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ABSTRACT

Lindane is an organochlorine pesticide, that has caused contamination of soil, water and air. This paper studies catalytic hydrodechlorination as a possible solution to the lindane problem in water streams. Several catalysts were tested. The effects of mass transfer and temperature was studied for a Ni-based and a Pt-based catalysts. A Ni-supported and a Pt-supported catalyst gave good results, but the best catalyst was Pd supported on active carbon, which provided 99% conversion in a few minutes at room temperature. Additional tests allow to discard adsorption instead of a catalytic effect. The amount of hexachlorocyclohexane compounds remaining as adsorbed on the catalyst surface was negligible.

1. Introduction

Currently, agriculture consumes about 70 % of water withdrawn from the environment [1]. In this activity, pesticides and various chemical compounds are often discharged into the environment. One of these contaminants is lindane, which is the gamma isomer of hexachlorocyclohexane (HCH), and is the only isomer with insecticidal properties [2]. Properties of the major HCH isomers can be found in the literature [3] [4]. Figure 1 shows the configurations of the five most important HCH isomers. This pesticide is commercialized in two forms: The so-called technical lindane contains a mixture of isomers, with 55-80%, 5-14%, 5-15%, 2-16% and 3-5% of α-HCH, β-HCH, γ-HCH, δ-HCH, ε-HCH, respectively [5], while pure lindane contains more than 99% of γ-HCH. In the production of pure lindane, only 5-15% of the reaction product is γ-HCH. Consequently, at least 85% of HCH produced was considered as waste, and it was discarded in landfills that were usually poorly managed [5, 6]. In addition, HCH has been used in agricultural soils for five decades because it was considered environmentally safe and not soluble in water. Nevertheless, it is a highly persistent compound in the environment. Although HCH is mainly found in landfills, the presence of the pesticide has been detected in soil [7], water (superficial, sediments and groundwater) [8][9][10] and air [11] in different concentrations. It is distributed by various means of transport such as water or atmosphere [12].
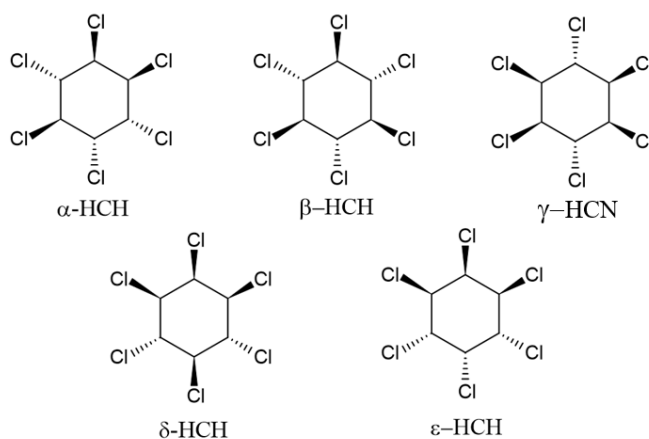
Fig 1. HCH isomers [13].

Lindane has been used in other functions apart from agriculture. Some examples include its use as a treatment for polymers or wood to repel insects, in health care to treat scabies and lice [14], and in military use [15]. However, it is a Persistent Organic Pollutant (POP) that is very difficult to degrade by light or microbial activity [2]. It is harmful for the environment and human health, and bio-accumulates in the food chain [16][10]. Lindane can bind to organic matter and it causes all kinds of harmful effects to many species that are exposed to it. It affects humans [17][18], plants [19] and animals [20][21]. Lindane is a common residue

in human tissues and fluids [22]. Lindane has also been identified in three quarters of the placentas of mothers who gave birth in public hospitals in a Spanish city [23][24][25].

According to Vijgen et al. [26], lindane production was estimated at 435.5 thousand tons, being Europe, Asia and America the major producers. With the classification of this pesticide as a persistent organic pollutant (POPs) in the Stockholm Convention (1972), it was banned in several places such as the European Union (EU). At present, there is only one known commercial lindane production plant in India.

In the EU, lindane was produced in a variety of countries such as Germany, the UK, the Czech Republic, France, Italy, Romania and Poland. Most of these countries had already stopped producing lindane from the 1990s, except for Romania, which continued to produce lindane until 2006. In Spain, there was a significant production of technical HCH. Large quantities of these wastes, even thousands of tons, were produced and stored in three locations: Sabiñánigo (Huesca) [27] , Vizcaya [28] and Porriño (Galicia) [29]. Evidence of the presence of the pesticide in the environment was found in North America [30][31][32] and different parts of Asia [33][34].

The leachates from the dumping areas and other contaminated sites constitutes a serious risk to the environment. A wide variety of techniques have been studied to achieve effective lindane removal. Some of the techniques include adsorption [35][36], electrochemical oxidation [37], dechlorination with catalysis on biological supports [38][39], use of Pd nanoparticles on a high-density polyethylene in supercritical CO_2 [40], non-zero valence ion-Cu nanoparticles supported on activated carbon [41], photocatalysis using CeO_2-TiO_2 [42], nanofiltration [43-44], or even degradation of lindane with tea extracts [45]. The most popular technique at water treatment plant level is adsorption with granular activated carbon. An example of this is the treatment plant located in Bailín (Spain) [46] to avoid the pollution of a near river with the leachate from the dumping site.

Catalytic hydrogenation is an interesting alternative, because it could avoid the consumption of activated carbon, and in addition it would destroy the pollutant instead of just transferring it to an adsorbent. Alonso et al. [47] reviewed the reactions employed for dehalogenation of organic compounds and Flid et al. [48] the catalysts and technologies for dechlorination. A review of heterogeneous catalysts in hydrodechlorination of chlorinated cyclic compounds (aromatic and HCH) is shown in Table 1. This table shows that hydrodechlorination of chlorinated aromatic compounds has been widely studied. Two main groups of catalysts can be seen: a) Those based on noble metals (Pt, Pd, Rh) and b) Those with Ni. In a few cases catalysts containing Mo, CoP, Au are employed. Many of those studies were made in gas phase (i.e. at high temperature) and the results are hardly applicable to the treatment of diluted pollutants in water, as is the case with lindane. In several cases, other compounds are added to the water (e.g. NaOH, KOH, or other bases, organic compounds). It may be expected that this addition would not be desirable in the treatment of polluted water, and thus the use of hydrogen as only reactant that should be added to the polluted water is preferable. Compared with the research on hydrodechlorination of chlorinated aromatic compounds

(chlorobencene, dichlorobencene, trichlorobencene, chlorotoluene, chlorophenol, etc), few previous works have studied catalytic hydrogenation of lindane in aqueous solutions: Schüth and Reinhard [49] tested this reaction for several chlorinated compounds with Pd/Al$_2$O$_3$ catalyst, and found that lindane was transformed to benzene; an original approach was presented by Zinovyev et al. [50], who used a multiphase reaction, i.e. in a medium containing water and iso-octane. In conclusion, few studies have been made on dechlorination of HCH with hydrogen in aqueous phase at room temperature.

