.5	-		3°	
	R10	-	-	-	0.5		1°	
	R11	-	-	-	0.5	5	2°	20
	R12	-	-	-	0.5		3°	
Dechlorination study, isomer's behaviour	R13	0.5	0.5	0.5	0.5	5	1°	20
Influence of wastewater composition	R1	0.5	-	-	-			
	R14	3	-	-	-	5	1°	20
	R15	6	-	-	-			
Temperature effect	R16	6	-	-	-			10
	R15	6	-	-	-	5	1°	20
	R17	6	-	-	-			30
Iron concentration effect	R18	6	-	-	-	1		
	R15	6	-	-	-	5	1°	20
	R19	6	-	-	-	10		
Ions presence effect	R20-R38*	6	-	-	-	5	1°	20

\* Described in detail in Table 7 of Section 4.4.

### 3.2.2 Fixed Bed Column Reactions

The dechlorination experiments in continuous mode were carried out using the experimental system represented on Figure 5. The “home-made” column was designed in order to present the same characteristics existing in batch reactions, such as the amount of Fe used (5 g/L) and the samples' extracting method. This column consists of a Teflon pipe of

10 cm length and 0.2 cm diameter. With the aim of supporting the iron microparticles, glass wool was placed below and above the fixed bed. Moreover, filters consisting on a combination of nylon between metallic mesh were placed between pipes connections and before the peristaltic pump.

The solution containing HCH isomers was conducted upwards through the column by action of a peristaltic pump and directed to the waste container or to a needle for sampling, using a three-way valve.

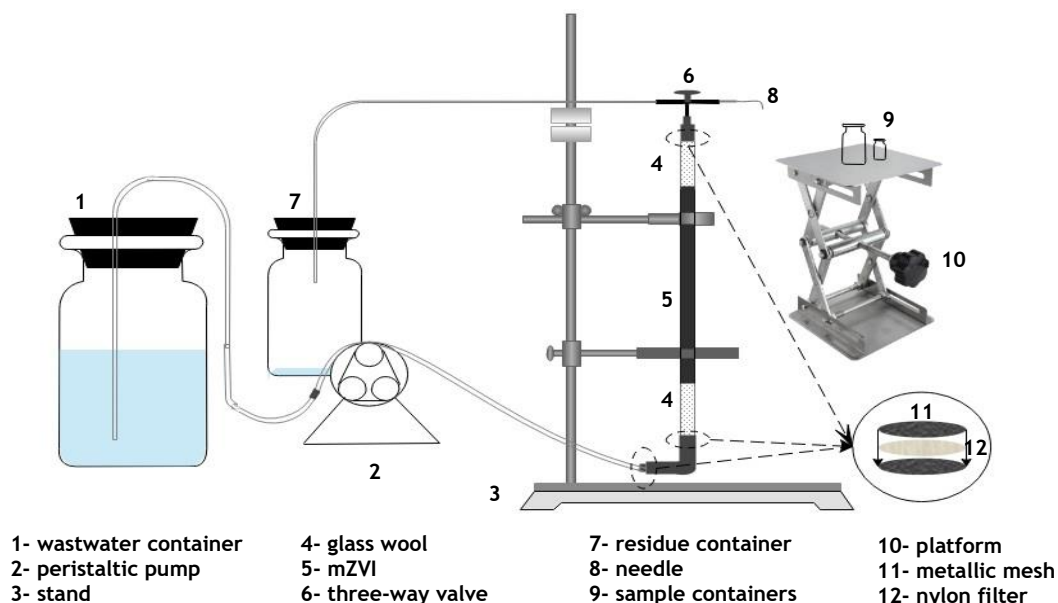


Figure 5: Scheme of the experimental procedure used in column experiments.

The studied variables in column reactions are presented in Table 6 containing details of each performed reaction.

Table 6: Objective and experimental conditions of the reaction runs carried out in continuous mode

Objective	Reaction	$C_{\gamma}$ (mg/L)	$C_{\alpha}$ (mg/L)	$C_{\beta}$ (mg/L)	$C_{\delta}$ (mg/L)	W/Q <sub>L</sub> (g*h/L)
Comparison Batch / Column	RC1	6	-	-	-	10 - 2778
Stability	RC2	6	-	-	-	167 and 2778
HCHs mixture behaviour	RC3	10	3	1.5	10	14 - 2778
HCHs mixture behaviour	RC4	5	1.5	0.5	5	42 - 2778

### 3.3 Analytical Methods

The progress of the dechlorination reactions was studied analysing liquid samples at different reaction times. To evaluate the efficiency of the process four analytical techniques were used.

#### 3.3.1 Gas Chromatography - Mass Spectrometry (GC-MS)

To identify and quantify the HCH isomers over reaction time, a HP6890 Gas Chromatograph coupled with a HP5973 Mass Spectrometric Detector using a CTC CombyPAL (GC samples 80) was used.

The extraction of the organic compounds was performed by solid phase microextraction (SPME) using polyacrylate coating fiber. The method used for this extraction had been previously optimized and consists in 3600 s at 38 °C followed by the desorption process conducted in the injector at 270 °C in splitless mode for 180 s.

The separation of all compounds takes place on a SPB-624 fused-silica-capillary column (30 m x 0.25 mm ID and 1.40 µm thickness). Helium was used as carrier gas in a constant flow-rate of 1 mL/min.

For each analysis the GC column was maintained at 45 °C for 10 minutes, ramped at a rate of 12 °C/min until 190 °C and held at this temperature for 4 minutes. After this, a second ramp starts with a 3 °C/min rate until it attains a temperature of 240 °C which is then retained for 20min. The process ends with a post run of 240 °C during 10 minutes.

In all experiments 4-methylcyclohexanone was used as an internal standard (ISTD) with the aim of minimizing experimental errors. The calibration curves used to quantify HCH concentration are displayed in Anex I. All samples corresponding to the dechlorination reaction's ending were measured in duplicate to confirm the results. This confirmation was achieved by comparing the chromatographic areas obtained with the ISTD areas.

#### 3.3.2 Ion Chromatography (IC)

The dechlorination degree was determined in based on the amount of chlorine ions released to the liquid phase. In order to quantify these ions, it was used an IC (Metrohm 761 Compact IC) with anionic chemical suppression using a conductivity detector. As stationary phase a Metrosep ASUPP5 column (5 cm length x 4 mm diameter) was used and as mobile phase, an aqueous solution of 3.2 mM Na<sub>2</sub>CO<sub>3</sub> along with 1 mM of NaHCO<sub>3</sub> flowing at 1 mL/min.

To quantify chlorine concentration some calibrations were made as described in Anex I.

### 3.3.3 High Performance Liquid Chromatography (HPLC)

Benzene was identified and quantified by HPLC (Agilend, model 1100) with an Agilent poroshell 120 SB-C18 column as the stationary phase.

The method used consisted on a mobile phase composed by a mixture of 4 mM H<sub>2</sub>SO<sub>4</sub> aqueous solution and acetonitrile with a 40 and 60% ration, respectively, at a 0.5 mL/min flow. The analysis was performed with a diode array detector (G1315A) at a 210 nm wavelength.

From each sample were extracted 20 µL which were then placed on the column which was maintained at 20 °C and 84,6 bar for the 30 min needed to obtain the spectrum and chromatogram.

The calibration curve used to quantify the benzene's concentration is described in Anex I.

### 3.3.4 pH

To ensure that the pH of each sample was maintained as intended and to observe if there were variations along with the reaction's time these measurements were performed using a Basic 20-CRISON pH electrode.



## 4 Results and Discussion

### 4.1 HCH's dechlorination reaction

#### 4.1.1 Reactivity of HCH isomers

Solutions containing 0.5 mg/L of each HCH isomer were treated in discontinuous mode at room temperature and for a mZVI concentration of 5 g/L. The results obtained at 72 h reaction time, in terms of HCH conversion, are shown in Figure 6. The reactivity order found for HCHs isomers were  $\gamma$ -HCH >  $\alpha$ -HCH >  $\delta$ -HCH >  $\beta$ -HCH, which is consistent with the expected attending to their chlorines position. Isomers with the largest ratio of axial to equatorial chlorines are expected to be more reactive towards iron microparticles dechlorination. Thus, obtaining a variation range from 93 % for  $\gamma$ -HCH to less than 50 % regarding to  $\beta$ -HCH.

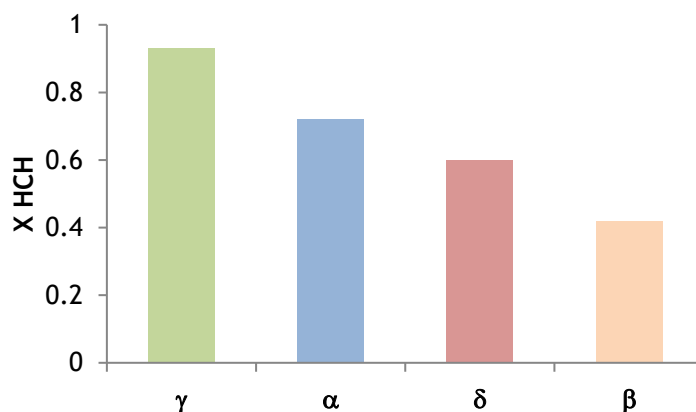


Figure 6: Reactivity order for HCHs isomers at 72 h reaction time ( $T=20^{\circ}\text{C}$ ,  $C_{\text{Fe}}= 5 \text{ g/L}$ ,  $C_{\text{HCH}_0}= 0.5 \text{ mg/L}$ ,  $\text{pH}_0=7$ ; R1, R4, R7 and R10).

As previously seen,  $\beta$ -HCH shows the most refractory behaviour. Besides that, due to the presence of all chlorine atoms in equatorial position (showed in Table 1 of Section 1.1) this isomer presents a reduced susceptibility to bio-chemical transformation [11] leading to a high bioaccumulation. Hence, some strategies were tested for its improvement.

It was found that an increase temperature reaction from 20 to  $30^{\circ}\text{C}$  did not lead to a significantly higher conversion. However, an increase in reaction time was more effective. A depletion of 85% of  $\beta$ -HCH was achieved at 312 h reaction time, working at room temperature. It is observed an increase of 38 % in  $\beta$ -HCH conversion comparatively with the

one obtained for 96 h of reaction previously performed. All the graphs presenting the obtained results in both attempts, in terms of  $1-X_{\beta\text{-HCH}}$ , can be found in Annex II.

#### 4.1.2 Iron Microparticles Stability

An extremely important aspect both for the economy and the applicability of this technology is the stability of the iron microparticles. It is intended that iron microparticles maintain the activity over a long period of time to be able to implement in the soil and ensure that they continue to react with the pollutant, in a stable manner.

In order to determine whether these microparticles keep stable throughout its use, three consecutive reaction cycles were performed for the treatment of each isomer, separately. After the first use, iron microparticles were recovered as previously explained in Section 3.2.1 and then used again in the next reaction without further treatment. The stability results are presented in Figure 7.

