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Hydrodechlorination of diuron in aqueous solution with Pd, Cu and Ni on activated carbon catalysts

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ABSTRACT

The hydrodechlorination (HDC) of diuron with hydrogen in aqueous phase was studied in a trickle bed reactor using different Pd, Cu and Ni catalysts supported on activated carbon. The reactor was fed with a diuron aqueous solution (2–30 mg/L) and a H_2/N_2 (1:1) gas stream. Wide ranges of temperature (35–100 °C) and space–time (64.8–647.5 kg_{cat} h/mol) were studied at a pressure of 1.4 bar. HDC of diuron with Pd on activated carbon (Pd/AC) catalyst with 0.5 wt.% Pd can be conducted successfully at 50 °C, reaching conversion values above 95%. The porous structure of the catalysts showed a significant effect on their activity. A nearly complete removal of diuron was achieved with the 0.5 wt.% Pd catalyst of high external (or non-microporous) area, whereas conversion values of around 70% were obtained with the highly microporous catalyst. The resulting effluents showed lower ecotoxicity values than the inlet diuron solution, thus indicating the evolution to less toxic species. Though the Pd catalysts showed a higher activity, the Cu and Ni ones also led to high conversions well above 80% at 2.5 wt.% metal load. Nevertheless, opposite to the Pd catalysts, a significant metal leaching was observed from the Ni and Cu ones, which affected negatively to the ecotoxicity of the final effluents, showing higher values than for the own initial diuron solution. To improve the anchorage of the active phase to the support, activated carbon was subjected to an oxidative treatment with HNO_3. A significant decrease of leaching was observed, leading to ecotoxicity values comparable to those obtained with the Pd catalysts.

1. Introduction

Contamination of surface and ground water with herbicides is of main concern for the environment and public health due to the toxicity and non-biodegradable nature of these pollutants [1]. Among the numerous agrochemicals developed, diuron (3-[3,4-(dichlorophenyl)-1,1-dimethylurea]) a substituted-urea herbicide, is widely used since the 1950s to control a variety of annual and perennial broadleaf and grassy weeds, as well as mosses. It has been also used on non-crop areas such as roads, garden paths and railway lines and on many agricultural crops such as fruit, cotton, sugar cane, alfalfa and wheat [2]. Undesirable side effects such as toxicity and carcinogenity confer to diuron the character of hazardous pollutant whose presence in water has to be carefully controlled since it was designated as persistent organic pollutant in EU legislation. Diuron has been detected in lakes, rivers and groundwater [3–6], in marine waters and sediments [7], in rain collected at urban and rural sites and in drainage water from agricultural soils [8]. The concentration in water bodies has been generally found to be from trace to higher concentrations (milligrams per liter) [9,10]. Although the use of diuron has been forbidden in some countries, it is still widely spread in many others; besides, large amounts of diuron are accumulated in soils and sediments and are slowly released to water bodies being a source of contamination even in countries where it is not in use at present.

Among the techniques proposed or used for the elimination of phenylurea herbicides from water, traditional methods such as adsorption are losing acceptance since they require a post-treatment to remove the pollutant from the newly contaminated environment. Biological methods, widely used for water treatment cannot be applied to efficiently remove diuron and related pollutants of biorecalcitrant nature [11]. In recent years, advanced oxidation processes (AOPs) have received a growing attention since a number of these techniques can promote relatively easy degradation of the contaminants to less harmful compounds. A number of studies can be seen in the literature using different AOP such as TiO_2-assisted photocatalysis [12,13], Fenton and Photo-Fenton processes [1,14–17], ozonization [14,18] and its coupling with photocatalysis [1,19]. Literature reports about the high consumption of chemical oxidants and/or energy in AOPs [20]. In the case of Fenton process, the most studied AOP, some relevant advantages such as simple operating conditions and equipment [21,22]

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and easy handling of reagents [23] are widely accepted. However, its applicability to real waters is limited by low selectivity and large consumption of reagents. Besides, complete mineralization is difficult to achieve [24]. Photocatalytic and UV processes have been shown to have a high mineralization potential, although they are in general more expensive than other AOPs. Operating costs can be drastically reduced if solar light is used [25,26] although large investment and discontinuities in solar radiation becomes a serious drawback for large scale applications. Though solar AOPs have been applied to diuron, it was also needed a further biological treatment to achieve a complete mineralization [16,27].

