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Deactivation of a Pd/AC catalyst in the hydrodechlorination of chlorinated herbicides

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ABSTRACT

This work analyses the stability of a palladium on activated carbon (Pd/AC) catalyst in the ambient-like conditions hydrodechlorination (HDC) of the organochlorinated herbicides 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) as well as 2,4-dichlorophenol (2,4-DCP), a precursor in the synthesis of the second. Continuous long term experiments (100 h time on stream) were performed at mild operating conditions (30 °C, 1 atm). The composition of the reaction effluents was analyzed and their ecotoxicity (Microtox) measured. In all cases, a significant decrease of ecotoxicity was observed due to the high dechlorination achieved. The Pd/AC catalyst maintained a constant activity along the HDC of 2,4-DCP, while it suffered an important deactivation in the HDC of 2,4-D and MCPA. From characterization of the fresh and used catalyst the adsorption/deposition of reaction byproducts on the active sites can be recognized as the main cause of deactivation. The use of activated carbon as support reduces the negative effect that the released chloride ions usually provoke on other HDC catalysts.

1. Introduction

Chlorophenoxy herbicides, like 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4-dichlorophenoxyacetic acid (2,4-D), are commonly used for the control of plant growth. On the other hand, 2,4-dichlorophenol (2,4-DCP) is used primarily as an intermediate in the preparation of the second one. These species have been identified in water bodies where they can enter by different ways [1–3]. Concentrations of pesticides from 10 to 100 mg/L have been found in aqueous wastes from pesticides containers cleaning and agricultural industries and within a wider range (1 to 1000 mg/L) in the wastewaters from pesticides manufacturing plants [4]. Low concentrations of these hazardous pollutants have been also detected in municipal wastewater treatment plants [5].

The high toxicity and low biodegrability of these compounds have caused that they are considered chemicals of main concern for the environment [6,7]. Different techniques have been used for the removal of these organochlorinated pollutants, including adsorption [8–11] and advanced oxidation processes (AOPs) [12–14]. The combination of advanced oxidation processes with biological treatment has been claimed as a promising cost-effective and environmentally friendly solution [1,15]. Reductive techniques have been used for the conversion of organochlorinated pollutants to less toxic compounds, thus providing a detoxifying step prior to biological oxidation. Some recent works have reported promising results on the use of electrocatalytic hydrogenolysis with Pd-modified cathodes, although further research is needed to achieve higher degradation efficiency at lower cost [16,17]. Catalytic hydrodechlorination (HDC) has demonstrated its capability to deal with aliphatic and aromatic organochlorinated pollutants, like chloroethlylenes, chlorobenzenes or chlorophenols or even more complex molecules as alachor, diuron or clopyralid in water using catalysts based on precious metals as active phase [18–24]. This process can operate under mild conditions (temperature and pressure) and is suitable within a wide concentration range. Pt, Rh, Ru and specially Pd have shown a high activity in that reaction and regarding the support, most of the hydrodechlorination studies in the literature have used alumina or activated carbon (AC). The stability of those catalysts is a crucial issue due to the high cost of precious metals. However, the catalysts developed so far for HDC usually have shown a short life due to rapid deactivation [19,25,26]. Different studies have associated that loss of activity to chloride poisoning, sintering, leaching of the active phase or accumulation of chlorine species on the catalyst surface [27–29]. Recent works on HDC of trichloroethylene and 4-chlorophenol in water with Pd catalysts have established a higher resistance to deactivation of the catalysts supported on AC compared to those on alumina [19,26].

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The better performance of Pd/AC catalyst could be associated to its high resistance to the chloride released during the reaction. The activated carbon interacts strongly with that chloride, protecting the metallic active phase.

The aim of this work is to study the HDC of three chlorinated compounds 2,4-DCP, 2,4-D and MCPA with an own-made Pd/AC catalyst, focusing the attention on its stability. In a previous study [20], this catalyst showed a very good performance for detoxification of chlorophenols-bearing synthetic wastewater through HDC, yielding a high activity with 4-chlorophenol, which was maintained upon long term experiments (100 h on stream) in a continuous stirred tank reactor. The objective now is to learn on the stability of the catalyst when dealing with more complex organochlorinated molecules. The causes of deactivation are analyzed in depth from the characterization of the fresh and used catalysts.