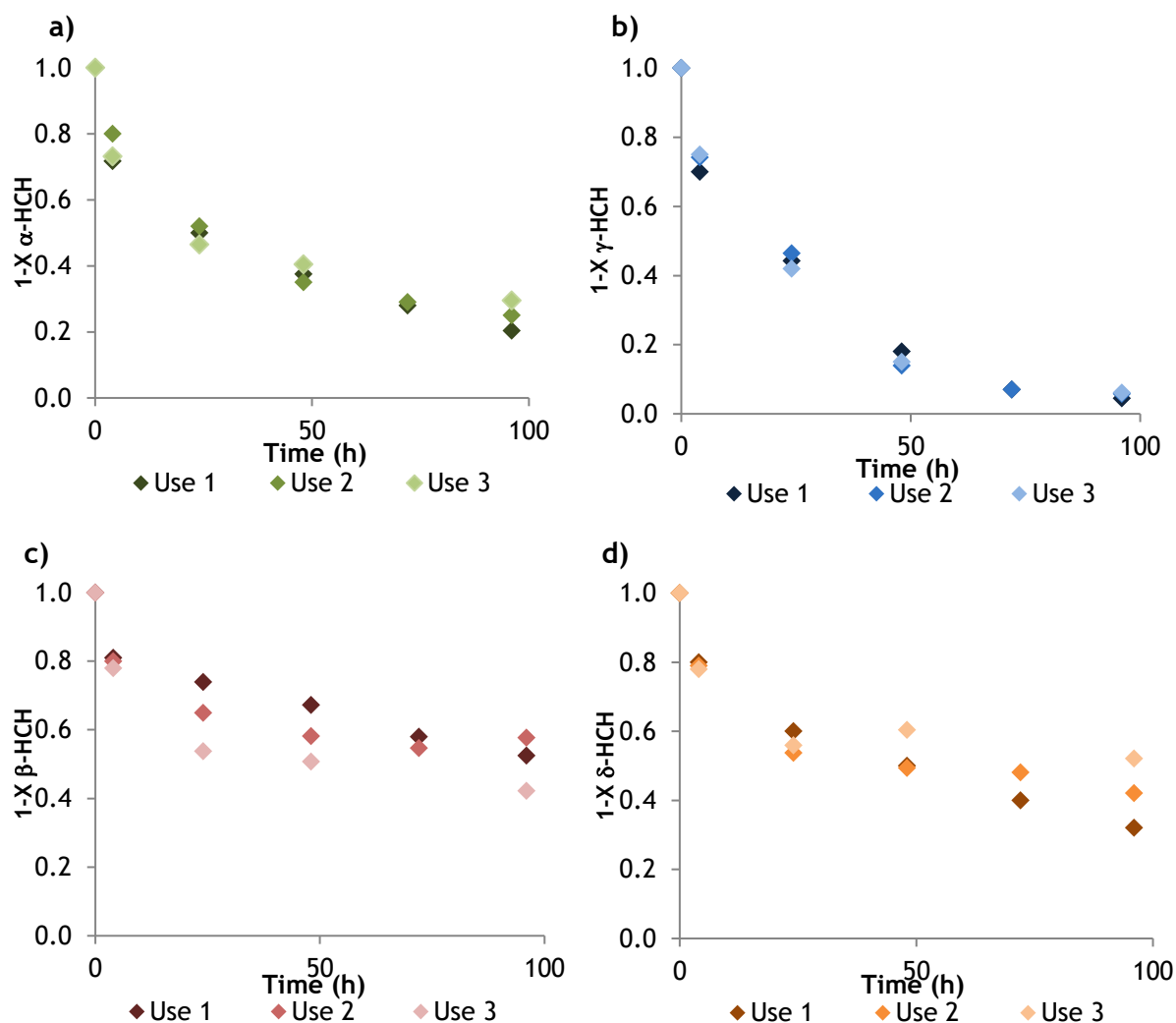


Figure 7: Degradation of HCH isomers in three successive runs ( $T=20^\circ$ ,  $C_{Fe}=5$  g/L,  $C_{HCH0}=0.5$  mg/L,  $pH_0=7$ ; R1-R12).

It is observed that the reactivity of iron microparticles, in the degradation of all isomers, is maintained in the three cycles tested.

This is a great result, since it presents an important advantage over the nanoparticles, currently presented as a better approach to this subject. Although microparticles activity is lower, they can reach the same results with a longer reaction time and have greater durability. Furthermore, microparticles do not require pre-treatments to their use or possess a protective layer that may initially obstruct the contact between the reactive, unlike nanoparticles [54].

#### 4.1.3 Influence of wastewater composition

The HCH isomers are not truly isolated, in reality these four isomers are mixed. Furthermore, with the goal of being more realistic, a solution containing the four isomers (0.5 mg/L of each) was treated with mZVI. The results, compared to those obtained for the isolated isomers, are presented in Figure 8.

It was observed that all isomers in the presence of mZVI behave in the same way, either in the mixture or isolated, maintaining the reactivity order previously shown (Figure 6 of Section 4.1.1). However, the final conversion in the mixture for each isomer is slightly higher than when they are isolated. This fact can be related to a possible instability of the iron surface, for short reaction times, that goes unnoticed when a bigger concentration of pollutant is used (2 mg/L in the mixture vs 0.5 mg/L when isolated).

Therefore, the presence of the other isomers doesn't interfere with the degradation of each one, which is an interesting point since it is a more realistic approach.

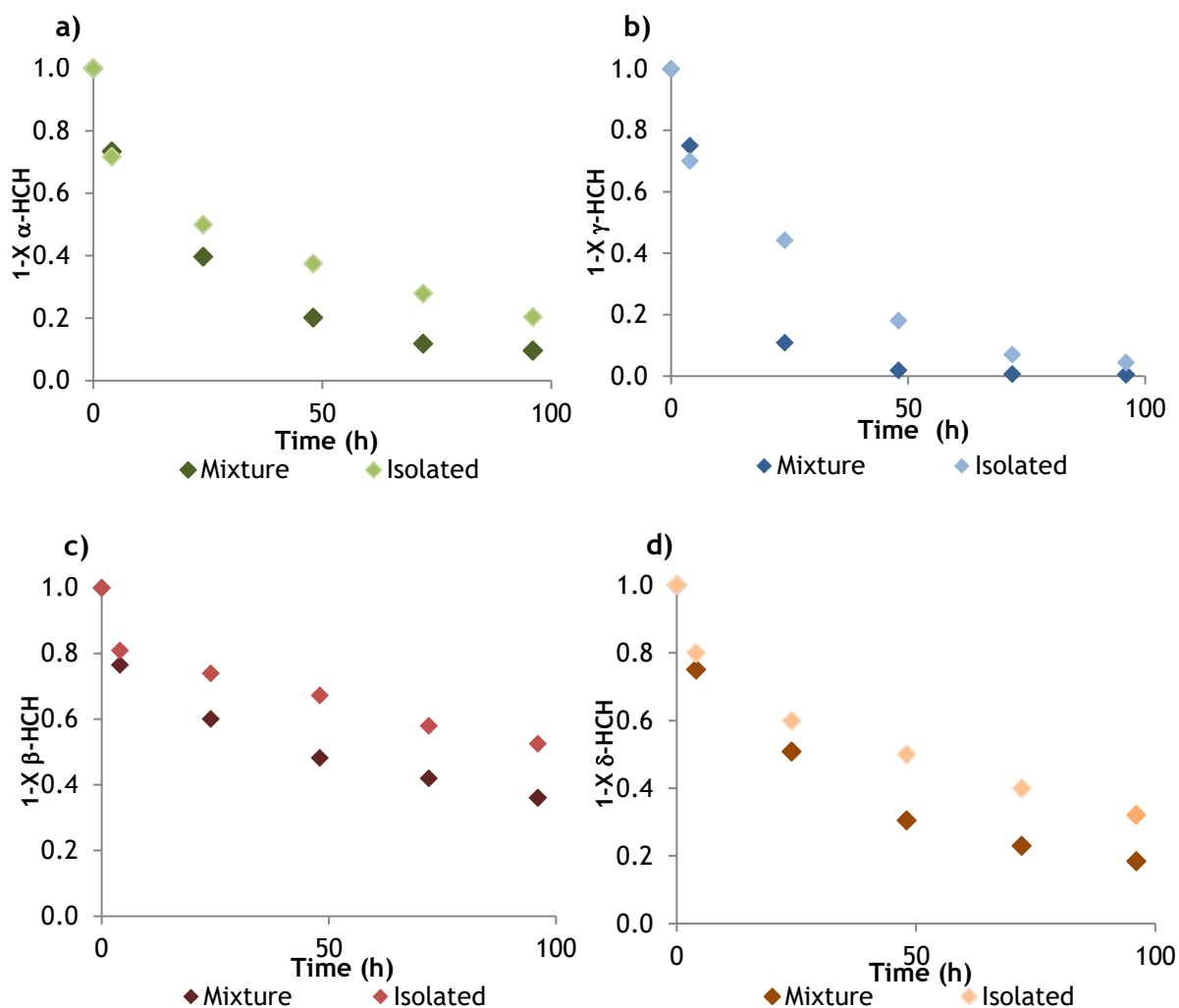


Figure 8: Degradation of isomers when in a mixture or isolated ( $T=20^{\circ}\text{C}$ ,  $C_{Fe}=5\text{ g/L}$ ,  $C_{HCHO}=0.5\text{ mg/L}$ ,  $pH_0=7$ ; R1, R4, R7, R10 and R13).

## 4.2 Influence of Operation Conditions

To learn more on the reduction of HCHs over zero-valent iron microparticles, the effect of several operating variables such as initial pollutant concentration, iron microparticles concentration and temperature were investigated following the evolution of lindane concentration as well as the formation of chorines with reaction time. This study has been performed using  $\gamma\text{-HCH}$  isomer due to its higher solubility. Therefore, in order to facilitate products identification and quantification, a concentration of 6 mg/L of lindane was chosen.

### 4.2.1 Concentration of pollutant

One of the important aspects to consider is the effect of pollutant concentration on its degradation. In order to understand that, three reactions were performed with three different concentrations of lindane. The degradation of this isomer and the mass balance for

$\text{Cl}^-$  (expressed as the relative amount of  $\text{Cl}^-$  measured in the bulk normalized by the chlorine content of the initial amount of lindane) is presented in Figure 9.

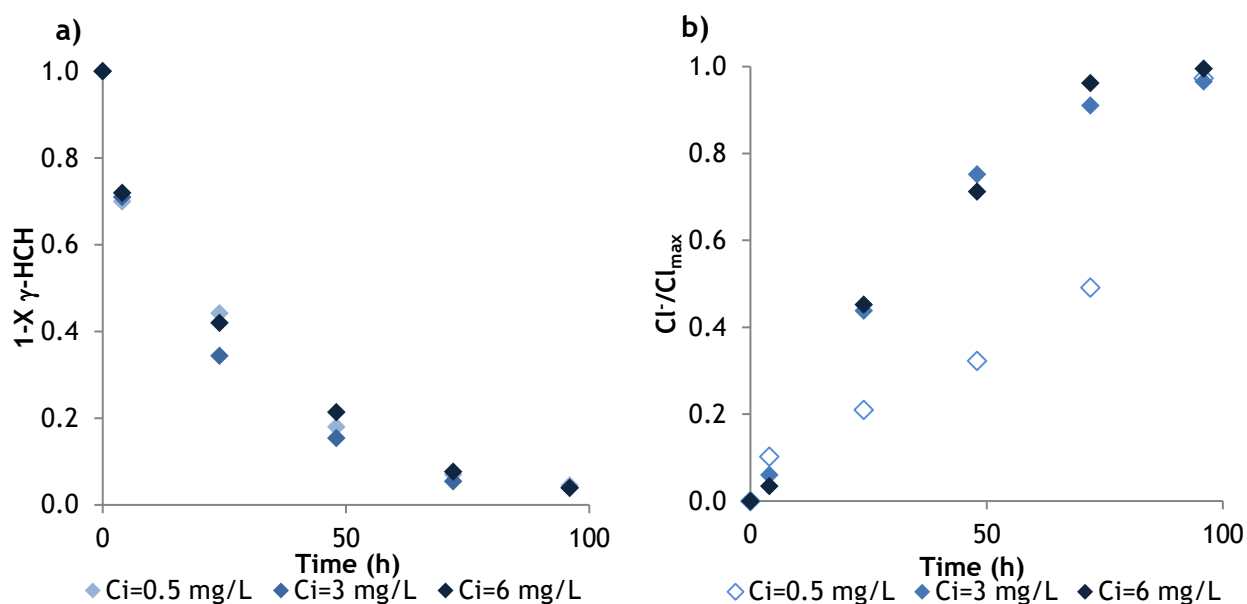


Figure 9 - Lindane concentration evolution (a) and  $\text{Cl}^-$  balance (b) in the presence of mZVI ( $T=20^\circ\text{C}$ ,  $\text{pH}_0=7$ ,  $C_{\text{Fe}}=5\text{ g/L}$ ) at different initial concentrations of lindane (reactions R1, R14 and R15).

Analysing Figure 9a it can be concluded that this reaction occurs according to first order law reactions, since the conversion curve obtained at different initial concentrations of lindane is maintained. In other words, the amount of initial pollutant does not interfere with the dechlorination reaction and the way it is conducted.

The same is confirmed by interpreting graph b), however it is necessary to point out that when working with very low concentrations of lindane (e.g. 0.5 mg/L) it is difficult to quantify chloride in solution (experimental limitations). Therefore, the data concerning to an initial concentration of 0.5 mg/L of lindane was discarded due to a possible lack of sensibility in the IC device.

#### 4.2.2 Concentration of Iron Microparticles

The effect of zero valent iron microparticles loading was analysed at room temperature and neutral pH. Thus, two additional reactions (R18 and R19) were performed at 1 and 10 g/L iron concentration and compared with the previously performed with 5 g/L (Figure 9) as shown in Figure 10.