HDC may be an alternative to AOPs in applications where selective removal of chlorinated organics is needed to increase the biodegradability of effluents prior to biological treatment. Likewise it can provide reduction of toxicity and hazardousness of water pollutants since the HDC reaction products are far less toxic than the starting chlorinated organics. This is a relevant advantage of HDC when compared to AOPs, since AOPs can lead to intermediate compounds more toxic that initial chlorinated organics if complete mineralization is not achieved [28]. Moreover, the formation of dioxins upon AOP has been reported recently [29].

The cost of HDC would be associated mainly to hydrogen consumption and catalysts. The non-reacted hydrogen can be recirculated to the reactor after scrubbing/absorption with water or alkaline solution to remove HCl, with would reduce substantially reagents costs [30]. With regard to catalysts, the majority of the HDC studies report the use of catalysts based on precious metals with a low concentration of active phase. Moreover, the use of much less expensive actives phases such as Ni and Cu reported can provide an important reduction in cost. In a previous work we have reported on the reasonably good activity of Ni and Cu catalysts capable of yielding conversion values in the range of 80–93% in the HDC of alachlor, a chloroacetanilide herbicide [31]. Nevertheless, there is still a lack of information in the literature on the potential application in the case of phenylurea herbicides.

In addition to metal phase, the catalyst support also plays an important role in both catalytic activity and stability, being alumina and activated carbon the most reported systems in the literature for HDC. Activated carbons have been extensively used in heterogeneous catalysis owing to their high surface area, chemical resistance and adsorption capacity coupled with a reasonable cost. Moreover, both carbon porosity and surface chemistry can be tuned upon the manufacturing and activation processes. In the case of metallic active phases supported on activated carbons, the surface chemistry is one of the factors determining metal dispersion since the presence of heteroatoms (mainly oxygen, hydrogen and nitrogen) introduces active sites on the activated carbon surface, which increases the dispersion and improve anchorage. The presence of oxygen groups can also modify the surface chemistry, decreasing the hydrophobicity of the support. The nature and concentration of surface oxygen functional groups can be modified through oxidation (in gas or liquid phase) and/or thermal treatment under inert atmosphere. Among the oxidizing agents in liquid phase nitric acid, hydrogen peroxide, ammonium persulfate and perchloric acid have been the most commonly used [32–34]. Previous works [35,36] reported that the use of nitric acid provided an increase in the amount of oxygen surface groups while the porous structure was not modified significantly.

In this work, we study the activity of several activated carbon-supported Pd, Cu and Ni catalysts in the HDC of diuron in aqueous phase at mild conditions. Moreover, since one of the drawbacks commonly reported for catalysts based on transition metals is the leaching of the active phase, the modification of the catalytic support is investigated as a way of improving the stability. Likewise, the effects of space–time and temperature as well as diuron initial concentration are studied. The catalytic activity is analyzed in terms of both diuron conversion and reduction of ecotoxicity.

2. Experimental

2.1. Catalyst preparation and characterization

Different own-made catalysts were tested. They were prepared by incipient wetness impregnation using activated carbon supplied by Merck and Chemviron as supports. Pd, Cu and Ni were used as active phases at metal loads within the 0.5–5 wt.% range. The impregnation was carried out with three different precursors $PdCl_2$, $CuCl_2 \cdot 2H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$. The volume of 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, heating up to 200 °C and calcination during 2 h at this temperature. Finally, the catalysts were reduced in H_2 atmosphere at 100 °C with a flow rate of 60 N mL/min. In some experiments, the activated carbon support was subjected to an oxidative treatment with nitric acid, which was carried out by boiling 1 g of activated carbon in 10 mL of 6N HNO_3 aqueous solution for 20 min [37]. The catalysts were identified by the % metal load followed by the abbreviature of the activated carbon used as support (Ch for Chemviron and Mk for Merck) and the symbol of the corresponding metal (i.e., 0.5Ch–Ni refers to the catalyst prepared with Ni over the Chemviron carbon at a nominal 0.5 wt.% load). In the case of Pd, the metal load was omitted since 0.5 wt.% was always used. A commercial Pd/AC catalyst supplied by Engelhard was also tested with the same content of Pd (Eng–Pd). The porous structure of the activated carbons and the catalysts was characterized by N_2 adsorption–desorption at 77 K (Autosorb-1 Quantachrome). The BET equation was used to obtain the surface area and the t-method for the micropore volume. The external or non-micropore surface area was also obtained from the t-method. The difference between the volume of N_2 adsorbed at 0.95 relative pressure (calculated as liquid) and the micropore volume was taken as the mesopore volume. The amount of oxygen surface groups of the activated carbons was determined by thermal programmed desorption (TPD), heating the samples up to 900 °C in He flow at a heating rate of 10 K/min and analyzing the CO and CO_2 evolved by means of a non-dispersive infrared absorption analyzer (Siemens, model Ultramat 22).