This work aims to provide insight on the feasibility of using catalytic hydrodechlorination to treat water polluted with HCH and to explore the use of non-noble metals for this reaction. To this end, a variety of catalysts have been tested for this reaction on a solution of HCH with a concentration similar to that expected in a polluted water stream. All catalysts were chosen based on their activity in other hydrogenation or dehydrogenation reactions. In this selection we included Ni-based catalyst, that are widely used in hydrogen production and Pd and Pt-based catalyst that are employed in hydrogenation and dehydrogenation reactions. Finally, the selection included a Mo/ZSM5 catalyst, that was previously employed in methane aromatization [51] and thus some hydrogen-activation effect could be expected. In addition, the presence of the zeolite could improve the adsorption effect, that could be a first step in the reaction.

Table 1. Previous studies on hydrodechlorination of chlorinated cyclic compounds

Ref	Catalyst(s)	Compound(s)*	Comments
Creyghton (1995)[52]	Pt/BEA	CB	T=175 ªC
Srinivas (1996)[53]	Pt -X/Al$_2$O$_3$	CB	X= V, Mo, W T= 140-200 ªC
Schuth (1998) [49]	Pd/Al$_2$O$_3$	CB, DCB, HCH	Kinetic model
Shin (1998)[54]	Ni/SiO$_2$	CPH	150-300 ªC
Ukisu (1998)[55]	Rh-Pt/TiO$_2$, Rh-Pt/C	CT	In propanol-NaOH solution
Yakovlev (1998)[56]	Ni/C, Pd/C, Pd-Ni/C	CB, TCB,HCB	Ethanol-NaOH solution, T=70 ªC
Cesteros (1999)[57]	Ni/Al$_2$O$_3$	TCB	150-250 ªC
Tavoularis (1999)[58]	Ni/SiO$_2$	CB, CPH, CT	150-250 ªC
Benitez (2000)[59]	Pt,Pd,Rh/C, Pd/Al$_2$O$_3$, Pd/SiO$_2$	CB	
Cesteros (2000)[60]	Ni/NiAl$_2$O$_4$	TCB	250 ªC
Ukisu (2000)[61]	Rh-Pt/C	CB,CT,CBPH	Isooctane+NaOH
Menini (2000)[62]	Ni/SiO$_2$	CB, CT, CPH, CBPh…	200-300 ªC
Schuth (2000)[63]	Pd/zeolite	DCB	Several zeolites
Cesteros(2001)[64]	Ni/MgAlO$_x$	TCB	Several supports, 150-250 ªC
Keane (2001)[65]	Ni/SiO$_2$	CB	200-300
Shindler (2001)[66]	Pd/C	CPH	C cloth as support
Serguchev (2001)[67]	Ni/Cr$_2$O$_3$	HCB,HCH	Kinetic study, 123-323 ªC

Chary (2003)[68]	Ni/Nb$_2$O$_3$	TCB	250 ªC
Hashimoto (2003)[69]	Pt/Al$_2$O$_3$	CB,DCB,TCB	Fixed bed reactor
Xia (2003)[70]	Pd/C	TCPE	Organic solvents
Yuan (2003)[71]	Pd/C, Pd/ Al$_2$O$_3$	DCPH	NaOH
Keane (2004)[72]	Ni/SiO$_2$	CB,DCB,TCB	T=200-300 ªC
Murena (2004)[73]	Pd/C	CB	Reports some MCB drops
Zynovyev, 2004 [50]	Pd/C, Pt/C, Raney Ni	HCH	Triphasic system
Hashimoto (2005) [74]	Pt, Pd/ S	CB	S=SiO$_2$,Al$_2$O$_3$,TiO$_2$
Kim (2005)[75]	Ni-Mg/Al$_2$O$_3$	DCB	300 ªC
MacKenzie (2005) [76]	C	HCH	
Wu (2005) [77]	Ni/C,Ni/ Al$_2$O$_3$, Ni/SiO$_2$, Raney Ni	CB	60-70 ªC, NaOH
Calvo (2006)[78]	Pd/C	CPH	50-75 ªC, 2.5 bar
Chary (2006) [79]	Ni/CeO2	CB	300 ªC
De Lucas-Consuegra (2006) [80]	MoC, MoC/SiO$_2$	CB, DCB	150-320 ªC
Golubina (2006)[81]	Pd/C, Pd-Fe/C	DCB,TCB,HCB	50 ªC,KOH,isooctane
Gryglewicz (2006)[82]	Ni-Mo/Al$_2$O$_3$	DCDPH	30 bar
Jujjuri (2006) [83]	Pd-Yb/SiO2	CB, DCB, TCB	150 ªC
Kawabata (2006)[84]	Pd–Al-MCM-41	Several aryl chlorides	Organic solvents
Mackenzie (2006)[85]	Pd/Al$_2$O$_3$	CB	Other halogenated compounds also
Pozan (2006)[86]	Pd, Rh/C	DCPH	
Yoneda (2006)[87]	Pd/C	Substituted Chlorobenzenes	hexadecane
Yuan (2007) [88]	Ni/SiO$_2$, Ni/TiO$_2$, Ni-Au/SiO$_2$, Ni-Au/TiO$_2$	DCPH	200 ªC
Amorim (2008)[89]	Pd/C	CB,DCB	Various supports 150 ªC
Chen(2008) [90]	Ni$_x$P/SO2	CB	300 ªC
Diaz (2008)[91]	Pt,Pd,Rh/ Al$_2$O$_3$	CPH	Kinetic study
Liu (2008)[92]	Ni$_2$P/SiO$_2$	CB	300ªC
Wee (2008)[93]	Pd/Al$_2$O$_3$	TeCB	Water-ethanol
Diaz (2009)[94]	Pd,Rh/ C	CPH	Kinetic study
Janiak (2009)[95]	Pd/C	CB	
Chen (2009) [96]	NiP	CB	Varios supports, 300 ªC
Meshesha (2009)[97]	Pd/Mg(Al)O	TCB	Gas pase (50-150 ªC)
Piechocki (2009)[98]	Ni-Mo/C	DDT, DCH	150-200 ªC
Xia(2009)[99]	Pd/C	CPH	
Jujjuri (2010)[100]	Pd/SiO$_2$	CB,DCB	150 ªC