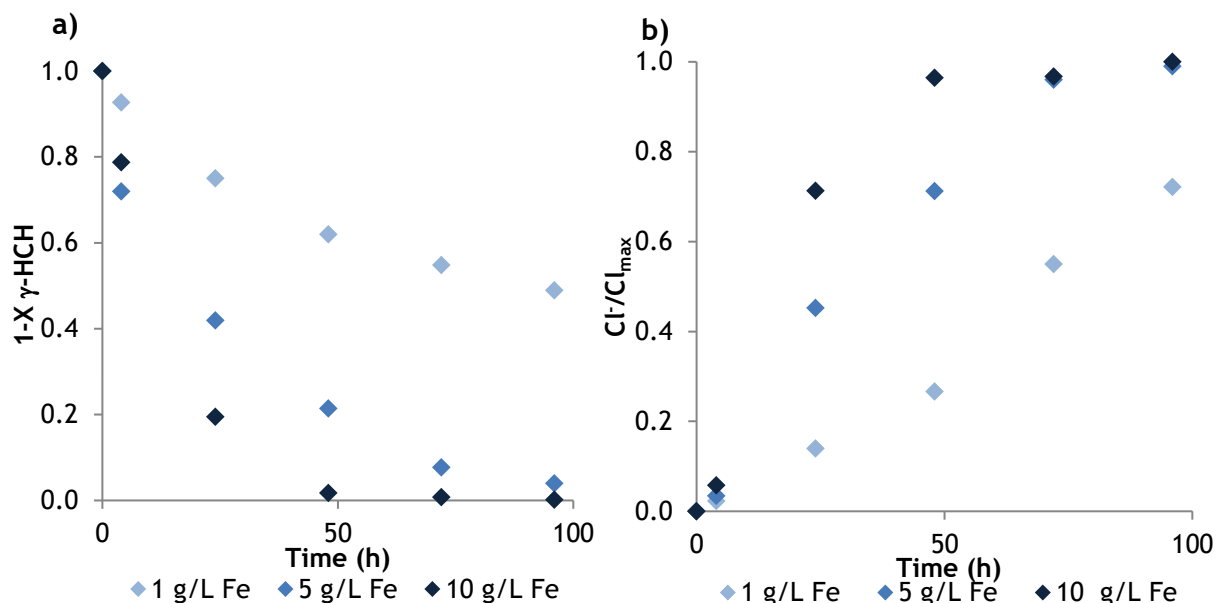


Figure 10: Lindane concentration evolution (a) and Cl<sup>-</sup> balance (b) in the presence of mZVI ( $T=20\text{ }^{\circ}\text{C}$ ,  $\text{pH}_0=7$ ,  $C_{\text{lindaneo}} = 6\text{ mg/L}$ ) at different iron concentrations (reactions R15, R18 and R19).

As expected, a higher concentration of iron microparticles led to a higher conversion of lindane (Figure 10a). The reaction's rate tends to be higher as the iron concentration increases. Additionally, for a longer reaction time it is expected that similar values are accomplished for lower concentrations of iron. The same conclusion withdraws from Figure 10b where the mass balance for chlorine is achieved faster for a higher amount of iron. In the reaction carried out with 1 g/L of iron microparticles, the chloride balance at final reaction time is not attained since at that time the degradation of HCH has not been completed yet.

#### 4.2.3 Temperature

A very important factor to take into consideration is the effect of temperature on the rate of degradation reaction. To analyse this effect two additional reactions occurring at 10 and 30 °C (R16 and R17) were performed to compare with the results obtained at 20 °C (Figure 9) as shown in Figure 11.

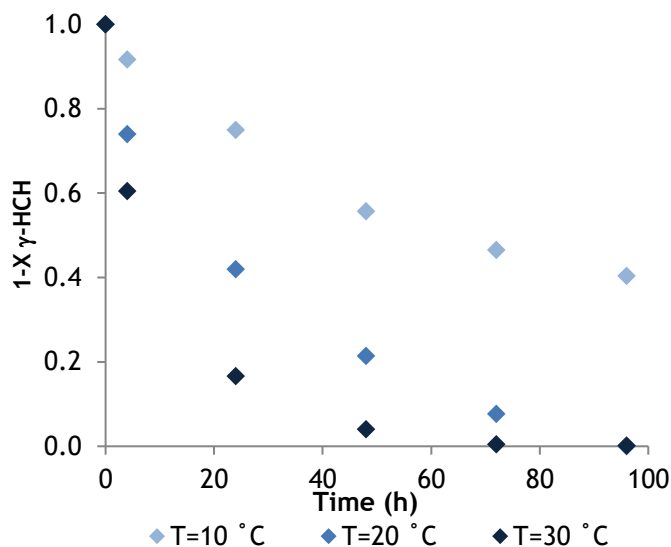


Figure 11: Lindane concentration evolution in the presence of mZVI ( $C_{Fe} = 5 \text{ g/L}$ ,  $pH_0 = 7$ ,  $C_{lindane0} = 6 \text{ mg/L}$ ) at different temperatures (reactions R15-R17).

Analysing figure 11, it is possible to conclude that at room temperature, total conversion of  $\gamma$ -HCH was obtained for 96 h of reaction. An increase in the temperature up until 30 °C allowed a total conversion after 72 h of reaction. Moreover, when the temperature is decreased to 10 °C the conversion is affected and drops to about 60% at 96 h. The form of the curve suggests that it will not reach total conversion. Therefore, it is assumed that an increase in temperature leads to an increase in the rate of reaction.

### 4.3 Kinetic Model

In order to establish a kinetic model for the degradation of lindane, the data obtained at different operation conditions (Section 4.2) was processed. All these reactions were performed in discontinuous mode that is equivalent to a stirred batch reactor. Accordingly, the mass balance of lindane can be determined by Equation 4.

$$-r_{lindane} = -\frac{dC_{lindane}}{dt} \left( \frac{mg}{L \cdot h} \right) \quad \text{Eq.4}$$

Considering the reaction scheme for lindane dechlorination in the presence of zero-valent iron microparticles presented in Section 2.4, Equation 4 was rewritten as shown in Equation 5. In these expressions  $K$  is the rate constant,  $C_{Fe}$  represents the mZVI concentration,  $C_{lindane}$  is lindane concentration, and  $n$  and  $m$  represent the reaction orders for iron and lindane concentration, respectively.

$$-\frac{dC_{lindane}}{dt} = k \times C_{Fe}^n \times C_{lindane}^m \quad \text{Eq.5}$$

As the reductant agent ( $\text{Fe}^0$ ) is in highly excess comparatively to the amount of lindane present in water, it is acceptable to assume that the iron concentration is maintained constant during the reaction. Afterwards, the expression in Equation 6 was incorporated in the mass balance of Equation 5, resulting in the presented expression in Equation 7.

$$k_{app} = k \times C_{Fe}^n \quad \text{Eq.6}$$

$$-\frac{dC_{lindane}}{dt} = k_{app} \times C_{lindane}^m \quad \text{Eq.7}$$

It was previously confirmed in Section 4.2.1 that the reaction follows a first order law, which means that  $m$  is equal to 1. Knowing this, it is possible to integrate the mass balance expression, resulting in Equation 8.

$$\frac{C_{lindane}}{C_{lindane_0}} = \exp(-k_{app} \times t) \quad \text{Eq.8}$$

In this regard, the apparent rate constants for different iron loadings, 1, 5 and 10 g/L ( $k_{app1}$ ,  $k_{app5}$  and  $k_{app10}$ ) can be calculated from the graph in Figure 12.

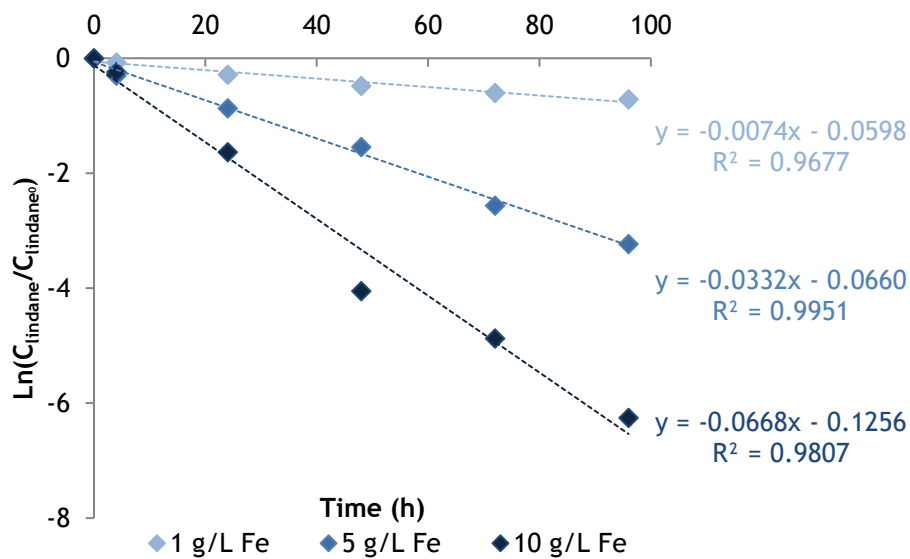


Figure 12: Apparent kinetic constants for different ZVI concentrations (R15, R18, R19).

From this representation it is observed that the values for  $k_{app1}$ ,  $k_{app5}$  and  $k_{app10}$  are 0.0074, 0.0332 and 0.0668  $\text{h}^{-1}$ , respectively.

With the purpose of determine the reaction order relative to iron concentration ( $n$ ), Equation 6 was changed to logarithmic form (Equation 9) and represented in Figure 13, showing a good linear association.

$$\ln(k_{app}) = \ln(k) + n \times \ln(C_{Fe}) \quad \text{Eq.9}$$

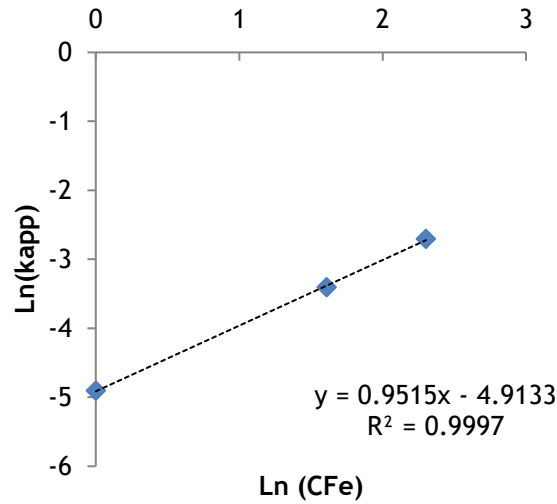


Figure 13: Determination of constant  $n$  by linear regression between  $\ln(k_{app})$  and  $\ln(C_{Fe})$ .

It follows that the slope of the straight line obtained is almost 1, indicating that lindane degradation can be considered as a first order reaction with respect to the mZVI concentration. This fact also suggests that the heterogeneous active sites are not encapsulated or deactivated during reaction.

For a given reaction the rate constant is related to the temperature of the system by Arrhenius Equation (Equation 10), from which it can be determined the activation energy. In this equation  $A$  is the pre-exponential factor,  $Ea$  is the activation energy (kJ/mol),  $R$  is the universal gas constant ( $8.314 \times 10^{-3}$  kJ/mol·K), and  $T$  is the absolute reaction temperature (K).

$$k = A \exp\left(-\frac{Ea}{RT}\right) \quad \text{Eq.10}$$

The rate constants were calculated for the three temperatures studied in Section 4.2.3, corresponding to 10, 20 and 30 °C ( $k_{app10^\circ C}$ ,  $k_{app20^\circ C}$  and  $k_{app30^\circ C}$ ), all with  $C_{Fe}$  equal to 5 g/L. As it can be seen in Figure 14, these constants were determined by the same method used for the ones related with mZVI concentration. The obtained  $k_{app10^\circ C}$ ,  $k_{app20^\circ C}$  and  $k_{app30^\circ C}$  correspond to 0.0147, 0.0314 and 0.0705 h<sup>-1</sup>, respectively. As expected, the apparent reaction rate increased rapidly with temperature.

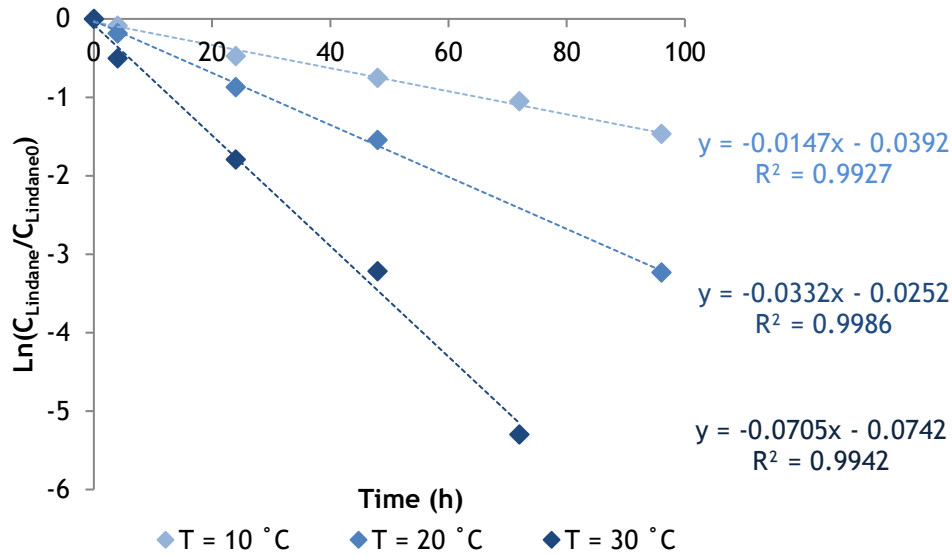


Figure 14: Apparent kinetic constants for different Temperatures with constant  $C_{Fe}$  and  $C_{Lindane0}$  (reactions R15-R17).