2. Experimental

2.1. Chemicals

Aqueous solutions of 2,4-DCP (>99.0% purity, Aldrich), 2,4-D, and MCPA (>98.0% purity, Aldrich) 0.352, 0.352 and 0.705 mM, respectively, were always used. Those concentrations are equivalent to 25 mg/L of organic chlorine. All the chemicals used were of analytical grade and supplied by Aldrich.

2.2. Catalyst preparation

The 0.5 wt.% palladium catalyst (Pd/AC) was prepared in our lab by incipient wetness impregnation of an activated carbon supplied by Merck (BET surface area ≈950 m^2/g; bulk density ≈ 0.5 g/cm^3; particle size ≈ 1.5 mm). The impregnation solution consisted in $PdCl_2$ (Sigma-Aldrich) dissolved in 0.1 N HCl. The volume of the impregnating solution exceeded by 30% the total pore volume of the activated carbon. Impregnation was followed by drying at room temperature for 2 h and overnight at 60 °C. Then, calcination at 200 °C in air atmosphere and reduction at 150 °C under continuous H_2 flow, were carried out.

2.3. Hydrodechlorination experiments

Two replicates of each hydrodechlorination run were carried out in a continuous basket stirred tank reactor (Carberry Spinning Catalyst Basket) from Autoclave Engineers, provided with temperature, pressure and gas flow control. The aqueous solution of each organochlorinated reactant was fed to the reactor at 4 mL/min and H_2 was continuously passed at 50 N mL/min. A catalyst loading of 2.95 g/L was always used, so that the space-time was fixed at 2.95 kg_{cat} $h/mol_{Cl.}$ All the experiments were performed at 30 °C, atmospheric pressure and 600 rpm stirring velocity. The progress of the reaction was followed by analyzing periodically samples of the exit liquid stream taken with a fraction collector (FC203B-Gilson) along the 100 h on stream of the experiments. The data reproducibility was better than ±5%. The existence of internal and external mass transfer limitations is discarded in our experimental conditions, as demonstrated in previous studies [30,31].

The organic compounds in the effluent from HDC of 2,4-DCP were analyzed by GC with a flame ionization detector (GC 3900 Varian) using a 30 m long × 0.25 mm i.d. capillary column (CP-Wax 52 CB). 2,4-D, MCPA and the aromatic reaction byproducts were quantified by HPLC (Varian Prostar 325) with a UV detector using a C18 as stationary phase (Valco Microsorb-MW 100-5 C18) at 280 nm and a mixture of acetonitrile and acid water (acetic acid 0.1%) as mobile phase at 0.5 mL/min. Analysis of chloride was performed by ionic chromatography (Metrohm 790 Personal IC). The pH was measured with a pH meter (CRISON).

Ecotoxicity measurements were carried out by a bioassay following the standard Microtox test procedure (ISO 11348-3, 1998), based on the decrease of light emission by the marine bacteria *Vibrio fischeri* (*Photobacterium phosphoreum*), using a Microtox M500 Analyzer (Azur Environmental), in order to determine of EC_{50} values of the reaction compounds.

2.4. Catalyst characterization

Several analytic techniques were used to characterize the fresh and used catalyst BET surface area, micropore volume and narrow mesopore volume (2–8 nm) were calculated from the 77 K N_2 adsorption–desorption isotherms obtained in a Micromeritics apparatus (Tristar 3020). Approximately 0.15 g of sample were used in each test. Samples were previously degassed for 12–16 h at 150 °C and a residual pressure at 10^{-3} bar in a Micromeritics sample degass system (VacPrep 061). The elemental composition of the catalysts was analyzed by a CHNS analyzer (LECO CHNS-932). Thermogravimetric analyses were performed in a Mettler SDTA851e model TGA apparatus under 50 N mL/min continuous air flow. A weighted amount (approaching always 20 mg) of sample was heated at 2 °C/min up to 110 °C, temperature that was maintained for 1 h in order to remove the humidity of the samples. Subsequently, the samples were heated at 2 °C/min up to 800 °C.

The bulk palladium content was determined by inductively coupled plasma–mass spectroscopy (ICP–MS) in a Perkin-Elmer model Elan 6000 Sciex apparatus equipped with an autosampler (Perkin-Elmer model AS 91). The samples were previously digested for 15 min in a microwave oven, using a mixture of several acids at 250 °C.