Fan (2010)[101]	XY$_2$O$_4$	HCB	X= Mg, Ca, Cu, Ni, Zn; Y =Al, Fe
Díaz (2011) [102]	Pd/C, Rh/C	MCPH	
Gryglewicz (2011) [103]	Ni-Mo/C	DCB,DCT,DCDPH	210-230 ªC, 30 bar
Baeza (2012)[104]	Pd	CPH	Unsupported Pd nanoparticles
Cecilia (2013)[105]	CoP/SiO$_2$	MCB	Various Co/P ratios
Gómez-Quero (2013) [106]	Au/Fe$_2$O$_3$	DCPH	Several solvents
Kar (2014)[107]	Pd/pillared clay	CPh	With hydrazine
Wu (2014)[108]	Ni/MCM	CB	In ethanol
Gupta (2015)[109]	Ag/reduced graphene oxide	HCH	TCB as product
Lokteva (2015) [110]	Pd/C	CB	C from sawdust pyrolysis, 150-350 ªC
Pizarro (2015) [111]	Pd, Rh/pillared clay	Chloro-cresol, TCPH	
Munoz (2016) [112]	Pt-Ni	CPH	Unsupported nanoparticles
Klokov (2016)[113]	Pd/C	CB, HCB	C from sawdust pyrolysis
Ruiz-Garcia (2018) [114]	Pt/C	CPH	
Yang (2018)[115]	Carbon Nanotubes	HCH	6 days
Ma (2020)[116]	Raney Ni	CPH	Adding bases
Yang(2020)[117]	Pd/C	HCH	Formic acid
Xiong (2021)[118]	Rh-La/SiO$_2$	CPH	
Lokteva (2022)[119]	Pd-Fe/Al$_2$O$_3$	CPH, bromophenol	Effect of reduction

* CB= chlorobenzene, CBPh=Chlorobiphenyl; CHC=Cyclohexyl chloride, CPH= Chlorophenol, CT=chlorotoluene, DCB= Dichlorobenzene, DCDPH= dichlorodiphenil, DCH= Dichlorociclohexane, DCPH=Dichlorophenol, HCH= Hexachlorociclohexane, HCB= Hexachlorobenzene, TCB= Trichlorobenzene , TCPE= trichloro-hydroxydiphenylether, TCPH = Trichlorophenol, TeCB= Tetrachlorobencene

2. Experimental

2.1. Materials

The solution of lindane was prepared with miliQ water. Extraction was made with hexane (Sigma-Aldrich, 98.5%). H$_2$ was supplied by Air Liquide. All materials were used as received.

Several commercial catalysts have been used: Ni-Mo/Al$_2$O$_3$ is a commercial catalyst produced by Haldor Topsoe (HT-500E), Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ is a commercial catalyst from BASF (Sg-9701), Pt-Cu/Al$_2$O$_3$ is a proprietary Pt based catalyst and Pd/C is commercialized by Sigma-Aldrich as Pd-5%/C. In addition, two home-made catalysts were used: Pt-Sn/MgAl$_2$O$_4$ and Mo/HZSM-5 with bentonite as binder (Mo/HZSM5). The preparation of

Mo/HZSM5 and Pt-Sn/MgAl$_2$O$_4$ catalysts has been described elsewhere [53,54]. Particle size was between 80 and 315 μm in all cases, except Pd/C that was below 80 μm.

2.2. Catalyst characterization

Textural properties of the catalysts were determined by N$_2$ adsorption-desorption analysis, with a Quantachrome Autosorb iQ3. These physical properties are shown in Table 2. Full adsorption-desorption isotherms are given in Supplementary Information.

Table 2. Textural properties of the employed catalysts.

Sample	Surface area (m^2·g^{-1})	Pore volume (cm^3·g^{-1})	Mean pore diameter (nm)
Ni-Mo/Al$_2$O$_3$	145.6	0.39	4.6
Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$	95.0	0.18	1.9
Pt-Cu/Al$_2$O$_3$	160.6	1.00	1.8
Pd/C	1,731.6	0.97	1.9
Pt-Sn/MgAl$_2$O$_4$	149.7	0.50	5.1
Mo/HZSM5	184.9	0.14	2.0

Mo/HZSM5, Pd/C and Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ show Type II-IV isotherms, corresponding to materials with macropores, although Mo/HZSM5 and Pd/C have a large volume of micropores. Macropores will not show restrictions up to high pressures. Therefore, the initial layers fill quickly. These pores will not be filled, and no condensation will occur. However, Pt-Cu/Al$_2$O$_3$ has a type III isotherm. It has a large pore size, although it has a small hysteresis loop. Therefore, the pore shape should be an inverted cone. Consequently, adsorption will take place easily, being difficult the exit from the pore. Finally, Pt-Sn/MgAl$_2$O$_4$ and Ni-Mo/Al$_2$O$_3$ show type IV isotherms, in which it is difficult to reach surface equilibrium when the pressure starts to drop. These catalysts have a large pore size and a large hysteresis cycle, which is often associated with ink-bottle shaped pores.

The chemical composition of the Pd/C, Pt-Sn/MgAl$_2$O$_4$ and Mo/HZSM5 catalysts was found in literature. Mo/HZSM5 catalyst included 5.7% of MoO$_2$, 70.8% of HZSM-5 and 23.6% of bentonite, as binder. The remaining catalysts were analyzed by X-ray fluorescence (Table). All components are given as a percentage by mass (wt%).

Table 3. Composition of the catalysts

Sample	Ni	MoO$_2$	Al$_2$O$_3$	MgO	La$_2$O$_3$	Pt	Na	Cu	Sn
Ni-Mo/Al$_2$O$_3$	5.7	21.2	73.1	-	-	-	-	-	-

Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$	39.7	-	38.3	10.4	11.6	-	3.4	-	-
Pt-Cu/Al$_2$O$_3$	0.4	-	98.1	-	0.2	0.25	-	0.5	-
Pt-Sn/MgAl$_2$O$_4$	-	-	49.7	49.7	-	0.3	-	-	0.3

X-ray diffraction measurements were carried out using a Ru2500 RIGAKU diffractometer, with a rotative Cu anode, operated at 40 kV and 80 mA and at room temperature. A graphite monochromator is used to select K$_\alpha$ radiation. The conditions were: diffraction angle (2θ) ranges from 5° to 70° with a 0.03° step and t = 1 s/step. XRD spectra are shown in Supplementary Information. The main phases found are given in Table 4. In some cases, the peak corresponding to the metal is not seen, because the small amount of metal and the high dispersion.