Using the obtained rate constants and considering Equation 6, the activation energy and pre-exponential factor were determined converting Equation 10 to its linear form, resulting in Equation 11. Then, the fitting of  $\ln(k)$  versus  $1/T$  yields a straight line throughout the temperature range ( $R^2 = 1$ ), as shown in Figure 15.

$$\ln(k) = -\frac{E_a}{RT} + \ln(A) \quad \text{Eq.11}$$

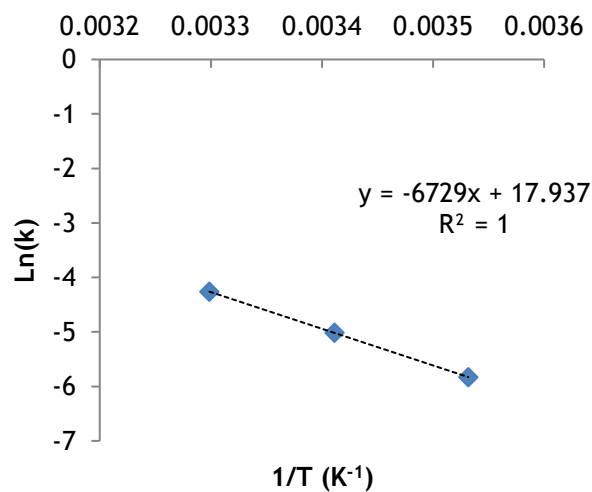


Figure 15: Representation of Arrhenius Plot.

The slope of the straight line gives an  $E_a$  of 55.44 kJ/mol, and the pre-exponential factor was calculated as  $6.17 \times 10^7$  from the intercept of the line.

Based on the results attained, the rate equation can be expressed as shown in Equation 12 by replacing the parameters determined and the values of each reaction.

$$-r_{\text{lindane}} = 6.17 \times 10^7 \cdot e^{-\frac{55.44}{R \cdot T}} \cdot C_{\text{Fe}} \cdot C_{\text{lindane}} \quad \text{Eq.12}$$

This expression shows the dependence of the lindane dechlorination rate (mg/L·h) on reaction temperature, mZVI concentration and initial lindane concentration. Furthermore, it allows the prediction of lindane reduction under different conditions, which is presented in Figure 16 with a comparison between experimental and simulated data characterized by an acceptable deviation ( $R^2=0.989$ ).

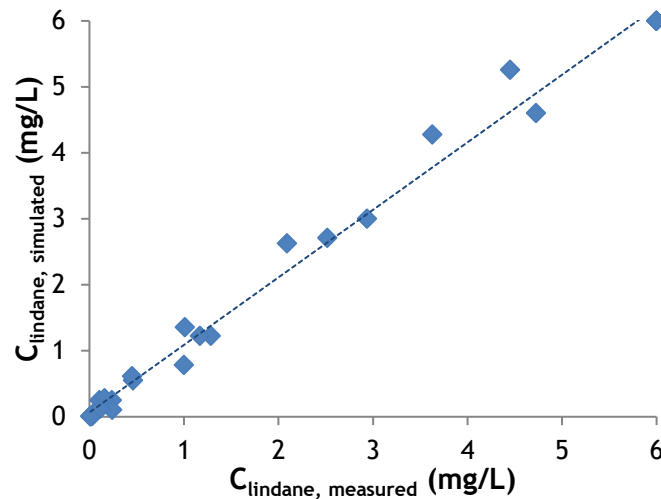


Figure 16: Comparison between the data predicted by the model and the measured data for lindane concentration at the different operation conditions tested.

#### 4.4 Effects of different ions on lindane degradation

Common anions and cations normally present in soil and water/groundwater might affect the dechlorination reaction of HCHs. In this regard, it is an important subject of study when planning to apply these technologies in real situations. In order to comprehend the influence of different ions (and their concentration) in the degradation of  $\gamma$ -HCH, some reactions were performed. For this purpose, an initial  $\gamma$ -HCH concentration of 6 mg/L and mZVI dose of 5 g/L were selected. Additionally, the concentration range for each salt was selected based on the typical values founded in this type of contaminated waters. All reactions were carried out at room temperature and the final reaction time elected was 48 h, corresponding to a conversion of around 76 %. These reactions are described in Table 7.

Table 7: Experimental conditions of reaction runs carried out in Batch in order to study the presence of different ions.

Objective	Reaction	Salt	C <sub>Salt</sub> (mM)
Anions effect	20		2.0
	21	NaHCO <sub>3</sub>	10.0
	22		20.0
	24		0.1
	25	Na <sub>2</sub> SO <sub>4</sub>	0.5
	26		2.0
	27		5.0
	28	NaCl	15.0
	29		50.0
Cations effect	30		1.0
	31	CaSO <sub>4</sub>	5.0
	32		10.0
	33		0.1
	34	MgSO <sub>4</sub>	1.0
	35		5.0
	24		0.1
	25	Na <sub>2</sub> SO <sub>4</sub>	0.5
	26		2.0

A very important factor to take into account during these reactions is the value of pH, which had been around neutral values and kept stable in reactions when no additional components were added to the reaction's medium. In addition HCH dechlorination reactions are favoured when the solution pH is between 4 and 7 [43]. When its value decreases to this minimum, the reaction efficiency increases because of a better solubility of Fe(II) and Fe(III). However, if it goes below that value an intensive corrosion of iron occurs due to extremely acidic conditions. At pH higher than 8, Fe(II) and Fe(III) formed in the mZVI surface and OH<sup>-</sup> ions in the alkaline solution can react and form precipitate iron oxides/hydroxides. These precipitates most likely will settle on the mZVI surface occupying the reactive sites blocking their access to HCHs, thus reducing its degradation [43].

Thereby, pH was measured before and after the dechlorination reaction in the presence of mZVI particles. These values have been compared with those obtained in a reaction performed without salts addition, as shown in Figure 17. As the pH value was preserved since the beginning of the dechlorination reaction until its end when no ions were added to the process, only one representing line was used in the graph of Figure 17.

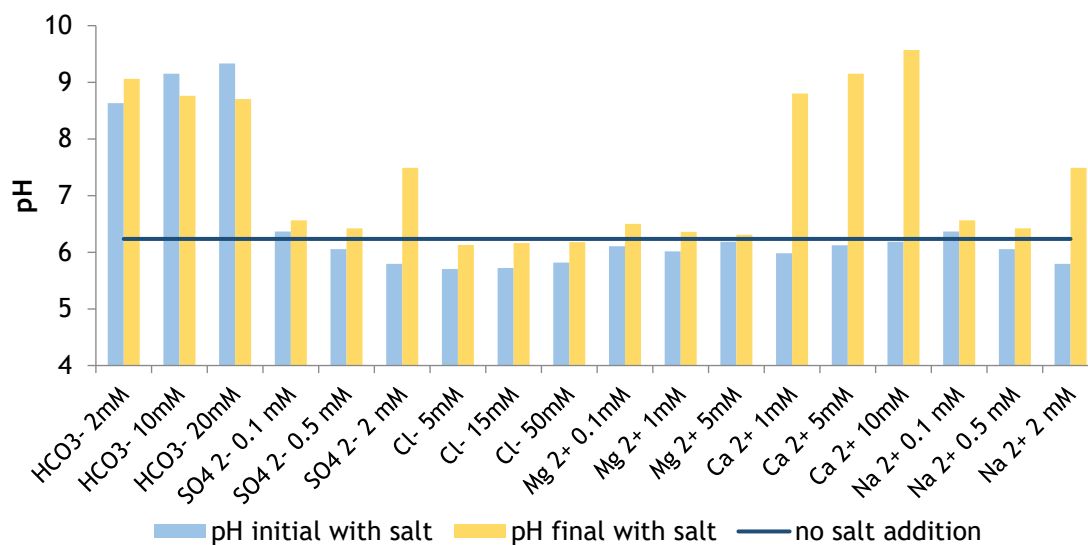


Figure 17: Effect of ions presence on initial and final pH in the lindane dechlorination reaction at  $T=20\text{ }^{\circ}\text{C}$ ,  $C_{\text{Fe}}=5\text{ g/L}$  and  $C_{\text{lindaneo}} = 6\text{ mg/L}$  (R15, R20-R38).

No significant changes on the initial pH were observed comparatively with the reaction without ions addition, except for the bicarbonates presence. In this case, the pH of the solutions increased greatly. Hence, these reactions took place in alkaline solutions with a pH range from 8.7 to 9.2, depending on the concentration of sodium bicarbonate used.

Analysing the pH evolution for the reaction it is possible to say that is maintained constant except for calcium, that greatly increases, and for sulphate and sodium which slightly increase. As already mentioned, from the beginning bicarbonates tend to increase the pH of the solution. However, no changes were observed along the reaction.

#### 4.4.1 Effects of anions presence

As described in Table 7, all anions were added in the form of sodium salts to maintain constant the possible influence of the cation. All reactions were performed in a 48 h reaction time, as so the conversion expected would be around 76%. The results presented in Figure 18, in terms of  $X_{\gamma\text{-HCH}}$  and  $\text{Cl}^-/\text{Cl}_{\text{max}}$ , are compared with reference values from a reaction with the same synthetic water but without ions (R15). In order to unify the ion addition analysis, it has been established an error range of 0.03 in lindane conversion represented in all graphs. When the studied anion was  $\text{Cl}^-$  it was not possible to measure chlorides since a high amount would saturate the IC column. Consequently, there is not a correspondent value for  $\text{Cl}^-/\text{Cl}_{\text{max}}$  in this reaction study.

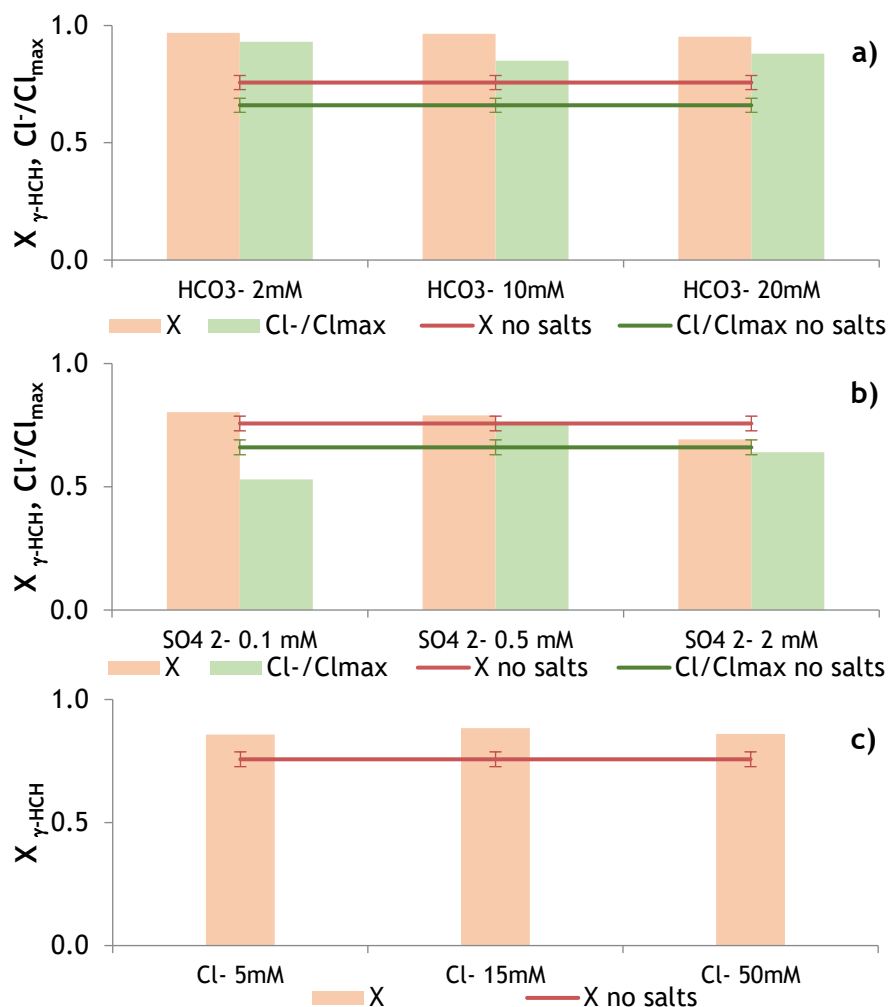


Figure 18: Effect of anions presence on the lindane dechlorination reaction in terms of  $X_{\gamma\text{-HCH}}$  and  $\text{Cl}^-/\text{Cl}_{\text{max}}$  at  $T=20\text{ }^{\circ}\text{C}$ ,  $C_{\text{Fe}}=5\text{ g/L}$  and  $C_{\text{lindane0}} = 6\text{ mg/L}$  (R15, R20-R29).