The metal content in the carbon-supported metallic catalysts was measured by means of the X-ray fluorescence technique with a TXRF EXTRA-II spectrometer (Rich & Seifert, Germany) after digestion of the samples by acid treatment (nitric, chlorhidric and sulfuric acids mixture) and high temperature. The catalysts were also characterized by XPS (Physical Electronics model 5700 apparatus equipped with α Mg Kα X-ray excitation source, 1253.6 eV) to determine Pd, Cu and Ni surface concentrations.

2.2. Hydrodechlorination experiments

HDC experiments of diuron (CAS number: 330-54-1) were conducted in a trickle bed reactor (stainless steel; 9 mm i.d. and 245 mm length) where 0.5 g of catalyst was placed with a particle size between 1 and 2 mm. The reactor was electrically heated and the liquid and gas streams were fed in co-current down flow. The aqueous solution of diuron was pumped by means of a chromatographic pump (Gilson 307) and the gas feed consisted of a hydrogen/nitrogen mixture (50%, v/v; 100 N mL/min) which was introduced through mass flow controllers (Bronkhorst High Technology). The liquid flow was varied between 0.1 and 1 mL/min allowing to work at different space–time (τ) values in the range of 64.8–647.5 kg_{cat} h/mol. The reactor effluent was cooled to 3 °C by means of a Peltier cell and finally the samples were collected. The

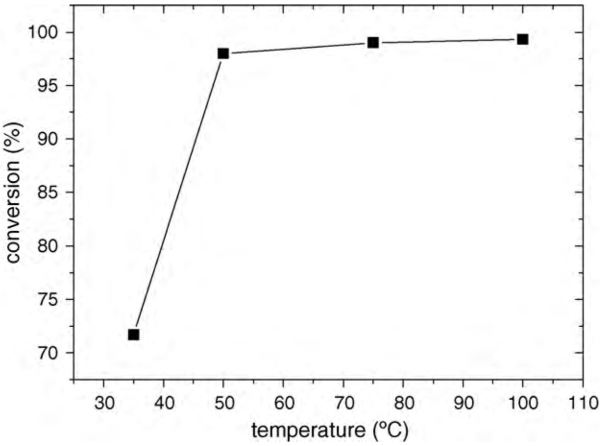

Fig. 1. Effect of temperature on diuron conversion with the Ch–Pd catalyst (τ: 260 kg_{cat} h/mol).

influence of reaction temperature was tested within the 35–100 °C range. A pressure value of 1.4 bar was maintained into the reactor in all the experiments thanks to a back pressure regulator. Additional data about the reaction system can be found elsewhere [38]. Before each run, the catalyst was saturated for 2 h in the initial herbicide solution for improving wetting, minimizing adsorption effects and reducing the time required for steady state. Diuron aqueous solutions in the range of 2–30 mg/L were prepared from Karcide, a 80 wt.% diuron commercial herbicide supplied by Agrodan.