Table 4. Species found in XRD for each sample

Sample	Species found by XRD
Ni-Mo/Al$_2$O$_3$	Al$_2$O$_3$, NiAl$_2$O$_4$, MoAl$_2$O$_4$
Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$	Al$_3$Ni, Mg$_4$Al$_2$(OH)$_{14}$.Al(OH)$_3$,MgO
Pt-Cu/Al$_2$O$_3$	Al$_2$O$_3$
Pt-Sn/MgAl$_2$O$_4$	MgAl$_2$O$_4$, Mg$_5$Al$_3$(OH)$_{16}$
Pd/C	Mostly amorphous

2.3. Procedures

An initial concentrated solution was made with 12 mg of lindane in 2 L. First, the solution was heated at 60 °C with vigorous stirring for two hours in a 3 L beaker. Then, the solution was stirred for 24 h at ambient conditions. The agitation time was long because of the low solubility of lindane in water. From this concentrated solution, a 600 ppb solution was prepared to be used in the experiments. That concentration was selected by considering control reports of lindane in different hydrographic sources in Spain, where the highest concentration reported was 618 ppb [120].

For the short-term experiments carried out, a 500 mL three-necked flask was used as a batch reactor. The flask was located in a water bath to reach working temperatures. For heating and agitation, a magnetic stirrer (STUART UC-152) was used. The temperature (T), H$_2$ flow rate (Q_{H_2}), stirring speed (Str), reaction time (t_r) and catalyst mass (W_{cat}) were the studied

variables. The working ranges for these parameters are collected in Table . The conditions that will be named as normal working conditions (nw) are a temperature of 20-24 ªC, Q_{H_2} of 50 mL·min^{-1}, stirring velocity of 662 rpm, 1 g of catalyst, t_r of 0.5 h and 300 mL of solution.

Table 5. Working parameter range.

T, ºC	20 – 60
Q_{H_2}, mL·min^{-1}	50 – 100
Stir, rpm	0 – 883
t_r, h	0.5 – 3
W_{cat}, g	0 - 1

The solution was added to the flask and heated to the working temperature and then the catalyst was introduced into the batch reactor and a stream of hydrogen was bubbled.

At the end of the reaction time, the solution was vacuum-filtered with a Büchner funnel, to remove the catalyst, and subjected to liquid-liquid extraction, to obtain a more concentrated solution. The working concentration of lindane is low, so two liquid-liquid extraction were carried out with hexane for 100 mL of problem solution. The objective was to increase the signal achieved in the GC-MS. 10 mL of hexane were used for the first extraction, and 5 mL for the second one. Both extractions need vigorous stirring for 15 min. The two phases are easily distinguished, and easily separable.

The same procedure was carried out for three experiments at room temperature conditions but without catalyst. Those experiments were intended to observe whether the reaction takes place only in the presence of H$_2$.

In addition, two more studies were performed using 2 L of solution in a beaker of 3 L where Pt-Cu/Al$_2$O$_3$ and Pd/C catalyst were used in standard working conditions. The reaction time was modified as a function of the catalyst due to the different reaction rate. In order to test if adsorption was affecting the results with the catalysts showing the highest conversion, the said catalyst was extracted in hexane once it had been removed from the reaction medium.

A gas chromatograph with mass spectrometry detector (Shimadzu GCMS-QP2010 Ultra) and a capillary column (TRB-50.2PONA 100 % dimethylpolysiloxane, 50 m x 0.20 mm and 0.50 μm internal width) was used to quantify the lindane concentration after filtration of the solution. The GC analysis conditions were: oven temperature 180 ªC, and the injection and detector temperatures 275 and 220 ªC, respectively.

The conversion of lindane was calculated from equation (1):

$$\text{Conversion (\%)} = \left(1 - \frac{c_f}{c_o}\right) \cdot 100 \qquad (1)$$

where C_o and C_f are the initial and final concentration of lindane in the solution (μg·L^{-1}).

In order to compare several catalysts, the kinetic constant has been obtained, assuming a first order reaction, according to equation (2), but using a kinetic constant per unit of catalyst

mass, in which case the variation of lindane concentration with time is related with the amount of catalyst, according to equation (3):

$$(-r_A) = -\frac{dC_A}{dt} = k_{obs} \cdot C_A \qquad (2)$$

$$-\frac{dC_A}{dt} = \frac{w}{V} \cdot k \cdot C_A \qquad (3)$$

where r_A is the reaction rate ($mol \cdot s^{-1} \cdot L^{-1}$), k_{obs} is the observed kinetic constant for lindane conversion (s^{-1}), k is an intrinsic kinetic constant per unit of catalyst concentration ($L \cdot s^{-1} \cdot g^{-1}$), t the time, V the working volume (L), w the mass of catalyst used (g) and C_A the concentration of lindane in the solution ($mol \cdot L^{-1}$). From equations (2) and (3), the intrinsic kinetic constant can be obtained from the conversion after a given time and the mass of catalyst:

$$Ln\ (1 - x) = -k \cdot \frac{t}{V} \cdot w \qquad (4)$$

where, x is the lindane conversion. The kinetic constants will be determined from equation (4). To make those experiments, different catalyst masses are used. Other experimental parameters were established as in the standard experiment.

3. Results and discussions

Preliminary experiments were made to check if the dehydrohalogenation reaction takes place in the working system without the presence of a catalyst. As shown in Figure 2, the reaction did not take place in the medium without the presence of catalyst. This can be stated because the conversion of lindane never reached in the blank experiments a percentage higher than 5%. When working with such low concentrations, this could be within the experimental error. Consequently, the reaction in the absence of catalyst was negligible.