It is notable that the presence of different anions does not interfere significantly on lindane degradation and on the dechlorination's degree achieved.

Analysing Figure 18a, it seems that an addition of bicarbonates to the reaction medium enhances the dechlorination reaction. As a result, the degradation efficiency attained was nearly 100%. Correspondingly, it is also observed a proportional increase in  $\gamma\text{-HCH}$  degradation along with the formation of  $\text{Cl}^-$  in solution. It is possible to conclude that the reaction pathway is conserved regarding the addition of this salt and the results obtained were the same independently the amount of salt added.

When sodium sulphate is added (Figure 18b) is possible to observe a slightly decrease for a high salt concentration. However, this variation is not significant in terms of lindane conversion. Regarding to chloride formation, the data does not show a clear tendency as the obtained differences were associated possible measurement errors.

As shown in Figure 18c, the presence of chloride ions is associated with an increase in the conversion of  $\gamma$ -HCH. This increase seems to be independent of the salt concentration as the conversion obtained was similar regardless the concentration of salt. This minor variation is certainly related with the GC-MS sensitivity measurements since it had been reported by others that the addition of chloride is associated with an improvement in dechlorination reactions [55].

#### 4.4.2 Effects of cations presence

In order to study the influence of cations presence in the lindane dechlorination reaction, different cations were added in the form of sulphate salts. The experiments were performed under the same conditions as was previously described for studying the anions presence effect (Section 4.1.4). The attained results are shown in Figure 19.

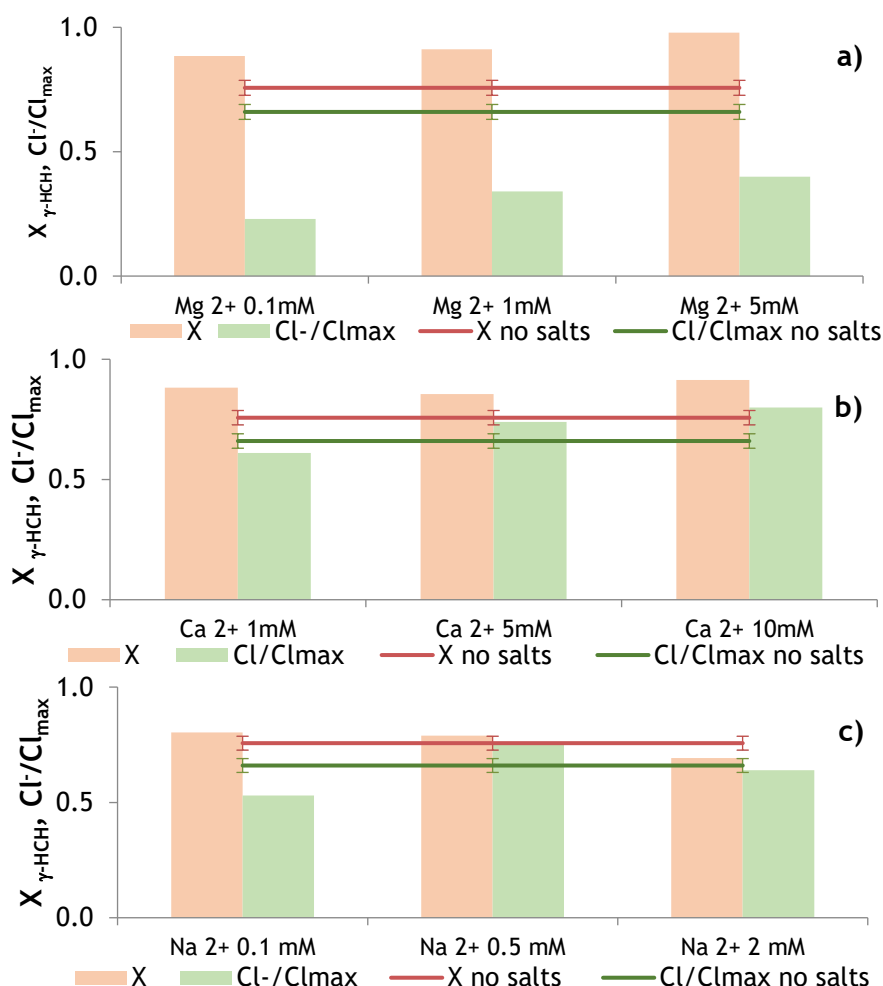


Figure 19: Effect of anions on the lindane dechlorination reaction in terms of  $X_{\gamma\text{-HCH}}$  and  $\text{Cl}^-/\text{Cl}_{\text{max}}$  at  $T=20\text{ }^\circ\text{C}$ ,  $C_{\text{Fe}}=5\text{ g/L}$  and  $C_{\text{lindane0}} = 6\text{ mg/L}$  (R15, R24-R26 and R30-R35).

In the presence of magnesium sulphate is outstanding the difference between the conversion of  $\gamma$ -HCH and the formation of  $\text{Cl}^-$ , noticeable in Figure 19a. The  $\gamma$ -HCH conversion seems to be increased by the addition of magnesium ions however the degree of

dechlorination attained is much lower than expected. This could be explained by a possible precipitation of  $\gamma$ -HCH, which solubility is already low in pure water [56]. Additionally, could as well occur the precipitation of intermediate chlorinated compounds or chlorides formed.

Moreover, the addition of calcium in the solution led to a slight increase in the  $\gamma$ -HCH conversion, as shown in Figure 19b. This increase seems to become more significant as the amount of  $\text{CaSO}_4$  used increases and it is followed by a rise in the concentration of chloride in solution, as expected.

Concerning the sodium addition (Figure 19c), as it was tested with sulphate, it has already been commented in Section 4.4.1.

## 4.5 Application to Fixed Bed Reaction Column

The implementation of HCH reduction by mZVI on a real situation (*in situ* treatment) would be performed in a similar way to reactive barriers, inserting these microparticles into the soil. Then, to bring the study to a more realistic situation, the experiments of HCH dechlorination were carried out using a tubular reactor (column).

### 4.5.1 Comparison between Batch and Column: Lindane degradation

In order to understand whether the column works properly, it was initially tested a reaction with the same operation conditions as the R15 Batch reaction. This way it is possible to compare the results in continuous and discontinuous mode, both using 6 mg/L of  $\gamma$ -HCH. The previously Equation 5 presented in Section 4.3, which represents the mass balance for a discontinuous reactor, can be manipulated into Equation 13. The mass balance for a continuous reactor is demonstrated in Equation 14. In this equation the amount of  $\text{Fe}^0$  used is normalized by the flow that goes through the column, by increasing or decreasing the contact time of the effluent with the mZVI.

$$-\frac{dC_{\text{lindane}}}{C_{\text{Fe}} dt} = k \times C_{\text{lindane}} \quad \text{Eq.13}$$

$$-\frac{dC_{\text{lindane}}}{d(W/Q_l)} = k \times C_{\text{lindane}} \quad \text{Eq.14}$$

Moreover, associating these two expressions yields the relation expressed in Equation 15. This expression represents a means to compare results obtained in continuous with results from discontinuous mode.

$$C_{\text{Fe}} dt = dW/Q_l \leftrightarrow C_{\text{Fe}} \times t = W/Q_l \quad \text{Eq.15}$$

Afterwards, knowing that in batch mode were used 5 g/L of mZVI and the maximum reaction time was 96 h, the value of  $Q_i$  was estimated to be 0.17 ml/min. With this value it is possible to attain total conversion using the same quantity of reducing agent.

After the column bed stabilization, a solution of 6 mg/L of lindane was treated at different values of  $W/Q_i$ , and the results are presented in Figure 20.

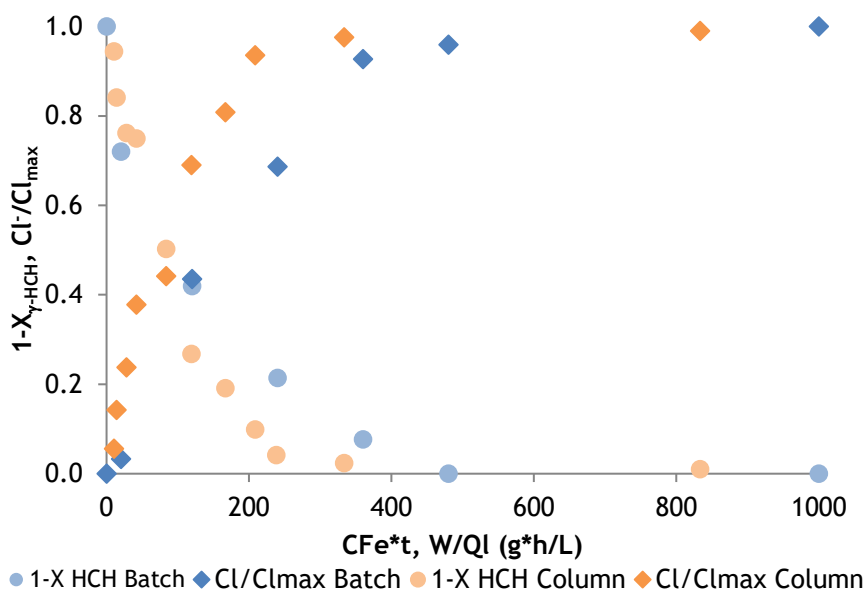


Figure 20: Lindane concentration evaluation in terms of  $1-X$  and  $Cl^-/Cl_{max}$  ( $T=20^\circ C$ ,  $C_{lindane0} = 6$  mg/L and  $pH_0=7$ ) for Batch and Column (R15 and RC1).

It can be noted that total conversion of lindane was obtained for shorter values of  $W/Q_i$  in column reactions, similarly to the chloride formation. This fact can be related to a better contact between the lindane solution and the microparticles. Even so, in both ways total conversion is attained and the resulting profile follows the same tendency. Subsequently, is verified that the results obtained batchwise can be extrapolated to a continuous mode.

#### 4.5.2 Long-term Stability Study

A very important aspect for the economy of these processes is the stability of iron microparticles with reaction time. In order to attest the mZVI stability, long-term experiments were performed in continuous mode with a time on stream of 10 days. For this purpose, two values of  $W/Q_i$  were selected. The lowest value corresponding to a flow of 0.5 ml/min ( $W/Q_i$  of 167 g\*h/L) and the higher one to 0.05 ml/min ( $W/Q_i$  of 2778 g\*h/L). The subsequent results are presented in Figure 21 where is notable that lindane conversion remains constant during 10 days of reaction. Accordingly, it is concluded that mZVI show a high stability.

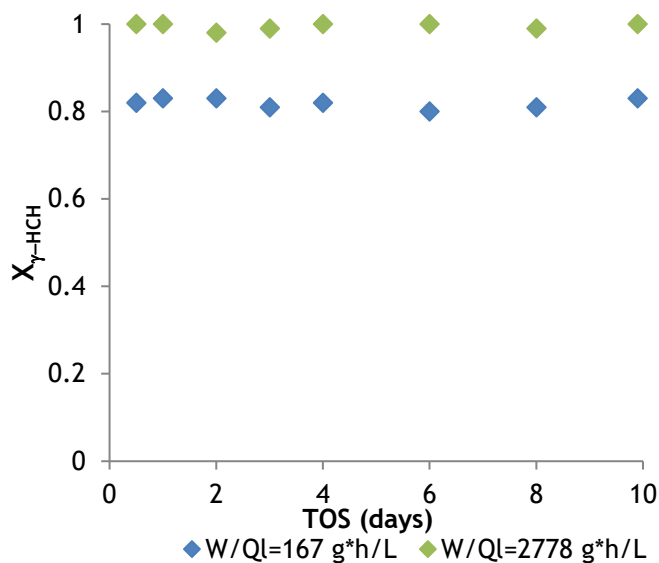


Figure 21: Lindane degradation reaction in column ( $T=20^\circ\text{C}$ ,  $C_{\text{lindane}0} = 6 \text{ mg/L}$  and  $\text{pH}_0=7$ ) for different  $W/Q_i$  values during 10 days (RC2).

#### 4.5.3 Mixture of $\gamma$ , $\alpha$ , $\beta$ , $\delta$ - HCH isomers in Column

In order to know if the dechlorination results obtained for lindane in continuous experiments also can be extrapolated to the rest of HCH isomers and to approximate the study to real operation conditions, synthetic wastewaters containing the four isomers were treated. Therefore, solutions with different concentration of HCH isomers were prepared depending on its water solubility as described in Table 5 of Section 3.2.2. The experiments were performed in a fixed-bed reactor column for a  $W/Q_i$  range between 14-2778  $\text{g}\cdot\text{h/L}$ , correspondent to 6 and 0.03  $\text{ml/min}$ , respectively.