2.3. Analytical methods

The concentration of diuron was determined by HPLC/DAD (Prostar, Varian) using a C_{18} column as stationary phase and a mixture of acetonitrile and water (1:1, v/v) at 1.0 mL/min as mobile phase. A wavelength of 254 nm was used for detection. The quantification of chloride ion was performed by ion chromatography (Metrohm 790 Personal IC). The ecotoxicity analysis was performed using the standard Microtox test procedure (Microtox® M500 Analyzer, Azur Environmental) with *Vibrio fischeri* bacteria at 5 and 15 min of exposure time. The bacteria were purchased from Azur Environmental as a freeze-lyophilized reagent and were stored at −20 °C and activated by hydration with a sterilized solution of sodium chloride before the test. The ecotoxicity was expressed in ecotoxicity units (T.U.), which correspond to the dilution factor that must be applied to the sample in order to obtain a 50% inhibitory effect. Pd, Cu and Ni in the reactor effluent were analyzed by total reflection X-ray fluorescence (TXRF) using a TXRF EXTRA II spectrometer. The concentration of Cu and Ni were also measured by colorimetric methods (Orbeco-Hellige 975 MP) according to 308C [39] and 316C [40] standard methods, respectively.

3. Results and discussion

Fig. 1 shows the effect of the temperature in the HDC of diuron with the Ch–Pd catalyst at an intermediate space–time. As can be seen, a modest increase of temperature within the lowest range tested substantially improves diuron conversion. At around 50 °C more than 97% was reached and then a further increase of temperature shows a low relative effect in terms of diuron conversion. Thus, HDC of diuron can be conducted successfully at around 50 °C with the Pd catalysts. The measured concentration of Cl^- ion and the uncorverted diuron in the outlet effluent matched in all the cases the chloride mass balance above 90%.

Diuron conversion upon space–time within the range investigated can be seen in Fig. 2 for all the Pd catalysts at 50 °C. All the catalysts showed a fairly similar Pd content determined by TXRF (Table 1). Nearly complete removal of diuron was achieved with the Mk–Pd and the Ch–Pd catalysts, whereas no more than 70% was reached with the Eng–Pd catalyst. The porous structure seems to play an important role in this case. The Eng–Pd catalyst showed a highly microporous structure with a very small contribution of mesoporosity, whereas the Mk–Pd and the Ch–Pd catalysts exhibit fairly nice values of mesopore volume and external, namely non-microporous area (Table 2). This provides a higher accessibility to the Pd active sites, since a higher proportion of this metal can be distributed in this part of the porous structure. In fact, when comparing the two own-prepared catalysts, although the Ch–Pd has 1.5 times more total (BET) surface area, both show close values of mesopore volume and area and their activity for diuron conversion becomes fairly close. Therefore, the lack of external surface seems to be an important limiting factor in the activity of the commercial catalyst tested as compared with the two own-prepared.

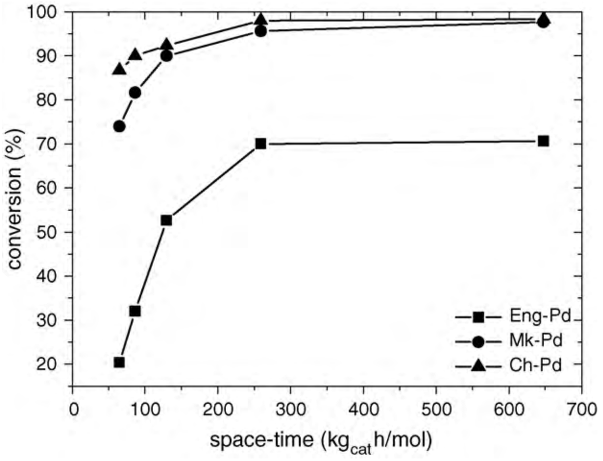

Fig. 2. Influence of the space–time on diuron conversion with the Pd catalysts (*T*: 50 °C).

Conversion of diuron upon HDC is accompanied by a substantial reduction of ecotoxicity as can be seen in Fig. 3. The ecotoxicity of the inlet 30 mg/L diuron solution (4.8 T.U.) dramatically reduced and the reduction percentages are quite similar to the conversion values indicating that the breakdown of diuron through HDC gives rise to by-products of very low ecotoxicity. Beyond 130 kg_{cat} h/mol, the ecotoxicity values were around 0.5 T.U. which can be considered a negligible level. The presence of HCl in the treated effluent proved chlorine removal from the diuron molecule leading to the formation of non-chlorinated compounds. From the analyses of chlorine ion and unconverted diuron in the effluents mass balances were calculated, which were found to match above 90% in all cases. Although the ecotoxicity of the treated effluent decreased with space–time within the whole range studied, the more marked drop was observed for the lower range.