Three repetitions of the experiments at 20 ªC also were carried out for the most extensively studied catalysts (Pt-Cu/Al$_2$O$_3$ and Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$). The obtained conversions were 24.9$\pm$2.0 and 93.4$\pm$2.4 for Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ and Pt-Cu/Al$_2$O$_3$ respectively. It can be concluded that the deviation of the conversion was not exceeding 3% in any case.
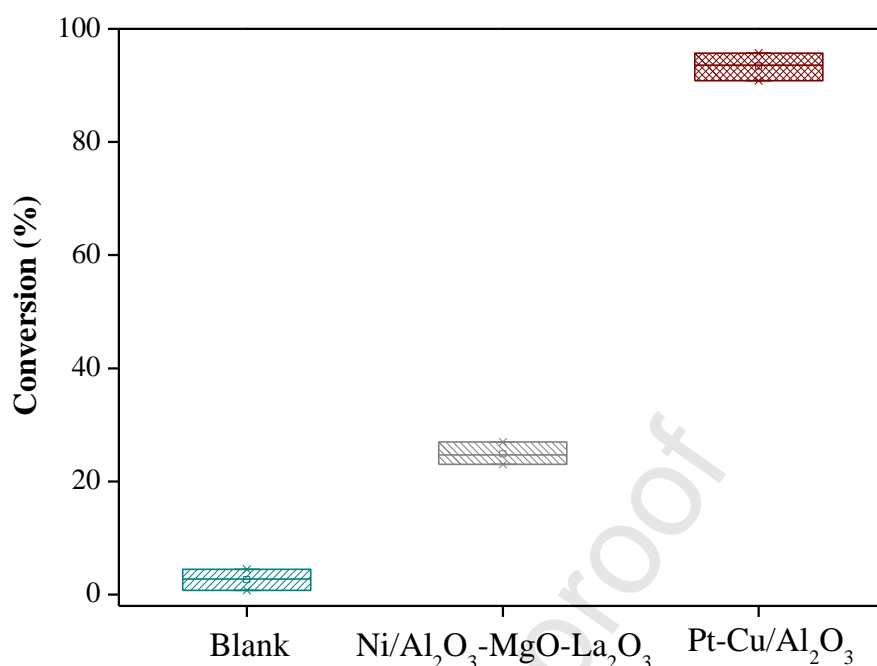
Fig 2. Reproducibility of catalytic dehydrohalogenation on two catalysts and blank experiment, based on three repetitions.

A series of test were carried out with different catalyst, both commercial and synthesised in our laboratory. All experiments were carried out in standard conditions (Table 5). As can be seen in Fig 3, in most cases the conversion improved by increasing operating temperature, as may be expected from Arrhenius' equation. However, for the Pt-Cu/Al$_2$O$_3$ catalyst, the observed behaviour was the opposite, with better conversion at lower temperatures. The best result were achieved with the Pd/C catalyst, where 100% conversions was achieved at both temperatures. However, it was considered that perhaps lindane was adsorbed by the activated carbon of the support, so that adsorption was masking the chemical reaction. This hypothesis will be checked later.

Although in general working at higher temperature increased the reaction rate, an industrial process requiring heating of the water would be too expensive. The following work will focus on the Pt-Sn/MgAl$_2$O$_4$, Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ and Pd/C catalysts, because they provided the best conversions at lower temperature.
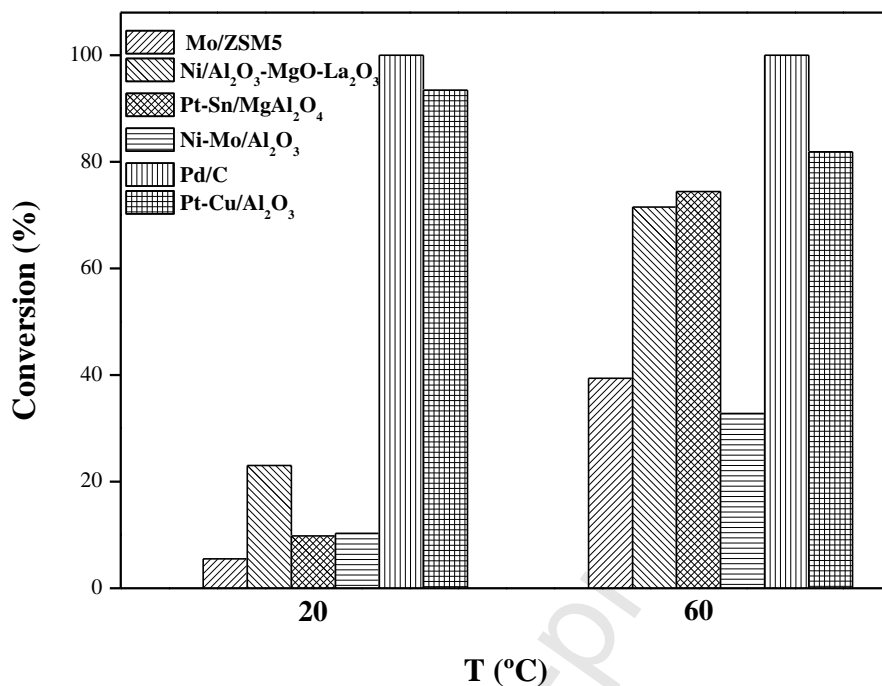
Fig 3. Catalyst screening.

The good conversion obtained by Pd/C (100%) was expected because previous studies on the removal of chlorinated aromatics with a similar Pd/C catalyst [56], already showed remarkable results. Concerning Ni catalysts, the conversion increases with temperature both for Ni-Mo/Al$_2$O$_3$ and Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$, although the second one achieved higher lindane removal (71.5%) at 60 ªC. However, the conversion at room temperature was poor, being 23% for Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$. This is not in agreement with a previous study of Ni-containing catalysts for this type of reaction [50], although in the last case a Ni-Raney catalyst was employed.

Pt-Cu/Al$_2$O$_3$ catalyst showed interesting results at both temperatures. Whereas at 20 ªC the conversion was 93.5%, at 60 ªC the conversion was reduced (81.9%). This catalyst is interesting because it contains also Ni, and Munoz et al. [112] found that the addition of Ni together with Pt stabilises the catalyst, so Pt is not deactivated.

Finally, the catalyst with Mo (Mo/ZSM5) presented uninteresting results at both working temperatures (<40%). Hagh and Allen [122] presented an effective and fast elimination of all chlorinated benzenes with a catalyst containing Mo. However, the working conditions in that work were less economically favourable (high reaction temperature, 325 ªC) and they employed a Ni-Mo catalyst in a different support.