Additionally, the results for this two experiments were compared with reaction R13 performed in batch (initial solution with 0.5  $\text{mg/L}$  of each isomer), as showed in Figure 22.

Notably, the chloride mass balance was not closed for these reactions. Regarding the mixtures that reacted in column, it was not expected achieving total  $\text{Cl}^-/\text{Cl}_{\text{max}}$ , since for these concentrations it is not possible to attain total conversion of HCH for the  $W/Q_i$  used. Nevertheless, the main reason for this low degradation degree is associated with the refractoriness of some HCH isomers, mostly  $\beta$ -HCH as mentioned in Section 4.1.1.

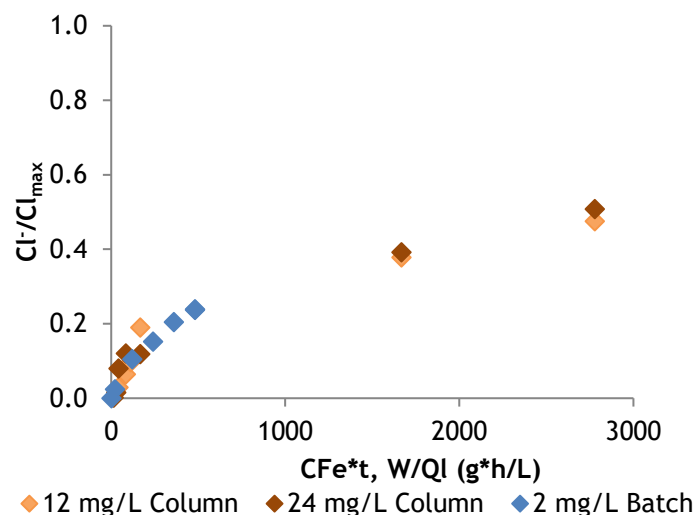


Figure 22: Degradation of different concentrations of HCH isomers in Batch and Column in terms of  $Cl^-/Cl_{max}$  at 20 °C (R13, RC3 and RC4).

#### 4.6 Reaction Pathway

It is known that Lindane degradation can occur by dechlorination (loss of 2 Cl<sup>-</sup> owing to the electron exchange between HCH molecule and zero-valent iron) or dehydrohalogenation (loss of HCl) [27, 29].

After analysing all reactions performed during the experiments, a reaction with 6 mg/L of  $\gamma$ -HCH (RC1) was elected to study the reaction pathway. In Figure 23, it is possible to observe the evolution of concentration of the different species identified and quantified during lindane dechlorination experiments.

It is notable that lindane abatement is accompanied by an increase in concentration of Cl<sup>-</sup> and benzene. Moreover, 3,4,5,6-Tetrachlorocyclohexene was detected in trace amounts by GC-MS, for short reaction times. However, it was not possible to quantify this intermediate due to its high instability [57].

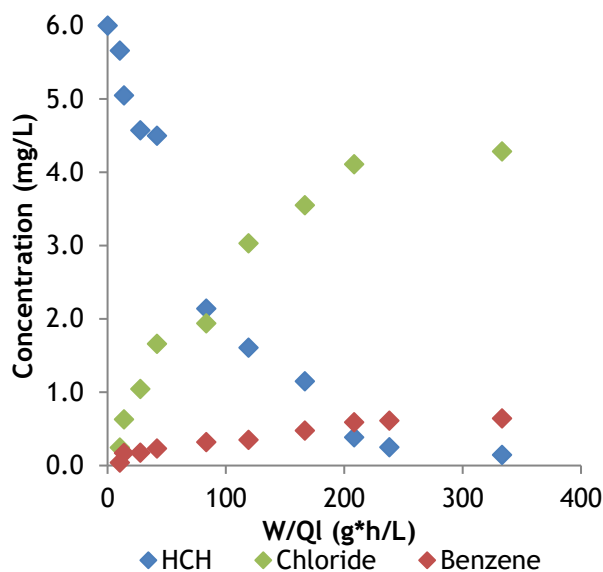


Figure 23: Concentration evolution for different compounds involved in the dechlorination of lindane ( $T = 20\text{ }^{\circ}\text{C}$ ,  $C_{\text{lindane}0} = 6\text{ mg/L}$ ,  $C_{\text{Fe}} = 5\text{ g/L}$  and  $\text{pH}_0 = 7$ ) in column (RC1).

Additionally, it was also studied the mass balance of chlorine and carbon (associated with benzene), showed in Figure 24. The curves of  $X_{\text{HCH}}$  and  $\text{Cl}^-/\text{Cl}_{\text{max}}$  are equal, meaning that the dechlorination reaction is complete and it occurs simultaneously with the formation of chloride. Moreover, from the initial HCH it is obtained chloride and benzene. Conversely, it was attained a low amount of benzene, around 40% of the theoretical expected value. This is associated with its high volatility, responsible for maintaining this compound mainly in the gas phase [58].

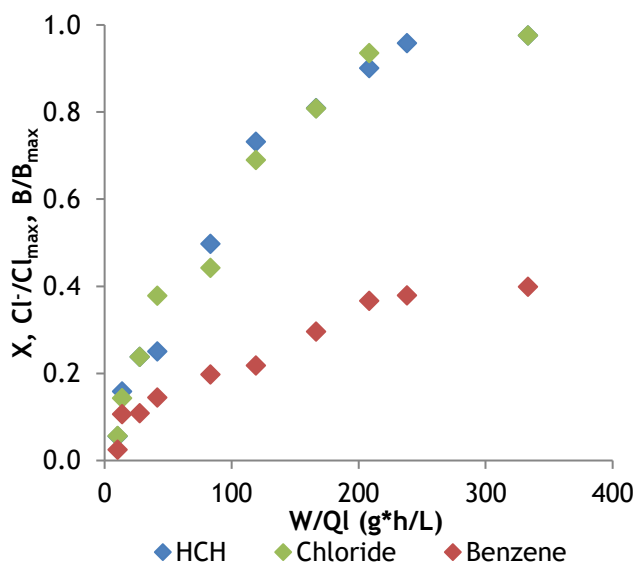


Figure 24: Evolution for different compounds involved in the dechlorination of lindane ( $T = 20\text{ }^{\circ}\text{C}$ ,  $C_{\text{lindane}0} = 6\text{ mg/L}$ ,  $C_{\text{Fe}} = 5\text{ g/L}$  and  $\text{pH}_0 = 7$ ) in terms of  $X$ ,  $\text{Cl}^-/\text{Cl}_{\text{max}}$ ,  $\text{B}/\text{B}_{\text{max}}$  (RC1).

Regarding the analysis of all the results obtained, there are two possible routes to occur lindane degradation in the presence of zero valent iron microparticles. It is estimated that this can occur by direct dechlorination to yield benzene or by a very fast three-stage dechlorination releasing two chlorides each time, resulting in the total release of 6 Cl<sup>-</sup> and the formation of benzene.

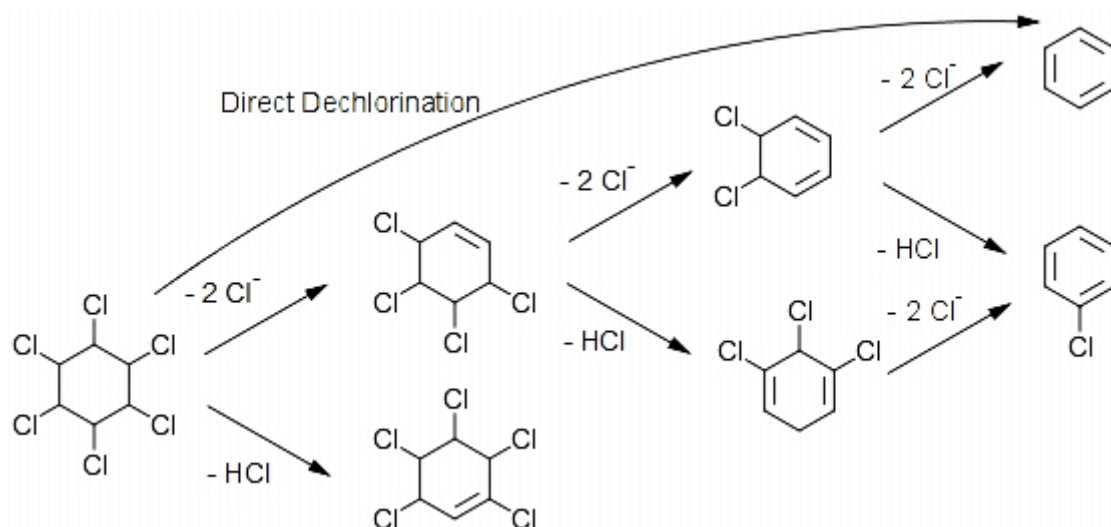


Figure 25: Proposed reaction pathway for degradation of lindane in the presence of zero valent iron microparticles.



## 5 Conclusions

### 5.1 Main Conclusions

To find a degradation process for hexachlorocyclohexanes is of extreme importance since this bioaccumulative component is spread worldwide. With this study it was possible to analyse several factors associated with its dechlorination, using zero valent iron microparticles. This process is selective towards the pollutant intended to eliminate, not deteriorating to the environment, and has a low economic cost associated when compared with similar technologies.

Firstly, dechlorination reactions for each isomer in separated were performed and the results attained for a 72 h reaction time led to establishing this reaction order:  $\gamma$ -HCH >  $\alpha$ -HCH >  $\delta$ -HCH >  $\beta$ -HCH, correspondent to a conversion of 0.93, 0.72, 0.6 and 0.45, respectively. The low value for  $\beta$ -HCH is a consequence of the refractory structure of this isomer, difficulting its degradation. Nonetheless, an experiment aside showed that is possible to attain a conversion of around 0.84 when the reaction time is extended to 312h.

In order to understand if the iron microparticles maintained their stability throughout time evolution, three consecutive reaction cycles were performed for each isomer separately. It was obtained the same conversion in all experiments, regarding the isomer in study, concluding that mZVI particles can be implemented in real situations without losing their activity. Additionally, it was analysed the coexistence of the four isomers and verified that this fact does not interfere with the degradation of each one.

A study on the operation conditions was carried out with isomer  $\gamma$ -hexachlorocyclohexane, which conclusions were then used in the development of the kinetic model. The analysis related to the effect of the initial lindane concentration, tested with 0.5, 3 and 6 mg/L, showed that the conversion attained was around 96% for all experiments. In other words, this reaction occurs according to first order law reactions, concerning the initial concentration of pollutant. Regarding the effect of the amount of iron used (1, 5 and 10 g/L), the reaction's rate achieved tends to be higher as the iron concentration increases. In order to complete this study and define a kinetic model, reactions were performed at different temperatures (10, 20 and 30 °C). It was obtained an increasing conversion along with the increase in temperature, corresponding to achieving total conversion for 72 and 96 h time reaction operating at 30 and 20 °C, respectively, and only 60% of conversion at 10 °C. Additionally, developing the kinetic model showed that the dechlorination reaction of lindane also corresponds to a first order law concerning to the amount of mZVI used. Furthermore, Arrhenius parameters were determined attaining an  $E_a$  of 55.44 kJ/mol with a pre-

exponential factor of  $6.17 \times 10^7$  which explains the considerable influence of temperature in the reaction. Nevertheless, at a temperature of 20 °C it is attainable total conversion for reasonable reaction times. Meaning that this reaction can occur normally, even in groundwater or soil with a temperature around this value. Furthermore, some data was simulated using the kinetic model established and it was confirmed its accuracy, comparing to real data attained for different operation conditions,

In order to simulate a more realistic situation, the addition of both anions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) and cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ ) was studied. In generally, these additions had no substantial effect on the conversion. However slightly bigger changes were detected when cations were present. In addition, reactions in column were also performed to approximate the study to an *in situ* treatment. For lindane degradation, the same degradation degree was attained when comparing with batch reactions. Additionally, mZVI stability and the effect of coexistence of isomers were also tested, attaining similar values to the previously tested in batch. In conclusion, the dechlorination of lindane shows a good efficacy, both in batch and column, being preferred this last one for real applications due to its continuously capacity to degrade contaminants.

To sum up, the experiments have yielded consistent results in both operating modes and it was possible to estimate the reaction pathway. Thereby, seems that the degradation of lindane occurs by direct dechlorination to yield benzene or by a very fast three-stage dechlorination releasing two chlorides each time, resulting in the total release of 6  $\text{Cl}^-$  and the formation of benzene.

## 5.2 Limitations and Future Work

Throughout this work, some limitations were faced in the experimental procedures. Some of which were not possible to overcome for a period of time, due to instruments malfunctioning which delayed the course of some experiments.

In the estimate of the reaction pathway it was notable that benzene was formed during the reaction. It is also known that this compound is characterized by a high volatility. Subsequently, for more accurate conclusions all the procedure should be optimized, minimizing the benzene lost in gas phase.