Table 1
Atomic and mass surface concentrations of Pd, Ni and Cu of the catalysts.

Catalyst	$Metal_{bulk}$ (wt.%)	$Metal_{XPS}$ (wt.%)	$Metal_{XPS}/Metal_{bulk}$
Eng–Pd	0.51	1.4	2.7
Mk–Pd	0.49	2.3	4.7
Ch–Pd	0.48	1.3	2.7
0.5Ch–Ni	0.50	2.2	4.4
2.5Ch–Ni	2.48	5.2	2.1
5Ch–Ni	4.95	29.8	6.0
0.5Ch–Cu	0.49	1.1	2.2
2.5Ch–Cu	2.45	2.8	1.1
5Ch–Cu	4.96	11.5	2.3

Table 2
Porous structure of the Pd, Cu and Ni catalysts.

Catalyst	BET area (m^2/g)	External area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)
Eng–Pd	899	9	0.45	0.02
Mk–Pd	917	119	0.37	0.14
Ch–Pd	1392	110	0.59	0.17
0.5Ch–Ni	1190	104	0.47	0.15
2.5Ch–Ni	1110	100	0.45	0.13
5Ch–Ni	1073	98	0.40	0.12
10Ch–Ni	1001	95	0.39	0.10
0.5Ch–Cu	1196	105	0.50	0.16
2.5Ch–Cu	1115	100	0.46	0.14
5Ch–Cu	1083	98	0.40	0.12

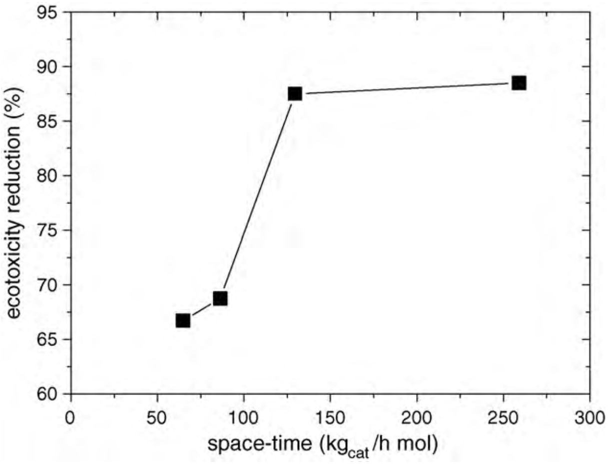

Fig. 3. Ecotoxicity reduction upon space–time with the Ch–Pd catalyst (*T*: 50 °C; inlet diuron concentration: 30 mg/L).

The HDC process was tested within a wide range of inlet diuron concentrations (2–30 mg/L) at 50 °C and 260 kg_{cat} h/mol space–time with the Ch–Pd catalyst. Conversion of diuron was maintained within 98% (for 30 mg/L) and 100% (2–5 mg/L). Therefore, HDC yields complete conversion of diuron at low concentrations and it is still highly efficient even when the concentration approaches the maximum water-soluble level (42 mg/L at 25 °C).

In spite of the fairly good results obtained with Pd, it is interesting to check the possibility of less expensive catalysts for HDC. Thus, Cu and Ni catalysts supported on activated carbon were prepared with metal loads within 0.5–5.0 wt.%. Table 3 summarizes the results obtained with these catalysts in terms of diuron conversion at 50 °C and 260 kg_{cat} h/mol space–time using a 30 mg/L diuron inlet concentration. Although Pd shows a higher activity, Cu and Ni also yielded conversion values within 80–90% range, somewhat higher for Cu. Increasing the metal load up to 2.5 wt.% slightly increases diuron conversion and then decreases at a 5 wt.% metal load suggesting a poorer dispersion of the active phase and/or partial blockage of pore entrances. The differences in activity became higher as the metal load increased, suggesting a better dispersion of Cu on the surface of activated carbon.

Table 3
Comparison of Pd, Cu and Ni catalysts (*T*: 50 °C; τ: 260 kg_{cat} h/mol).