3.1. Pt-Cu/Al$_2$O$_3$ and Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ catalysts

Figure 4A shows the behaviour of catalyst Pt-Cu/Al$_2$O$_3$ under different temperatures, for two hydrogen flow rates. At 20 and 40 ªC, the achieved lindane conversion was independent of the hydrogen flow. However, working at 60 ªC there is a noticeable difference in lindane conversion with either H$_2$ flow rates. The conversion is notoriously worse with lower hydrogen flow rate. This may be due to a lower presence of hydrogen in the medium, as the solubility of hydrogen in water decreases at higher temperatures, this effect being increased by the lower mass transfer when the H$_2$ flow rate was smaller.
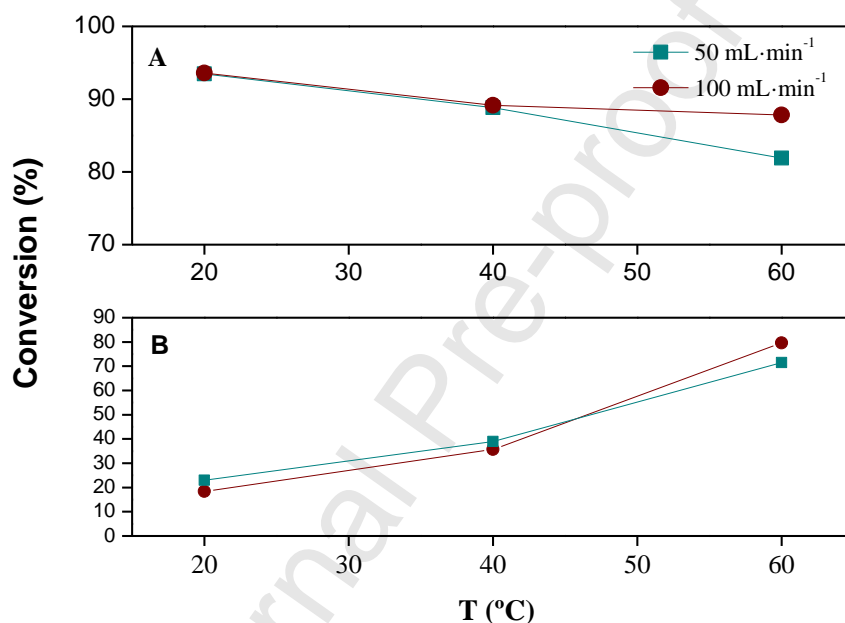

Fig 4. Conversions at several temperatures and H$_2$ flows. A: 3.1.   Pt-Cu/Al$_2$O$_3$ catalyst; B: Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ catalyst

Fig 4B shows the behaviour of Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ by varying the hydrogen flow and the temperature. The catalysts show different trends with varying temperature. While Pt-Cu/Al$_2$O$_3$ shows a clear tendency to work better at low temperature (Fig 4A), Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ shows better results with increasing temperature (Fig 4B). The better conversion with Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ at high temperature may be explained by the usual increase in kinetic constant with temperature according to the Arrhenius equation. However, Pt-Cu/Al$_2$O$_3$ shows better performance at low temperatures. An explanation is that for Pt-Cu/Al$_2$O$_3$, which is the most active catalyst, the lower solubility of hydrogen at higher temperature makes the mass transfer become the rate determining step.

Regarding the effects caused by modifying the hydrogen flux, both catalysts showed similar conversions at the two lowest temperatures (variation of less than 5% between the two

experiments). The difference with respect to the flow rate for Pt-Cu/Al$_2$O$_3$ is not too noticeable when working at 60 °C. The decrease in conversion at lower flow rate may be due to a lower mass transfer coefficient for hydrogen. Therefore, the medium does not have the same concentration as in the high flow case. Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ (Fig 4B) shows slightly lower conversions at 60 °C than those of catalyst P. On spite of the effects of temperature and hydrogen flow rate, we have considered that it is more interesting to follow the study at room temperature, because it would be too expensive to heat the water in a treatment plant. In addition, a flow rate of 50 mL·min^{-1} will be employed, since at low temperature this gas flow rate provided the same conversion as a higher one.

The next study carried out concerns the stirring speed (Fig 5). The other parameters were fixed according to normal working conditions. Stirring speed was varied between 0 and 833 rpm. An increase of lindane removal from the medium is clearly visualised with increasing the agitation. This result suggests an important influence of the mass transfer on the reaction, at least with the most active catalyst and the stirring rates below 700 rpm. This effect may be even more relevant for low concentrations of the residue. The agitation did not affect either catalysts equally. While with Pt-Cu/Al$_2$O$_3$ the conversion increased drastically (63.8%), with Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ increased only by 17.4%. Clearly, the effect of mass transfer limitations at low stirring rates was more visible for the highest reaction rates.
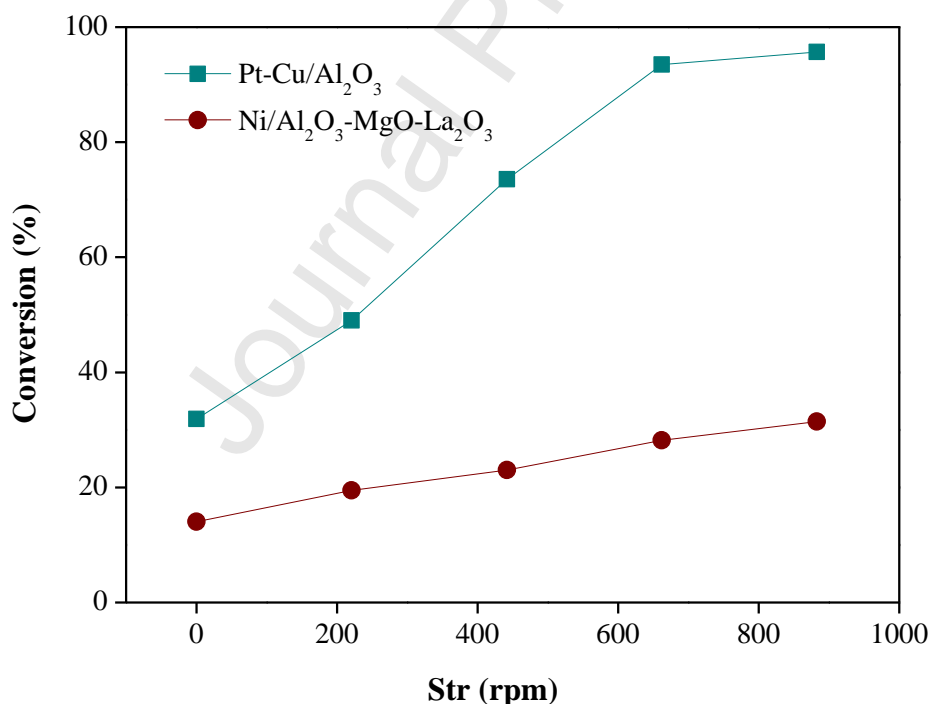

Fig 5. Pt-Cu/Al$_2$O$_3$ and Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ with variable stirring rate.

From linear plot of ln (1-x) respect to catalyst mass, according to equation 4, observable kinetic constants were determined (Figure 6). The conversions obtained by Pt-Cu/Al$_2$O$_3$

were higher, so its kinetic constant is higher (1.25 L·s^{-1}) than by Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ (0.16 L·s^{-1}). Despite the higher reaction rate of Pt-Cu/Al$_2$O$_3$, this does not mean that it is economically profitable, due to the different chemical composition of the catalysts. Pt-Cu/Al$_2$O$_3$ contains 0.3 wt% in Pt, which makes this catalyst significantly more expensive. We will compare both catalysts by relating the kinetic constant with the price of the most expensive metal contained in the catalyst and the content of such metal in the catalyst. Equation (5) will be used for this comparison.

$$\frac{k}{€} = \frac{k}{m_{\%wt} \cdot C} \tag{5}$$

where $m_{\%wt}$ is the percentage in mass of the most valuable metal and C is the price of metal per mass unit (€·g^{-1}).