The catalyst surface was analyzed by X-ray photoelectron spectroscopy (XPS) with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer (pass energy of 20 eV) and a Mg KR ($h\nu$ = 1254.6 eV) X-ray source, powered at 120 W.

Metal dispersion on the catalysts was determined from CO chemisorption at room temperature in a Micromeritics Chemisorb 2750 automated system equipped with ChemiSoft TPx software. Before chemisorption measurements, the samples were reduced in H_2 flow at 150 °C for 2 h and then cooled down to ambient temperature in He flow. The stoichiometry of CO adsorption on Pd was assumed to be 1:1 [32].

3. Results and discussion

3.1. HDC of 2,4-DCP, 2,4-D and MCPA

Fig. 1 shows the results from the long-term HDC experiments. Adsorption onto the activated carbon lead to C and Cl unbalances during the early stages before the steady state was reached. After that, those balances were always closed in more than 93 and 95%, respectively. Fig. 2 shows the reaction pathways deduced in each case from the identified reaction products. The HDC of 2,4-DCP led to the formation of 2-chlorophenol (2-CP) and phenol (Ph) in addition to HCl. Previous works have reported that HDC of 2,4-DCP proceeds via 2-CP as the sole partially dechlorinated byproduct due to the occurrence of steric hindrance, where the Cl atom in *ortho* position is less susceptible to attack [33–35]. Although phenol was the most hydrogenated byproduct identified, others previous works have demonstrated that HDC of 2,4-DCP, under different operating conditions can produce more hydrogenated byproducts, like cyclohexanone and cyclohexanol [36,37].

The reaction products identified from 2,4-D HDC were 2-chlorophenoxyacetic acid (2-CPA) and phenoxyacetic acid (PA). Yamanaka et al. [38] studied the HDC of 2,4-D with several Pd catalysts and concluded that the formation of PA upon successive

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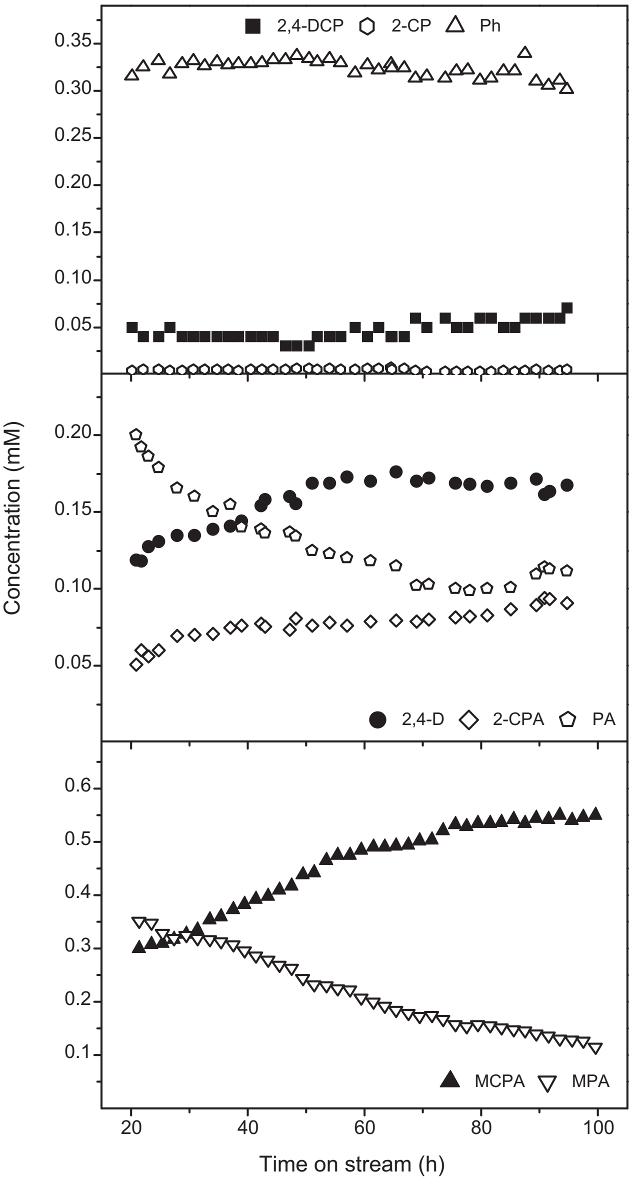

Fig. 1. Exit concentrations upon time on stream from HDC of 2,4-DCP (a), 2,4-D (b) and MCPA (c) with a Pd/AC catalyst (30 °C, 1 atm, 2.95 kg_{cat} h/mol_{Cl}).