Catalyst	Diuron conversion (%)
Ch–Pd	98
0.5Ch–Cu	87
2.5Ch–Cu	91
5Ch–Cu	85
0.5Ch–Ni	85
2.5Ch–Ni	89
5Ch–Ni	79

To learn on these Ni and Cu catalysts in more depth, the porous structure (Table 2) and surface concentrations (Table 1) were determined. The incorporation of Cu and Ni in the activated carbon reduces somewhat the BET surface area, affecting mainly to the microporous structure and in a lower extent also to the mesoporosity. A relatively small but monotonical decrease can be observed in the values of Table 2 as the total load increases.

The differences observed in the porous structure cannot explain by themselves the different catalytic behavior since the higher diuron conversion does not correspond to the catalyst with both higher BET area and mesopore volume. Thus, it should be considered the metal surface concentrations of the active phase, which are summarized in Table 1 as determined by XPS. In all the catalysts tested, the metal concentration measured by XPS is substantially higher than the bulk metal concentration. In all the cases the ratio Ni_{XPS}/Ni_{bulk} is higher than 1 (well above except for the 2.5 wt.% Cu catalyst), indicating that a significant part of the active phase is located at the external surface, thus favouring the accessibility to the reactants. However, the amount of active phase cannot be increased indefinitely without leading to agglomeration of the metal particles and to the consequent loss of dispersion. For both Cu and Ni catalyst, nominal load of 2.5 wt.% seems to maximize the metal surface available to reactants. On the other hand, the metal concentration measured by XPS was always lower in the Cu than in the Ni series, suggesting a better dispersion of this metal within the porous structure.

The results obtained with these Cu and Ni catalysts show the potential of these metals for their use in HDC reactions. However, the possible leaching of Cu and Ni from the catalysts is an important feature regarding their stability and performance that must be considered. Some studies have reported the leaching of the active phase from catalysts based on transition metals, mainly in acidic media [31,41,42]. To check the possible leaching, Cu and Ni concentration were analyzed in the reactor effluent upon time-on-stream and the results are shown in Figs. 4 and 5. As can be seen, during the initial 5–6 h an important metal leaching took place. Moreover, the concentration of the leached metal was always higher for the catalysts with a higher content of active phase. Beyond 7–8 h on stream the leaching of the active phase substantially decreased and was maintained at rather low values, especially in the case of the Ni catalysts. Besides, the dependence of metal load on the metal concentration in the effluent was much lower. The amounts of metal leached and the corresponding percentages relative to the initial metal load after 12 h on stream are collected in Table 4. From these results a relationship between the nominal metal load and the percentage leached is not likely, although the lowest relative loss was observed for both metals at a 2.5 wt.% nominal load.

Besides the loss of the active phase metal by leaching has a detrimental effect on the quality of the effluent since the presence of Cu and Ni represents an important contribution to the ecotoxicity. As

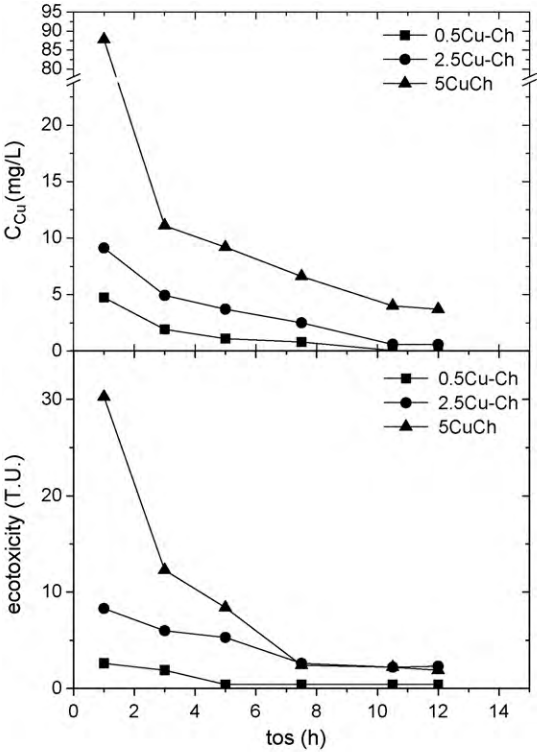

Fig. 4. Cu concentration and ecotoxicity of the reactor effluent (*T*: 50 °C; *τ*: 260 kg_{cat} h/mol).

can be seen in Figs. 4 and 5 ecotoxicity values even more than six times that of the inlet 30 mg/L diuron solution (4.8 T.U.) were measured upon the first hour of time-on-stream, which is linked to the highest metal leaching.