By using equation (5), 8.23 and 18.46 (L·s^{-1}·€$^{-1}$) are obtained for Pt-Cu/Al$_2$O$_3$ and Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$, respectively. With these values, it may be deduced that the use of Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ would be economically advantageous over Pt-Cu/Al$_2$O$_3$. Other economic factors may affect the decision, such as the higher volume of reactor needed in the case of the Ni-based catalyst.
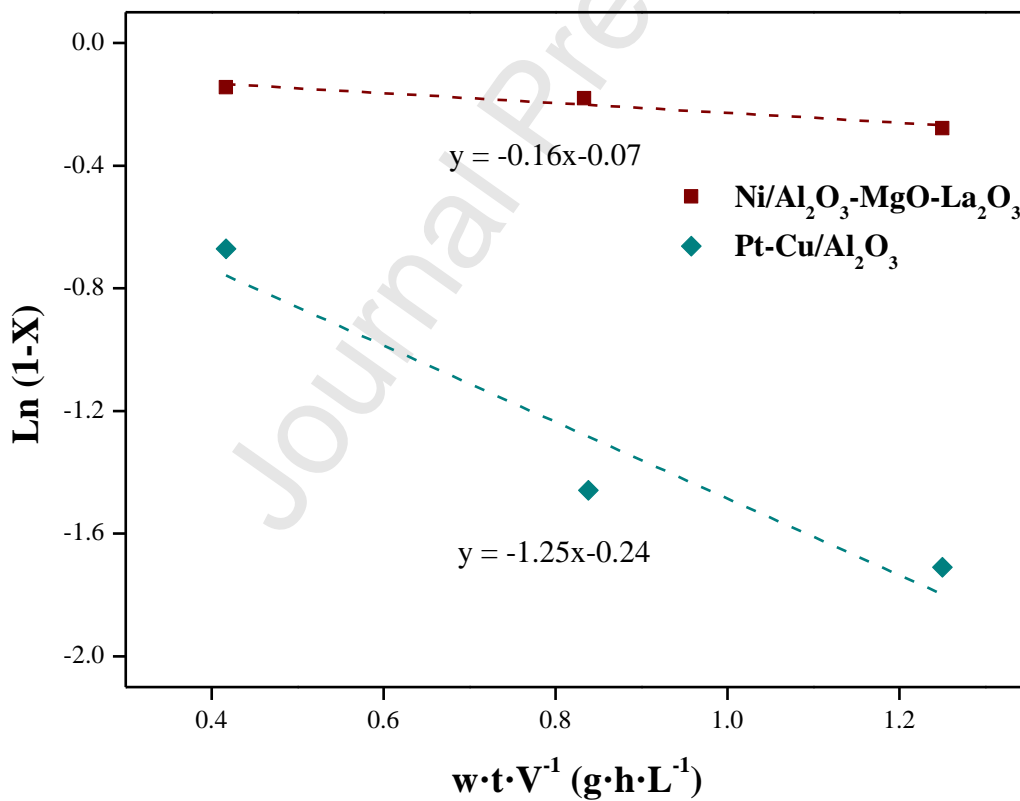

Fig 6. Evaluation of the kinetic constant for two catalysts using experiments with variable amount of catalyst.

Otherwise, we considered the possibility that the catalyst was adsorbing the pesticide, without hydrogenation occurring. For this reason, we carried out experimentation with the used catalyst, with the purpose of demonstrating the non-accumulation of contaminant in the catalyst. We found similar conversions (91.7 %), which suggests that the adsorption was not playing a significant role in the removal of pollutant, but was mainly a catalytic reaction.

Finally, an experiment was carried out with a 7 ppm solution, i.e. with a much more concentrated solution than in previous experiments. Normal working conditions were employed, except for time and volume, which were increased to 3 h and 2 L. A conversion of 48.5 % was achieved, falling short of the levels obtained for lower volumes and concentrations. This conversion was smaller than the expected value according to equation 4 (the larger volume should be compensated by the larger time). Two hypotheses could explain this lower conversion: a) The catalyst was working by adsorption and since the ratio mass of lindane/mass of catalyst was much higher, the maximum amount of adsorption had been achieved, and b) The lower agitation in terms of energy per unit of volume resulted in a lower mass transfer coefficient. To remove doubts about the possible saturation of the catalyst, an extraction with hexane was applied on the used catalyst, and 0.03 μg of lindane were found as adsorbed amount. This mass represents 0.0002% of the total initial mass contained in the batch reactor, so we can discard the adsorption of lindane as the main reason for the disappearance from the solution. Therefore, the lower energy per unit of volume and therefore the smaller mass transfer coefficient was considered as the reason for the low conversion in that experiment.

3.2. Pd/C catalyst

A series of experiments was carried out with the Pd/C catalyst, which achieved excellent conversion (99.7%). This could be due to adsorption, because activated carbon a good adsorbent, and in fact it is used as standard adsorbent for the retention of lindane in water treatment plants [46]. Under normal working conditions, no traces of lindane were detected with GC-MS. These results are in agreement with those presented in Xia et al. [70], where almost complete conversions of lindane in aqueous media were achieved within 35 min.

Moreover, the amount of catalyst was reduced in other experiment (0.25 g) in order to check its conversion and possible lindane retention. The conversion was still excellent (99.15%). Furthermore, experiments with 0.25 g at different times (Fig 7) show that the remmal of lindane with the Pd/C occured at very short times. This behaviour is agrees with the work by Yang et al. [117], where the same catalyst was used for 4 cycles and the lindane conversion was not affected.

Experiments by modifying different operational parameters would be meaningless, because the changes made did not denote an improvement in the pollutant conversion. For this reason, experiments were carried out at higher concentrations and volumes of solution.

