



# Application of catalytic hydrodechlorination for the fast removal of chlorinated azole pesticides in drinking water

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## ABSTRACT

Catalytic hydrodechlorination (HDC) is regarded as a promising purifying technology for drinking water treatment. So far, it has proved to be highly effective for the removal of different groups of chlorinated micropollutants including pharmaceuticals, neonicotinoid pesticides, personal care products or chloroacetic acids. The azole pesticides, recently included in the EU Watch Lists (Decisions 2020/1161 and 2022/1307), are a group of micropollutants of particular concern for drinking water given their high toxicity, persistence, and bio-accumulation potential. In this work, the feasibility of HDC for the removal of a representative group of chlorinated azole pesticides tebuconazole (TEB), tetraconazole (TET), prochloraz (PCZ), penconazole (PEN), metconazole (MET) and imazalil (IMZ) is demonstrated, and their reactivity is compared with that observed for other halogenated micropollutant groups. Notably, all the pesticides investigated in this work (100 µg L<sup>-1</sup>) were completely dechlorinated within 30 min under ambient conditions using a 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst concentration of 0.25 g L<sup>-1</sup> and a H<sub>2</sub> feeding of 50 mL N min<sup>-1</sup>. The experimental data were accurately described by a pseudo-first order kinetic equation and rate constant values in the range from 1.08 to 2.60 L g<sup>-1</sup> min<sup>-1</sup> were obtained. These values are quite close to those achieved for the most reactive neonicotinoid pesticides and significantly higher than the obtained for chloroacetic acids and most pharmaceuticals (e.g. diclofenac, sertraline or chlorpromazine). From the identification of the generated reaction intermediates and the final non-chlorinated products, sequential reaction pathways were proposed for each pollutant. Remarkably, despite the high toxicity exhibited by the azole pesticides tested, with LC<sub>50</sub> values within the 0.4–7.0 mg L<sup>-1</sup> range using *A. salina*, HDC effluents were non-toxic in all cases. Furthermore, the catalyst showed a remarkable stability upon three consecutive runs. Finally, the versatility of the process was demonstrated in the treatment of real aqueous matrices such as DWTP and tap water, where no significant differences were found either in terms of activity or stability.

## 1. Introduction

The access to safe and clean drinking water is crucial for human health and thus, it is considered a basic human right. Drinking water treatment plants (DWTPs) are the responsible for guaranteeing that potable water quality fulfills the requirements established in the regulation. Accordingly, these treatment plants are designed for the removal of microorganisms, turbidity, and natural organic matter, paying special attention to the general appearance, odor and taste of water. Nevertheless, the fresh waters employed by DWTPs generally contain a wide range of micropollutants that so far have not been considered in the regulation. A particularly relevant example is the occurrence of pesticides, widely employed in agriculture to enhance food production by

preventing or eliminating pests, weeds and fungal diseases [1]. Among pesticides, fungicides play an essential role in modern agriculture, representing over 35% of the global pesticide market share, which is expected to increase due to population growth and increasing fungal resistance [38]. Furthermore, fungicides are also widely used in urban landscapes, building boards and paints [18]. Azole compounds represent one of the most employed fungicides nowadays [14]. Apart from their desired antifungal properties, these compounds are characterized by high a persistence and remarkable toxicity, representing a high risk for both the environment and public health. Residual azole fungicides in the aquatic environment could cause adverse effects on different levels of organisms such as toxic effects on algal growth as well as endocrine disruption in fish [9]. For these reasons, a representative group of azole

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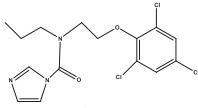
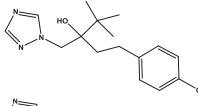
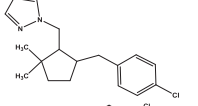
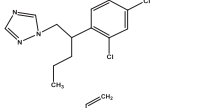
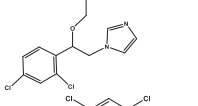
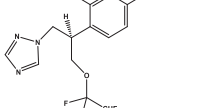
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**Table 1**

Main properties of the chlorinated azole pesticides tested in this work.