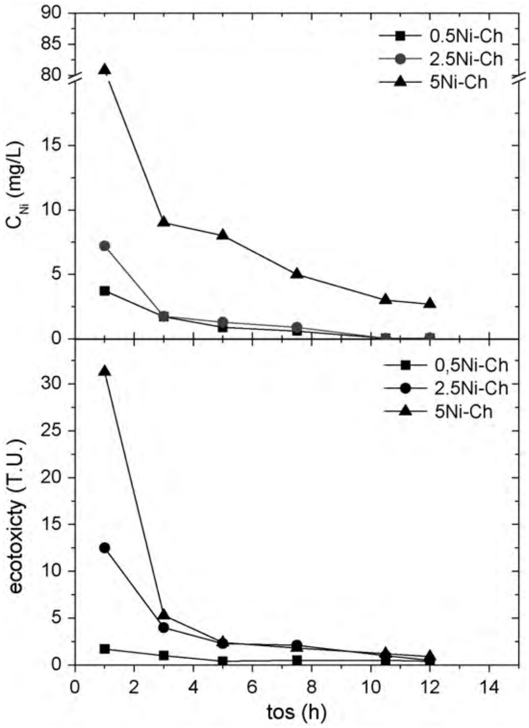

Fig. 5. Ni concentration and ecotoxicity of the reactor effluent (*T*: 50 °C; *τ*: 260 kg_{cat} h/mol).

Table 4
Metal leached from the Cu and Ni catalysts after 12 h on stream (*T*: 50 °C; *τ*: 260 kg_{cat} h/mol).

Catalyst	Metal leaching (%)	Total metal leaching (mg[a])
0.5Ch–Cu	8.4	0.42
2.5Ch–Cu	4.2	1.05
5Ch–Cu	9.6	4.8
0.5Ch–Ni	4.4	0.22
2.5Ch–Ni	2.0	0.5
5Ch–Ni	7.5	3.75

[a] 1 g catalyst basis.

Table 5
CO and CO_2 evolved upon TPD of the activated carbons and the catalysts.

Sample	CO_2 evolved (μmol/g)	CO evolved (μmol/g)
Ch	136	357
ChN	1335	3927
2.5Ch–Cu	154	457
2.5ChN–Cu	1489	4210
2.5Ch–Ni	146	449
2.5ChN–Ni	1399	3945

Table 6
Diuron conversion and ecotoxicity of the effluents from HDC with catalysts prepared from the starting and oxidized activated carbon (*T*: 50 °C; *τ*: 260 kg_{cat} h/mol).

Catalyst	Conversion (%)	Metal leaching (%, 12 h tos)	T.U.		
			Tos (1 h)	Tos (3 h)	Tos (12 h)
2.5Ch–Cu	92	4.2	8.3	5.9	2.2
2.5ChN–Cu	93	2.1	3.3	3.3	0.9
2.5Ch–Ni	90	2.0	12.5	5.0	2.1
2.5ChN–Ni	92	0.2	3.8	2.1	1.0
Ch–Pd	98	Non-detected	0.2	0.2	0.3

An attempt was made to achieve a more stable anchorage of the active phase onto the support which could minimize metal leaching from the catalysts. The starting activated carbon from Chemviron was subjected to oxidative treatment with nitric acid. The catalyst prepared using the resulting activated carbon as support was designated by the same nomenclature but indicating N after Ch. Table 5 shows the amount of CO and CO_2 evolved upon TPD of catalysts prepared with the starting and the oxidized activated carbon. In this table, data for the activated carbon supports have included as well. As can be seen, the oxidation treatment increases dramat-