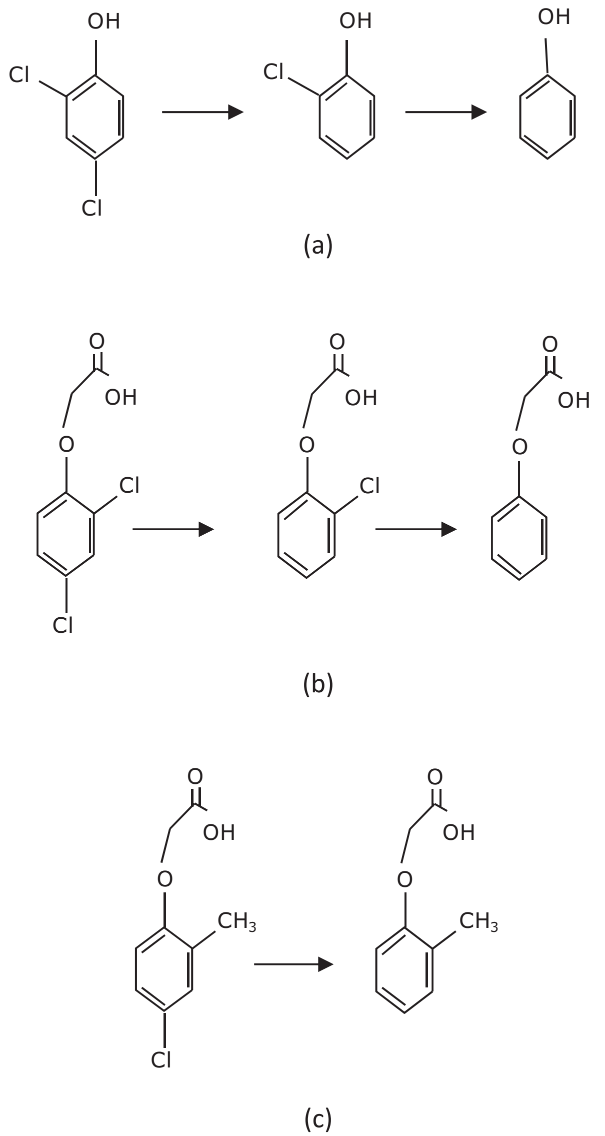

Fig. 2. HDC pathways for (a) 2,4-DCP, (b) 2,4-D and (c) MCPA.

reactions through 2-CPA and 4-chlorophenoxyacetic acid (4-CPA). According to the products selectivity, these authors suggested that the HDC of 2,4-D occurred faster at *para* than *ortho* position and, consequently, 4-CPA is not always detected. The same reaction pathway has been described for the electrocatalytic reductive dechlorination of 2,4-D [17,39,40].

In the HDC of MCPA, 2-methylphenoxyacetic acid (MPA) was the only reaction product detected in addition to HCl and no further hydrogenation was observed under the operating conditions used.

The efficiency of HDC for the abatement of ecotoxicity has been evaluated from EC_{50} values of the starting compounds and the reaction products determined by the Microtox test. Table 1 summarizes the results obtained as well as the range of values reported in the literature by other authors. The byproducts from HDC showed significantly higher EC_{50} values than those of the corresponding starting compounds, thus indicating the reduction of ecotoxicity achieved upon HDC. The experimental EC_{50} values determined in this work are in general in reasonable agreement with those reported in the literature although it is also true that the literature range is fairly wide in some cases. The highest EC_{50} values correspond in all cases to the non-chlorinated byproducts.

3.2. *Catalyst stability*

Catalyst deactivation represents an important drawback for potential application of HDC. Among the different causes of deactivation of Pd catalysts poisoning by HCl is the most widely accepted [19,41,42]. Nevertheless, so far there is no a general agreement

Table 1
EC_{50} values obtained by the Microtox test and reported in literature.

Compound	This work EC_{50} (mg/L)	Other authors EC_{50} (mg/L) range	Reference
2,4-DCP	3	1–6	[7,36,54,55]
2-CP	22	1–34	[36,55,56]
Ph	24	15–42	[36,57]
2,4-D	130	20–60	[7,58]
2-CPA	148	–	–
PAA	300	75	[59]
MCPA	75	12–75	[7,60–62]
MPA	150	300	[60]

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and whereas several authors suggest that the HCl released during the HDC reaction does not have any significant effect [43,44] some other state that it causes an important loss of activity even at low concentrations [16,26,41].