Compound	Abbreviation	Structure	pKa	Molecular weight (g mol <sup>-1</sup> )
Prochloraz	PCZ		3.8 [32]	376.6
Tebuconazole	TEB		5.0 [6]	307.8
Metconazole	MET		11.3 [16]	319.8
Penconazole	PEN		5.2 [6]	284.2
Imazalil	IMZ		6.5 [13]	297.2
Tetraconazole	TET		0.6 [16]	372.1

pesticides have been included in the most recent Watch Lists approved by the EU (Decisions 2020/1161 and 2022/1307). Azole pesticides may reach the aquatic environment mainly by surface run-off, spray drift and soil seepage [15]. Therefore, they are practically ubiquitous in water bodies, being tebuconazole (TEB) the most frequently detected fungicide in surface waters worldwide [31].

DWTPs are not specifically designed for the removal of micropollutants, and they are particularly ineffective for azole compounds elimination [3]. In fact, these compounds or their metabolites have been commonly detected both in the catchment water, treated water, and tap water samples [18]. High detection frequencies of azole pesticides in catchment waters have been reported by several authors [10,11], and most of them are inadequately removed after the conventional drinking water treatment processes. For instance, the detected concentration of TEB in raw water samples ranged from 5 to 510 ng L<sup>-1</sup>. Accordingly, the development of advanced water treatments to warrant the complete removal of such persistent species is crucial. Adsorption of azole pesticides onto activated carbon has proved to be quite effective in the removal of these pollutants [12]. Nevertheless, this is a non-destructive process, which requires further management of the saturated adsorbent. Advanced oxidation processes, in particular Fenton and photo-Fenton, have been also explored for the elimination of several azole pesticides like imazalil and TEB with mineralization yields between 75% and 85% in the Fenton and photo Fenton processes, respectively [7,29]. However, the possible formation of reaction intermediates even more toxic than the parent compounds clearly limits its implementation for drinking water treatment [4,5].

In recent contributions, the effectiveness of catalytic hydrodechlorination (HDC) for the removal of different chlorinated micropollutant groups like pharmaceuticals, personal care products, neonicotinoid pesticides or haloacetic acids was demonstrated [24,36]. Nevertheless, to the best of our knowledge, HDC was not explored so far for the elimination of azole compounds. Since the number and nature of halogenated substituents in the structure of the micropollutants influences its reactivity, as well as the different heteroatoms and functional groups contained in the parent molecule, the evaluation of the effectiveness of the HDC process for these pollutants is of great interest.

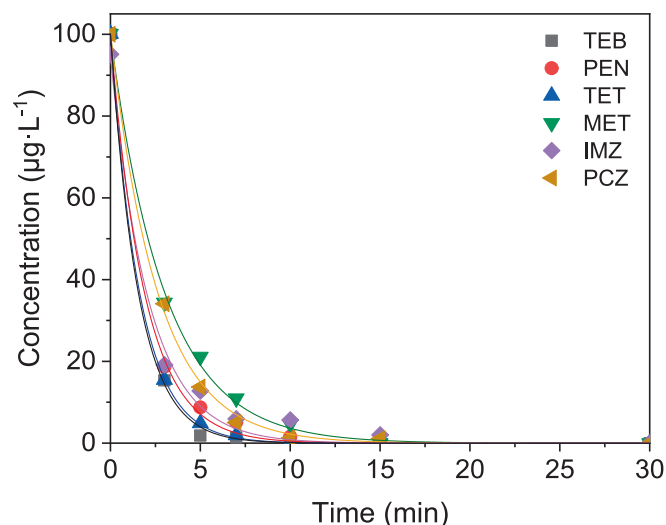
Upon HDC, organochlorinated compounds react with hydrogen in presence of a solid catalyst, resulting in the formation of chlorine-free products and the release of hydrochloric acid [2]. This transformation usually leads to a significant reduction of the ecotoxicity of the effluent. Furthermore, HDC reactions can be carried out under ambient operating conditions, being also effective for the treatment of wide range of initial pollutant concentrations.