Concerning the study of ions addition to the dechlorination reaction, it was not possible to attain concrete results due to time restrictions. Therefore, it would be necessary to perform a more meticulous analysis in order to comprehend exactly how ions presence can affect the reaction in a real situation.

Since some important factors, such as mZVI stability, concentration of pollutant and reducing agent were already studied, the next step would be to add some soil to the fixed-bed reactor, simulating what would happen when introduced into the soil. Afterwards, this study should be performed with real wastewaters, instead of the synthetic ones used in this work, to verify the efficacy of the dechlorination when subject to uncontrolled factors.



## References

1. Unsworth, J. (2010). History of Pesticide Use. Retrieved 21/04/2016, from [http://agrochemicals.iupac.org/index.php?option=com\\_sobi2&sobi2Task=sobi2Details&catid=3&sobi2Id=31](http://agrochemicals.iupac.org/index.php?option=com_sobi2&sobi2Task=sobi2Details&catid=3&sobi2Id=31).
2. WHO and FAO, *The International Code of Conduct on Pesticide Management*. 2014.
3. Center, N.P.I., *Understanding Pesticide Risks*. 2016.
4. EPA (2011). Pesticides Industry Sales and Usage. Retrieved 21/04/2016, from [https://www.epa.gov/sites/production/files/2015-10/documents/market\\_estimates2007.pdf](https://www.epa.gov/sites/production/files/2015-10/documents/market_estimates2007.pdf).
5. EPA (2016, 21/04/2016). Insecticides. Retrieved 21/04/2016, from [https://www3.epa.gov/caddis/ssr\\_ins\\_int.html](https://www3.epa.gov/caddis/ssr_ins_int.html).
6. Vijgen, J., et al., *Hexachlorocyclohexane (HCH) as new Stockholm Convention POPs—a global perspective on the management of Lindane and its waste isomers*. Environmental Science and Pollution Research, 2011. 18(2): p. 152-162.
7. Manonmani, H.K., *Bioremediation of Hexachlorocyclohexane Contaminated Soil: Field Trials*, in *Pesticides in the Modern World - Pesticides Use and Management*, D.M. Stoytcheva, Editor. 2011.
8. European Food Safety, A., *Opinion of the Scientific Panel on contaminants in the food chain [CONTAM] related to gamma-HCH and other hexachlorocyclohexanes as undesirable substances in animal feed*. EFSA Journal, 2005. 3(7): p. n/a-n/a.
9. Program, N.T. (2014). Report on Carcinogens. Retrieved from <https://ntp.niehs.nih.gov/ntp/roc/content/profiles/lindane.pdf>.
10. KL, W., U. EM, and H. RA, *Differential toxicity and environmental facts of hexachlorocyclohexane isomers*. Environ Sci Technol, 1998.
11. N, N. and L. R, *Hexachlorocyclohexane Contamination and Solutions: Brief History and Beyond. Emerging Model to Study Evolution of Catabolic Genes and Pathways*. J Bioremed Biodeg, 2016. 7.
12. ATSDR (2005). Hexachlorocyclohexane. Retrieved from <http://www.atsdr.cdc.gov/toxfaqs/tfacts43.pdf>.
13. UNEP (2005). Consideration of chemicals proposed for inclusion in Annexes A, B and C of the Convention: Lindane. Retrieved from [http://www.pops.int/documents/meetings/poprc/meeting\\_docs/en/K0582616%201-8%20edited%20EJF.pdf](http://www.pops.int/documents/meetings/poprc/meeting_docs/en/K0582616%201-8%20edited%20EJF.pdf).
14. UNEP (2009). Report of the Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants on the work of its fourth meeting Retrieved from <http://chm.pops.int/Programmes/NewPOPs/DecisionsRecommendations/tabid/671/language/en-US/Default.aspx>.
15. UNEP, *Listing of POPs in the Stockholm Convention*.
16. Iwata, H., et al., *Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate*. Environmental Science & Technology, 1993. 27(6): p. 1080-1098.
17. Loomis, G.W. and O.-S.W.T.C.a.t.U.o.R. Island (1996). Soil Based Wastewater Treatment. Retrieved 15/06/2016, from <https://www.ces.ncsu.edu/plymouth/septic/loomis.html>.

18. EPA, *In Situ Treatment Technologies for Contaminated Soil: Engineering Forum Issue Paper*. 2006.
19. TechnologyWater (2014). Types of Soil Remediation Techniques and Methods. Retrieved 15/06/2016, from <http://www.technologywater.com/post/104761516702/types-of-soil-remediation-techniques-and-methods>.
20. FAO (1992). Wastewater treatment and use in agriculture. Retrieved 15/06/2016, from <http://www.fao.org/docrep/t0551e/t0551e05.htm>.
21. Authority, M.W. (2011). How Wastewater Is Treated. Retrieved from <http://www.maconwater.org/how-wastewater-is-treated>.
22. Badea, S.L., et al., *Stable isotope fractionation of gamma-hexachlorocyclohexane (lindane) during reductive dechlorination by two strains of sulfate-reducing bacteria*. Environ Sci Technol, 2009. 43(9): p. 3155-61.
23. Matsumoto, E., et al., *Bioremediation of the organochlorine pesticides, dieldrin and endrin, and their occurrence in the environment*. Appl Microbiol Biotechnol, 2009. 84(2): p. 205-16.
24. Alvarez, A., et al., *Bacterial Bio-Resources for Remediation of Hexachlorocyclohexane*. International Journal of Molecular Sciences, 2012. 13(11): p. 15086-15106.
25. Nienow, A.M., et al., *Hydrogen peroxide-assisted UV photodegradation of Lindane*. Chemosphere, 2008. 72(11): p. 1700-5.
26. Liu, X., et al., *Effects of FeS on the Transformation Kinetics of  $\gamma$ -Hexachlorocyclohexane*. Environmental Science & Technology, 2003. 37(9): p. 1822-1828.
27. Singh, R., et al., *Degradation of lindane contaminated soil using zero-valent iron nanoparticles*. J Biomed Nanotechnol, 2011. 7(1): p. 175-6.
28. Yang, S.C., et al., *Application of zerovalent iron (Fe(0)) to enhance degradation of HCHs and DDX in soil from a former organochlorine pesticides manufacturing plant*. Chemosphere, 2010. 79(7): p. 727-32.
29. Wang, Z., P. Peng, and W. Huang, *Dechlorination of gamma-hexachlorocyclohexane by zero-valent metallic iron*. J Hazard Mater, 2009. 166(2-3): p. 992-7.
30. Usman, M., et al., *Chemical oxidation of hexachlorocyclohexanes (HCHs) in contaminated soils*. Science of The Total Environment, 2014. 476-477: p. 434-439.
31. Liang, C., et al., *Persulfate oxidation of trichloroethylene with and without iron activation in porous media*. Chemosphere, 2008. 70(3): p. 426-35.
32. Xue, X., K. Hanna, and N. Deng, *Fenton-like oxidation of Rhodamine B in the presence of two types of iron (II, III) oxide*. J Hazard Mater, 2009. 166(1): p. 407-14.
33. Rodriguez-Garrido, B., et al., *Reductive dechlorination of alpha-, beta-, delta-, and gamma-hexachlorocyclohexane isomers by hydroxocobalamin in the presence of either dithiothreitol or titanium(III) citrate as reducing agents*. Environ Sci Technol, 2004. 38(19): p. 5046-52.
34. Mertens, B., et al., *Biocatalytic dechlorination of lindane by nano-scale particles of Pd(0) deposited on Shewanella oneidensis*. Chemosphere, 2007. 66(1): p. 99-105.
35. CityChlor, *In Situ Chemical Reduction using Zero Valent Iron Injection* 2013.

36. Vellanki, B.P., B. Batchelor, and A. Abdel-Wahab, *Advanced Reduction Processes: A New Class of Treatment Processes*. Environmental Engineering Science, 2013. 30(5): p. 264-271.
37. EUGRIS, *Ex situ treatment technologies*
38. Environmental, E. In-Situ Remediation. Retrieved from <http://www.ecologia-environmental.com/index.php/remediation/in-situ-remediation/>.
39. Battelle, *In Situ Chemical Oxidation (ISCO): Current Advancement*. 2009.
40. Services, E.R., *Chemical Oxidations VS Chemical Reduction - Choosing the Right Application*.
41. Schlimm, C. and E. Heitz, *Development of a wastewater treatment process: Reductive dehalogenation of chlorinated hydrocarbons by metals*. Environmental Progress, 1996. 15(1): p. 38-47.
42. EPA, *A Citizen's Guide to In Situ Chemical Reduction*. 2012.
43. Singh, R., et al., *Degradation of gamma-HCH spiked soil using stabilized Pd/FeO bimetallic nanoparticles: pathways, kinetics and effect of reaction conditions*. J Hazard Mater, 2012. 237-238: p. 355-64.
44. Shoiful, A., et al., *Degradation of organochlorine pesticides (OCPs) in water by iron (Fe)-based materials*. Journal of Water Process Engineering, 2016. 11: p. 110-117.
45. Paknikar, K.M., et al., *Degradation of lindane from aqueous solutions using iron sulfide nanoparticles stabilized by biopolymers*. Science and Technology of Advanced Materials, 2005. 6(3-4): p. 370-374.
46. Cong, X., et al., *Reductive dechlorination of organochlorine pesticides in soils from an abandoned manufacturing facility by zero-valent iron*. Sci Total Environ, 2010. 408(16): p. 3418-23.
47. Elliott, D.W., H.-L. Lien, and W.-X. Zhang, *Degradation of Lindane by Zero-Valent Iron Nanoparticles*. J. Environ. Eng, 2009.
48. Group, A., *In Situ Chemical Reduction (ISCR) Technologies for Soil, Sediment and Groundwater Remediation*. 2007.
49. ITRC, *Permeable Reactive Barrier: Technology Update*. 2011.
50. Forum, T.I.H. (2015). 13th HCH & Pesticides Forum. Retrieved 15/06/2016, from <http://www.hchforum.com/>.
51. Vega, F.A., E.F. Covelo, and M.L. Andrade, *Accidental organochlorine pesticide contamination of soil in Porrino, Spain*. J Environ Qual, 2007. 36(1): p. 272-9.
52. Confidencial, E. El Chernóbil Español. Retrieved 15/06/2016, from [http://www.elconfidencial.com/espana/2016-01-27/sabinanigo-agua-contaminada-aragon-chernobil\\_1138180/](http://www.elconfidencial.com/espana/2016-01-27/sabinanigo-agua-contaminada-aragon-chernobil_1138180/).
53. Romero, A., et al., *Degradation of Hexachlorocyclohexanes (HCHs) By Zero-Valent Iron (ZVI) Microparticles*. Chemosphere, 2016 (Pending Publication).
54. Vodyanitskii, Y.N., *Artificial permeable redox barriers for purification of soil and ground water: A review of publications*. Eurasian Soil Science, 2014. 47(10): p. 1058-1068.
55. Xu, J., et al., *Dechlorination of 2,4-dichlorophenol by nanoscale magnetic Pd/Fe particles: Effects of pH, temperature, common dissolved ions and humic acid*. Chemical Engineering Journal, 2013. 231: p. 26-35.
56. Commission, E., *Common Implementation Strategy for the Water Framework Directive*. 2005.

57. Chang, C., F. Lian, and L. Zhu, *Simultaneous adsorption and degradation of  $\gamma$ -HCH by nZVI/Cu bimetallic nanoparticles with activated carbon support*. Environmental Pollution, 2011. 159(10): p. 2507-2514.
58. ATSDR (2011). Toxic Substances Portal. Retrieved 25/06/2016, from <http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=14>.

## Annex I. Calibrations

In the course of the experimental work accomplished three calibrations were necessary to obtain the results shown previously. The results showed concerning the efficiency of the dechlorination process by degradation of HCH, release of chlorines and the formation of benzene were correlated with the integration area of the peaks obtain from GC-MS, IC and HPLC, respectively.

The eligible characteristics for a good peak are clear separation between the different peaks, absence of tails and some narrowness. An ideal analysis comprehends these features and an accurate calibration curve correlating areas with concentrations in order to optimize the results. Therefore, were tested different calibration curves and selected those with the higher R2 for each analysis.

The treatment of results was executed measuring the areas of each peak available on the analysis software and writing them in an excel sheet.

Following are the results of the calibrations used to analyse the experimental results and the respective concentration window that they can be used with desirable and trustworthy results.

### HCHs

The calibration method used to identify different HCH's isomers had been prepared previously and applied to the data processing program. The calibration curves associated with each isomer are presented in Figure A I 1 along with the specific peaks for each one. The chromatogram present in this image compares reaction R1 at time zero and at the end (96h). It is easy to observe the decrease on the concentration of each isomer and the difference in the efficiency of their removal.