The HDC of 2,4-DCP, 2,4-D and MCPA was carried out at the same concentration of organic chloride ($C_0 = 25$ mg/L). The initial rate of HDC ($(-r_{\mathrm{HDC}})$, $\mathrm{mmol_{Cl}/kg_{cat}\,h}$), defined as the rate of Cl removal once the pseudo-steady state was reached (≈20 h time on stream), was determined from the concentration of $\mathrm{Cl^-}$ in the effluent. Values of 289, 200 and 181 $\mathrm{mmol_{Cl}/kg_{cat}}$ h were obtained with 2,4-DCP, 2,4-D and MCPA, respectively. Some authors have analyzed the dependence of HDC activity on the number and position of chlorine atoms and the presence of some other substituents in the aromatic ring. Nevertheless, there is no general consensus. Benitez and Del Angel [45] using a Pd/C catalyst established the following order of reactivity: chlorophenol > chlorotoluene > dichlorobenzene, for HDC water–methanol medium, suggesting that the rate of HDC of those molecules is increased by the presence of electron donor groups such as $-\mathrm{CH_3}$ and $-\mathrm{OH}$. Janiak and Okal [25] found the following sequence: 3-chlorotoluene < 1,3-dichlorobenzene < 3-chloroanisole < 1-chloro-3-fluorobenzene < 3-chloroaniline, stabilizing a correlation with the electronegativity of the heteroatom bound to the chlorobenzene ring. Regarding the number of chlorine atoms of the molecule, Keane [42] observed that the HDC rate of several chlorophenols decreased as the number of chlorine atoms increased. A similar conclusion was obtained by Xia et al. [46] with a wider diversity of polychlorophenols: monochlorophenol > dichlorophenol > trichlorophenols > pentachlorophenol. This conclusion is consistent with the reduction of the electron density of the aromatic ring associated to the presence of Cl substituents [47].

The performance of the Pd/AC catalyst upon 100 h on stream in the HDC of 2,4-DCP, 2,4-D and MCPA in terms of reactant conversion is shown in Fig. 3. In the case of 2,4-DCP, the catalyst showed a fairly stable behaviour with only slight changes upon the 100 h on stream ($X_{20\,\mathrm{h}} \approx 85\%$; $X_{95\,\mathrm{h}} \approx 80\%$). The concentration of the chlorinated intermediate, 2-CP, remained also practically constant along the experiment. This stability of Pd on activated carbon catalysts in the HDC of chlorophenols has been previously reported [20,26,36]. However, in the case of 2,4-D and MCPA a progressive decrease of conversion upon time on stream can be observed, indicative of an important deactivation of the catalyst. In the former case, the exit concentration of 2,4-D and 2-CPA increased and that of PA decreased up to around 50 h on stream and then the catalytic activity remained practically stable yielding an almost constant 50% conversion of 2,4-D. A quite similar behaviour showing a constant residual activity was observed by Ordoñez et al., [19], in the HDC of trichloroethylene with a commercial Pd/AC catalyst. The experiment with MCPA showed a progressive deactivation of the catalyst upon the whole time on stream tested which becomes less pronounced at the end of the experiment where the MCPA conversion trends to stabilize at a fairly low value around 20%. Thus, the Pd/AC catalyst suffered a severe deactivation in this case.

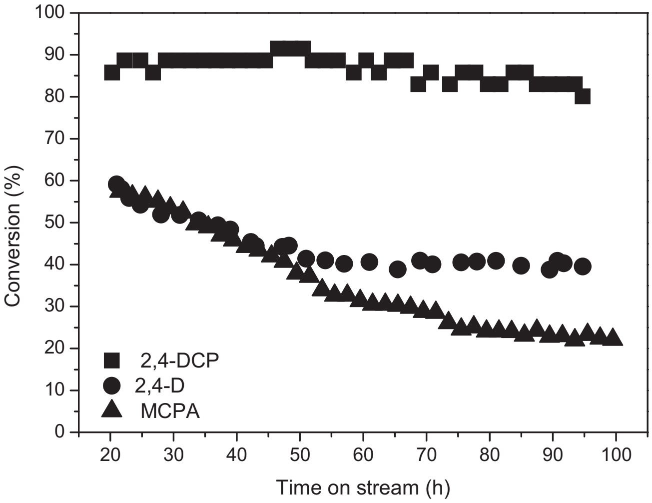

Fig. 3. Conversion of 2,4-DCP, 2,4-D and MCPA upon time on stream.