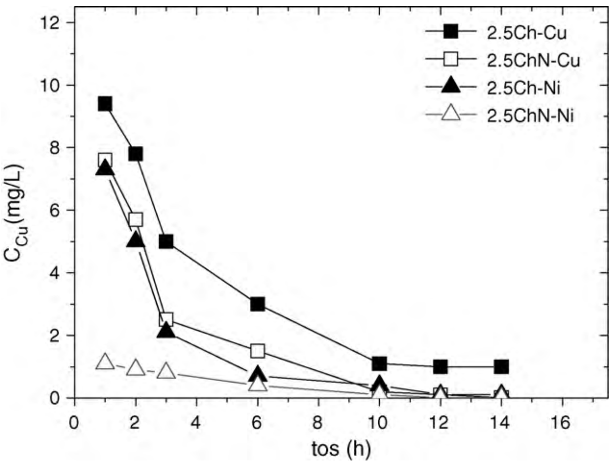

Fig. 6. Comparison of the evolution of Cu and Ni leaching with time-on-stream for the catalysts prepared with untreated and oxidized support (*T*: 50 °C; *τ*: 260 kg_{cat} h/mol).

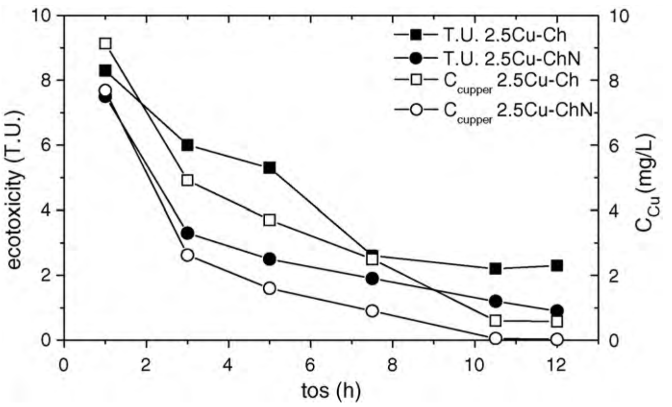

Fig. 7. Comparison of the ecotoxicity effluent and evolution of Cu leaching with time-on-stream for the catalysts with untreated and treated support (T: 50 °C; τ: 260 kg_{cat} h/mol).

ically the amount of oxygen surface groups in both the support and the catalysts. The results of HDC experiments with these catalysts are summarized in Table 6. The diuron conversion did not show significant differences between the catalysts prepared with the oxidized and untreated support, although a slight improvement was observed with the second, which can be related with a somewhat better distribution of the metal due to the higher availability of anchoring sites [31]. The evolution of Cu and Ni concentrations in the effluent was also followed and the results are depicted in Fig. 6. The percentage leached after 12 h on stream are given in Table 6. The comparison of the results for the catalysts prepared from untreated and oxidized activated carbon shows a noticeable decrease of leaching as a result of the oxidative treatment of the support and that decrease leads to a substantially lower ecotoxicity of the resulting effluent (Table 6) and (Fig. 7).

4. Conclusions

Pd, Cu and Ni catalysts supported on activated carbon were tested in the HDC of diuron in aqueous phase using hydrogen in a trickle bed reactor. The results showed that HDC of diuron over a 0.5 wt.% Pd catalyst supported on activated carbon can be conducted successfully at 50 °C, reaching almost complete conversion if a carbon with a well developed mesoporosity is used as support. The use of a highly microporous carbon as support substantially reduces the efficiency in terms of diuron conversion. In addition of a high activity the Pd catalysts showed a very good stability being the leaching of Pd almost negligible. Although less active than Pd, Cu and Ni catalysts led also to high conversions, above 90%. Maximum diuron conversion was reached for a nominal metal load of 2.5 wt.% for both Cu and Ni catalysts. This nominal load makes possible to maximize the metal surface available to the reactants. An important leaching of Cu and Ni was observed which besides the loss of active phase entails negative effect in the quality of the effluents by significantly increasing the ecotoxicity. To control leaching, activated carbon was subjected to an oxidative treatment prior to metal impregnation, which provided an improvement in the anchorage of the active phase to the support. Thanks to this treatment a noticeable decrease in leaching was observed, which resulted in very low ecotoxicity values, comparable to those obtained with Pd catalysts.

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