To prove that lindane removal was not only because lindane was adsorbed, experiments were carried out by reusing the catalyst (0.1 g). The initial concentration was increased, to 6 ppm lindane. The rest of the parameters were those defined by normal working conditions. The average conversion for the three experiments was 99.9%. An extraction with hexane was carried out on the catalyst. The analysis of the hexane solution revealed that the amount of lindane present on the catalyst was only 0.18 mg, representing only 6.53% of the lindane fed to the reactor. Consequently, most lindane was not retained in the AC by adsorption, and catalytic dehydrohalogenation was the main reason for the lindane removal, also with the Pd/AC catalyst.
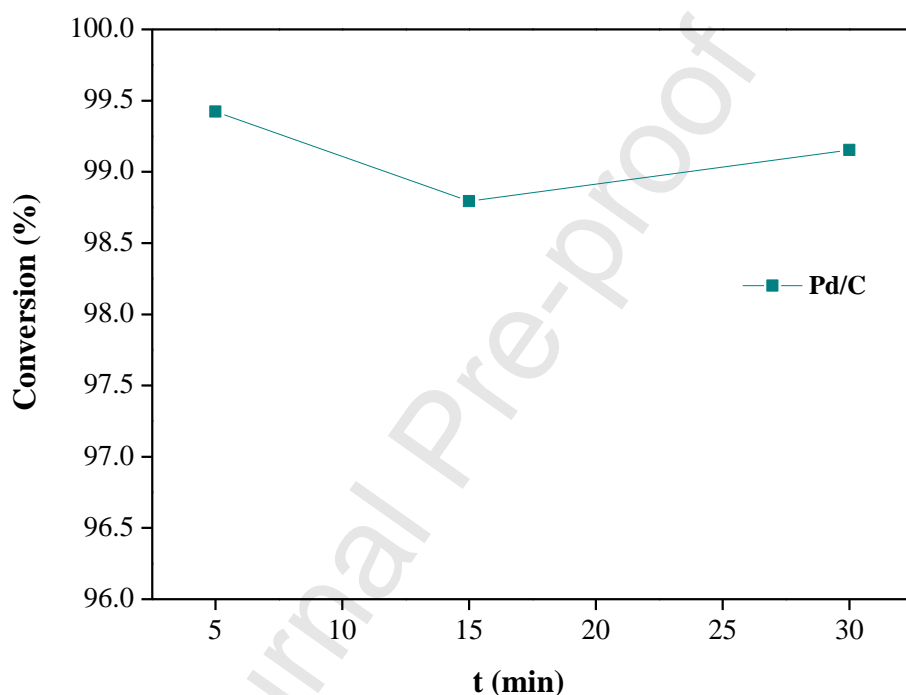
Fig 7. Conversion vs time using Pd/C catalyst.

Finally, an experiment was carried out with a larger volume of solution (2 L) with a concentration of 7 ppm. The reaction took place over a period of 1 h. The remaining conditions of the experiment are those specified as nw. The conversion was 99.95 %, while the lindane retained on the catalyst represented only 0.12 % of the total initial feed. This experiment was the only one in which a product of the dehydrohalogenation reaction has been identified. GC-MS quantified the presence 0.48 mg of δ-PCH (Pentachlorohexene, Fig 8). This amount of product represents 3.9% of the initial lindane addition. This byproduct is not found in other publications [47] [48], although δ-PCH has been identified in studies involving palladium-FeO composite catalysts [61]. Therefore, dehydrohalogenation of lindane is taking place inside the catalyst, but this product was partially retained in it. Furthermore, no other potential products of lindane dehydrohalogenation, such as 1,3,5-

trichlorocyclohexane, were found. This fact points to a fast removal of chlorine after the first two atoms are substituted by hydrogen.
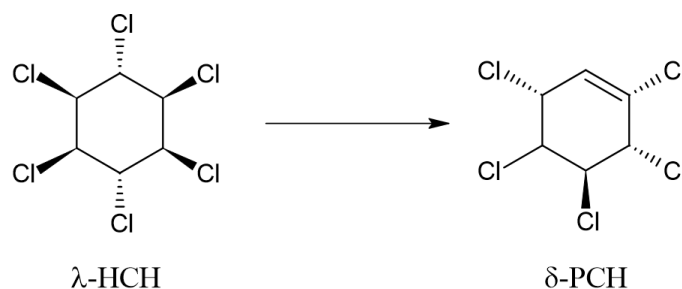

Fig 8. Lindane hydrogenation to δ-PCH

4. Conclusions and outlook

A study was carried out on lindane hydrogenation, with several catalysts used in other hydrogenation or dehydrogenation reactions.

Firstly, a screening was carried out to determine which catalysts are the most effective in removing lindane. at room temperature, and Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$, Pt-Cu/Al$_2$O$_3$ and Pd/C showed the best conversions.

Secondly, tests were done with Ni/Al$_2$O$_3$-MgO-La$_2$O$_3$ and Pt-Cu/Al$_2$O$_3$ by modifying different operational parameters. Conditions to avoid mass transfer effects on reaction rate were studied. Of these two catalysts, Ni/Al$_2$O$_3$-MgO- La O$_3$ is more cost-effective, although Pt-Cu/Al$_2$O$_3$ provided higher reaction rate. Finally, the adsorption of lindane in Pt-Cu/Al$_2$O$_3$ was found to be negligible, confirming that the removal of lindane was due to a catalytic reaction and not to adsorption.

Among the tested catalyst, Pd/C has exhibited the most promising results. With this catalyst at normal working conditions, conversions higher than 99.1% were always achieved. In fact, pesticide removal is relatively fast, with similar conversion achieved at times between 5 and 30 min. No lindane was found after extraction with hexane on the used catalyst, which suggest that it was removed by catalytic dehydrogenation, and not simply adsorbed on the activated carbon of the support.

The achieved lindane removal in those experiments did not meet the water quality standards for human consumption (0.1 μg·L^{-1} for all HCH isomers according to the EU water quality commission). However, the combination of catalytic dehydrohalogenation with other processes could be advantageous. For example, the combination of catalytic hydrodehalogenation with activated carbon adsorption would reduce the amount of activated

carbon used in water treatment plants. As a result, the costs of the plant operation could be reduced.

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CRediT authorship contribution statement

Ruiz-Gutierrez: Investigation, Data curation, Writing – original draft. J. Lasobras: Methodology, Formal analysis, Writing –review & editing. M. Menéndez: Conceptualization, Resources, Writing – review& editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

+H$_2$

γ-HCH

Ni/Al$_2$O$_3$
Pt/Al$_2$O$_3$
Pd/C
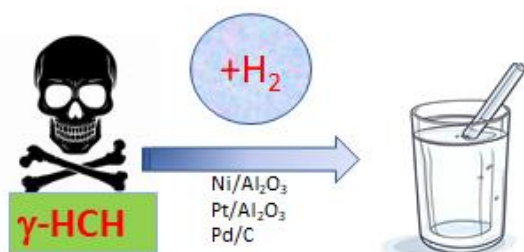
Highlights

- Several catalysts tested for hydrodechlorination of lindane in water

- Pt based is more active than Ni based catalyst on a mass basis

- Ni based catalyst is preferable than Pt catalyst in a cost/performance basis

- Pd on active carbon was the most active catalyst tested

- The potential effect of adsorption masking catalytic activity was discarded