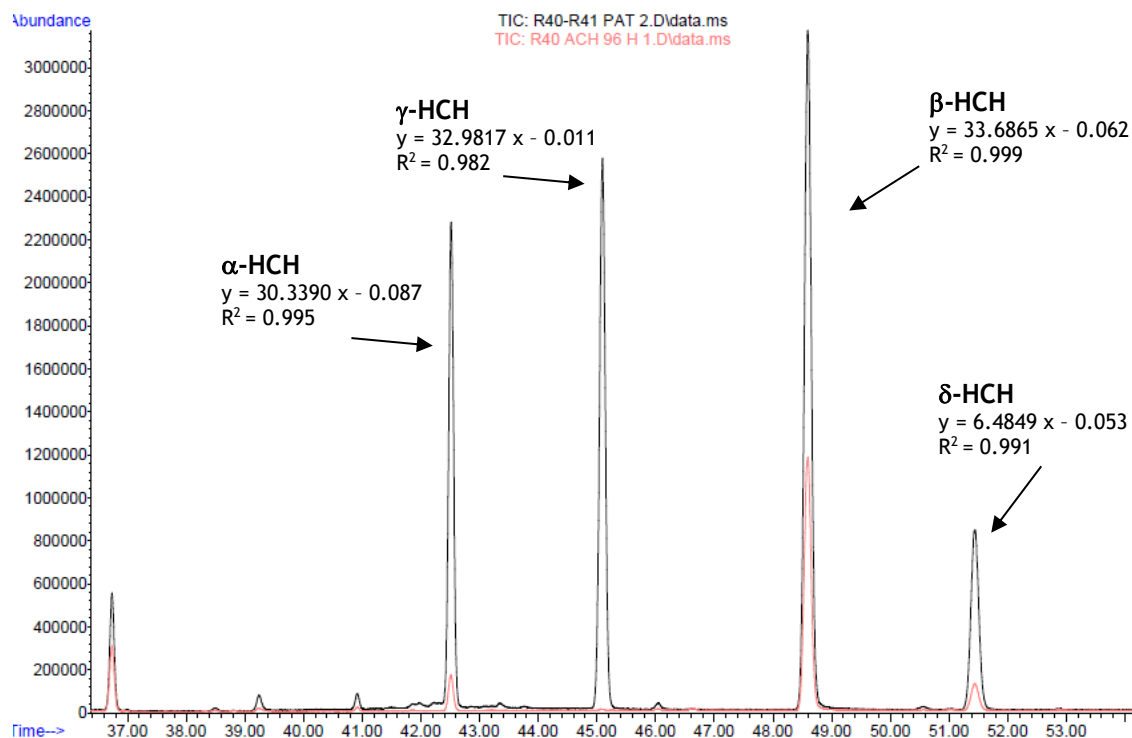


Figure A I 1: Chromatogram obtained by GC -MS for all HCH isomers and calibration curves.

## Chloride

A main solution with 1 g/L concentration in a 500 mL volumetric flask was prepared to obtain samples with different concentrations of chloride ions. A determined amount of NaCl was dissolved in ultrapure water considering a purity of 99.0% and that chlorine has a molar mass of 35 g/mol. From this solution, a designated volume was taken to attain a new solution with 20 mg/L concentration from which three other solutions were prepared in order to obtain 10, 5 and 1 mg/L.

The curve obtained is showed in Figure A I 2 and it's easy to understand that a linear regression should be drawn separately for low and high concentrations. Then, as showed in Figure A I 3 and Figure A I 4 linear regressions were obtained, one for concentrations under 2.5 mg/L and another for higher ones.

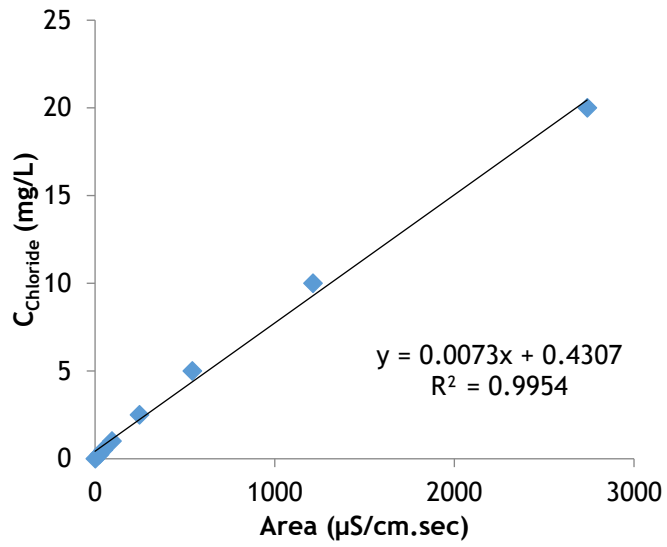


Figure A I 2: Chlorides calibration curve.

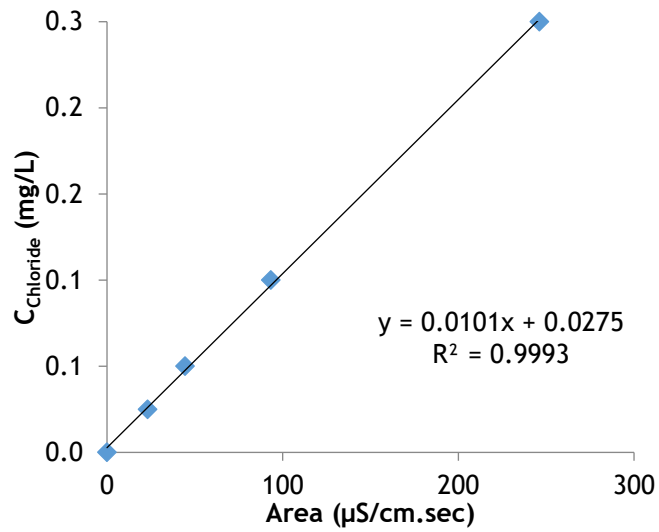


Figure A I 3: Calibration curve for low concentration of chlorides.

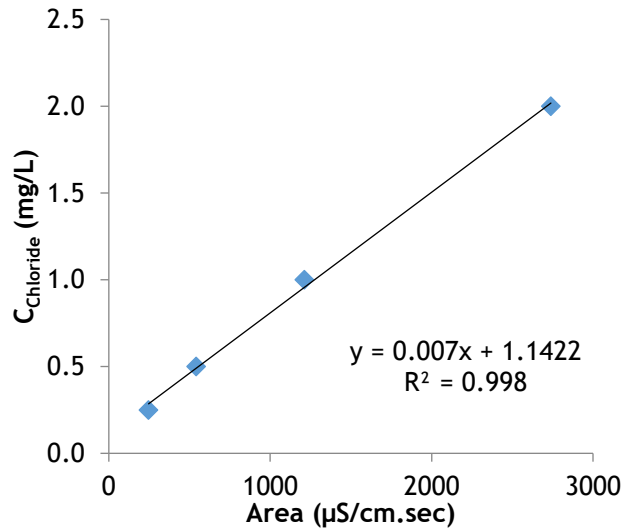


Figure A I 4: Calibration curve for high concentration of chlorides.

## Benzene

A 1 L solution with a 100 mg/L concentration was prepared knowing that benzene has a molar mass of 78 g/mol and a density of 876,5 g/L. From this main solution designated volumes were taken in order to obtain 10, 5, 2.5, 1, 0.5, 0.25 mg/L. As showed in Figure A I 5 and Figure A I 6, the polynomial curve has a better R2 but the range of concentrations used to analyse the results includes the lowest concentrations. Therefore, a new linear regression focused on low concentrations was estimated in Figure I 6, defining an intercept on the origin.

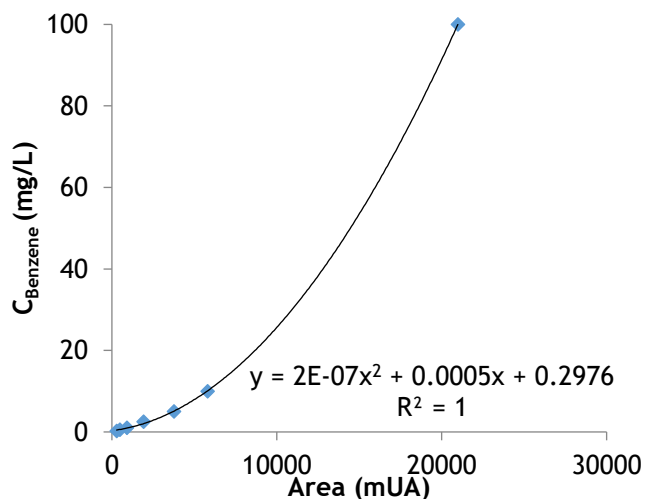


Figure A I 5: Benzene calibration curve.

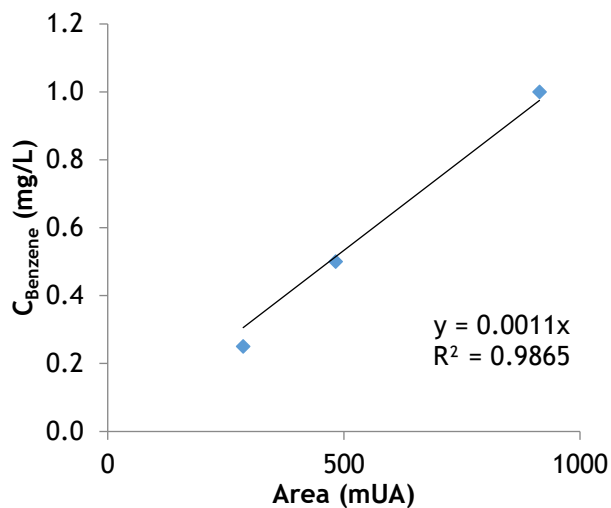


Figure A I 6: Calibration curve for low concentration of benzene.

## Annex II. Strategies to enhance $\beta$ -HCH decay

In order to improve the degradation of the isomer  $\beta$ -HCH two methods were implemented. One is to increase the reaction temperature and the other to increase its reaction time.

### Increase of Reaction Temperature

When raising the temperature to 30 °C it was found that there were no significant changes in conversion, still keeping this isomer with the lowest conversion of all four. This is easy to observe in Figure A II 1.

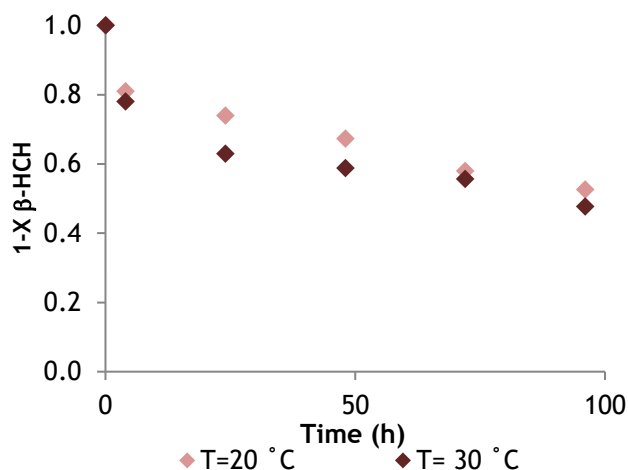


Figure A II 1: Degradation of 0.5 mg/L of  $\beta$ -HCH in terms of 1-X at different temperatures.

### Increase of Reaction Time

The reaction time was extended up to 312 hours, at which it has achieved a conversion 85% as can be seen in Figure A II 2. That is, there was an increase of about 38% compared to the conversion obtained for 96h. This is a very good result as this isomer is found aplenty in real contaminated waters and is one of the compounds listed as POPs in Stockholm Convention list [14].

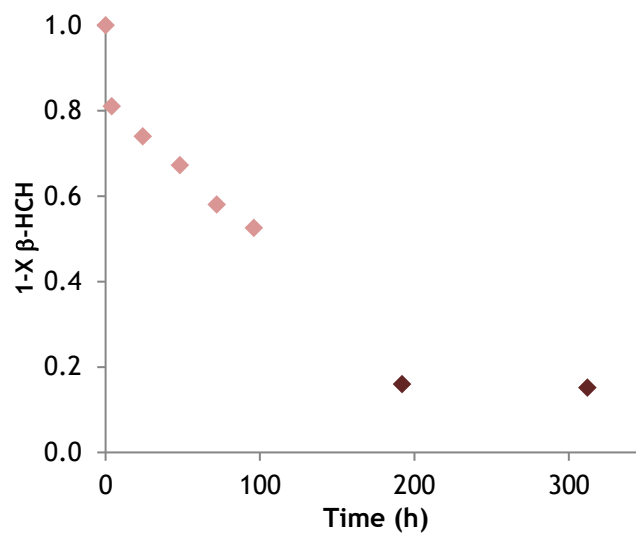


Figure A II 2: Degradation of 0.5 mg/L of  $\beta$ -HCH in terms of 1-X for longer reaction time.