The following well-known equation has been used to describe the rate of deactivation:

$$-\frac{da}{dt} = k_d \times (a - a_\infty) \qquad (1)$$

where k_d is the deactivation kinetic constant ($\mathrm{h^{-1}}$) and a is the catalyst activity (dimensionless, from 0 to 1) defined as the ratio between the values of reaction rate (2,4-D or MCPA disappearance) at time t and the initial. From the mass balance in a continuous stirred tank reactor, the following expression is obtained:

$$a = \frac{(-r)_t}{(-r)_0} = \frac{X_t}{X_0} \qquad (2)$$

where X_0 and X_t correspond to the conversion of the starting compound at the initial and t time, respectively. Integration of Eq. (1) with limits $t = 0$; $a = 1$; $t = t$; $a = a$; (corresponding $t = 0$ to the time when the pseudo-steady state in the effluent was reached) leads to:

$$a = \frac{X_t}{X_0} = (e^{-k_d \times t}) \times (1 - a_\infty) + a_\infty \qquad (3)$$

Fitting of the experimental data to Eq. (3) was accomplished using non-linear regression (Origin 6.1). The results are depicted in Fig. 4 and the values of the deactivation kinetic constant and the

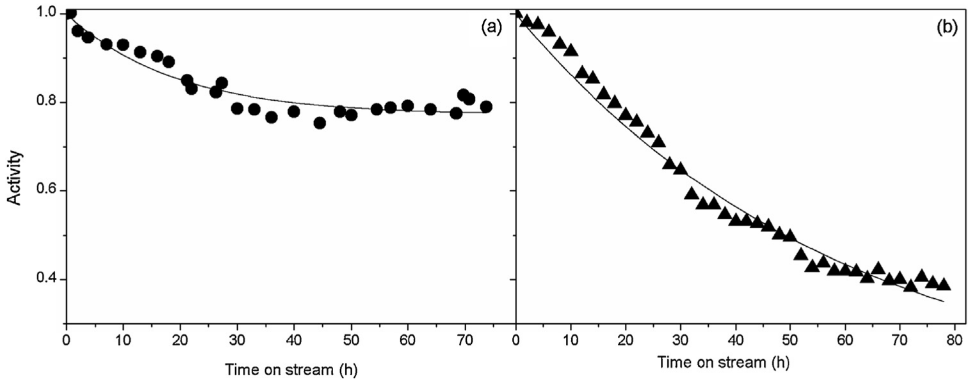

Fig. 4. Fitting of the experimental results from long term experiments of 2,4-D (a) and MCPA (b) HDC to the deactivation model.

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Table 2
Values of the deactivation kinetic constant and residual activity of Pd/AC catalyst in the HDC of 2,4-D and MCPA.

Catalyst	Starting compound	k_d (h^{-1})	a_∞	$\Sigma\chi^2$	r^2
Pd/AC	2,4-D	0.0533 ± 0.0071	0.7721 ± 0.0097	0.0005	0.918
	MCPA	0.0170 ± 0.0017	0.1142 ± 0.0535	0.0008	0.982

Table 3
Characterization of the fresh and used Pd/AC catalyst.

Catalyst	Fresh	Used in 2,4-DCP HDC	Used in 2,4-D HDC	Used in MCPA HDC
A_{BET} (m^2/g)	1025	360	119	93
A_{ext} (m^2/g)	175	96	79	81
$V_{micropores}$ (cm^3/g)	0.35	0.09	0.02	<0.01
$V_{mesopores}$ (cm^3/g)	0.040	0.030	0.027	0.024
Dispersion (%)	32	26	18	8
C (%)	88	79	78	82
Pd_{bulk} (wt.%)	0.48	0.32	0.22	0.20
Pd_{XPS} (wt.%)	2.55	1.41	0.80	0.98
Cl_{XPS} (wt.%)	1.9	6.7	8.6	4.1

residual activity are collected in Table 2. The deactivation rate constant is significantly higher for HDC of 2,4-D, where deactivation takes place within a shorter time giving rise to a much higher residual activity than in the case of MCPA. With this second, the value of residual activity indicates that the catalyst undergoes almost complete deactivation. The results obtained suggest that poisoning by the chloride ions released upon HDC reactions must not be the only cause of deactivation of the Pd/AC catalyst. The high stability shown in the HDC of 2,4-DCP suggests a strong interaction of the activated carbon support with the chloride ions due to its adsorption capacity. This prevents the potential poisoning effect on the metallic active phase [26]. On the other hand, the deactivation observed in the HDC of 2,4-D and MCPA, severe in the second case, can be associated with the nature of the starting compounds and the reactions products which can be strongly adsorbed or deposited on the metal surface restricting the access of the reacting species [48]. Albers et al. [49] in their study on the poisoning and deactivation of Pd catalysts used mainly in hydrogenation reactions, revealed the easy formation of a stable CH_3–Pd complex, provoking catalyst deactivation.

To learn more in depth on the deactivation, different techniques were used for the characterization of the fresh and used catalyst. The results are summarized in Table 3.

The Pd/AC catalyst presents a basically microporous structure with a contribution of mesoporosity which represents 17% of the BET surface area and a fairly small fraction of the pore volume. After 100 h on stream a dramatic decrease of the surface area was observed, affecting mainly to the microporosity. This can be attributed to partial blockage of the entrance of micropores by species adsorbed or deposited on the catalyst surface. The higher decrease of BET area observed in the cases of 2,4-D and MCPA can be explained by the higher molecular size of the starting compounds and reaction byproducts. Moreover, the slightly lower pH of the reaction media would favour the adsorption of those species [41,50]. The accumulation of organic substances on the catalyst upon HDC runs was also checked by thermogravimetric analysis (TGA). A significant loss of weight occurred around 186 °C for all the used catalysts, being more important for the catalysts used in the HDC of 2,4-D and MCPA.

In a previous work it was found by STEM that the fresh Pd/AC catalyst presents a narrow distribution of the Pd particles (2–6 nm) and a mean particle size of 3.7 nm corresponding with a dispersion of 30% [20]. This dispersion values is in good agreement with the reported now in Table 3 as obtained by CO chemisorption. As can be seen, the used catalyst shows a loss of dispersion which is much more pronounced after HDC of MCPA and 2,4-D, consistently with the respective loss of activity. Since agglomeration of the metal particles appears unlikely under the operating conditions of the HDC experiments, the dispersion values of the used catalysts must be conditioned by the deposition of species onto the catalyst surface. This fact must be also affecting to the measured bulk Pd content of the used catalyst since the leaching of Pd was lower than 5% in all the experiments. That leaching occurred during the early stages of the HDC process and cannot be considered a significant contribution to catalyst deactivation in aqueous HDC reaction [19,20]. This aspect should be remarked because the catalyst is mainly constituted by Pd particles lower than 4 mm, which are considered more susceptible to leaching by the HCl produced [18,51–53]. The Pd content of the fresh catalyst determined by XPS is much higher than the bulk Pd content, indicating that the metal is mainly distributed in the outermost surface. Thus, the HDC reaction must be occurring predominantly in the external or non-microporous surface of the catalyst. A remarkable decrease of that surface was observed in the used catalyst, more pronounced upon HDC of 2,4-D and MCPA. This is also the case of XPS Pd content. The accumulation of organic species on the catalyst surface can explain those findings. A very important increase of the surface Cl content was detected by XPS in the used catalyst, supporting the abovementioned adsorption/deposition of organic compounds, which must correspond in great part to organochlorinated species.

4. Conclusions

The HDC of 2,4-DCP, 2,4-D and MCPA was carried out efficiently with an own-made Pd/AC catalyst at mild operating conditions, leading to a significant reduction of ecotoxicity. The catalyst showed a high resistance to poisoning by the chloride released upon the HDC reaction due to the strong interaction of activated carbon with it. Neither structural changes nor leaching of Pd were significant causes of deactivation. The more plausible explanation for the loss of activity appears the accumulation of organic species (mainly organochlorinated) on the catalyst surface. The stronger interaction of phenoxyacetic compounds compared to phenolic ones can explain the more severe deactivation accompanying HDC of the chlorophenoxy herbicides 2,4-D and MCPA in contrast with 2,4-DCP.

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