This work aims to evaluate the feasibility of HDC for the removal of a representative group of chlorinated azole pesticides included in the last EU Watch Lists: prochloraz (PCZ), tebuconazole (TEB), tetraconazole (TET), imazalil (IMZ), metconazole (MET) and penconazole (PEN). A commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was used given its prominent role in this field [19]. The kinetics of the HDC reactions was investigated and reaction pathways were accordingly proposed. Furthermore, the treatment of azole pesticides mixtures was also studied, and the reactivity of this group of micropollutants towards HDC was compared with that showed by other families like neonicotinoid pesticides, pharmaceuticals, personal care products and chloroacetic acids. The effectiveness of the treatment was further demonstrated by evaluating the ecotoxicity breakdown of the effluents. Furthermore, the stability of the catalyst was proved in three consecutive runs and the versatility of the process was demonstrated in real aqueous matrices.

## 2. Materials and methods

### 2.1. Materials

The azole pesticides (>98%) tested in this work were supplied by Sigma-Aldrich. Table 1 collects their main properties. Sodium carbonate (99.8%) and sodium bicarbonate (99.9%) were provided by PanReac and Sigma-Aldrich, respectively. Acetonitrile (99.9%) and hydrogen (99.999%) were delivered by Fisher Scientific and Praxair, respectively. The powdered (~24 µm) Pd/Al<sub>2</sub>O<sub>3</sub> (1% wt.) catalyst was supplied by Alfa Aesar. This catalyst was fully characterized elsewhere [26]. Briefly, the Pd content was 0.95% wt., the Pd nanoparticles showed a mean particle diameter of 3.3 nm, the specific surface area was 147 m<sup>2</sup> g<sup>-1</sup> and the pH<sub>PZC</sub> value was close to 7.6. Regarding the oxidation state of Pd, a



**Fig. 1.** Evolution of the isolated azole pesticides upon HDC reaction ([Pesticide]<sub>0</sub> = 100 µg L<sup>-1</sup>; H<sub>2</sub> = 50 N mL min<sup>-1</sup>; [Pd/Al<sub>2</sub>O<sub>3</sub>] = 0.25 g L<sup>-1</sup>; 25 °C). Experimental (symbols) and model fit (solid lines).

molar Pd<sup>0</sup>/Pd<sup>n+</sup> molar ratio of 1.04 was determined. Unless otherwise indicated, deionized water was used as reaction matrix.

## 2.2. Experimental procedure

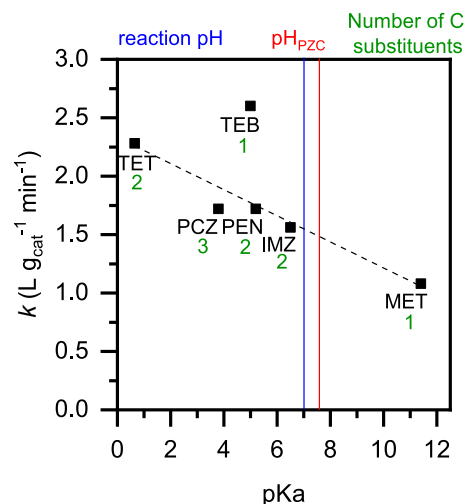
HDC runs were carried out in a batch-wise slurry-type reactor (450 mL) under ambient conditions (1 atm and 25 °C) and neutral pH at 900 rpm stirring rate (to avoid external mass transfer limitations) [23]. The initial pesticides concentration was established at 100 µg L<sup>-1</sup>, although it was raised up to 10 mg L<sup>-1</sup> in a particular set of experiments to allow the identification of the reaction intermediates and final products. The catalyst concentration and H<sub>2</sub> feed were set at 0.25 g L<sup>-1</sup> and 50 N mL min<sup>-1</sup>, respectively. The hydrogen was bubbled from the bottom of the reactor using a diffuser to achieve small diameter bubbles and high gas to liquid transfer surface. Blank experiments were performed in the absence of H<sub>2</sub> to discriminate the role of adsorption along the HDC process. All experiments were carried out in triplicate, being the standard deviation below 5%.

## 2.3. Analytical methods

The evolution of HDC reactions was followed by analyzing the samples periodically withdrawn from the reactor. Prior analysis, samples were centrifuged to separate the solid catalyst. The target pollutants, intermediates and products were measured by an HPLC-UV (Shimadzu, model Prominence-i, LC2030C LT) using an-Agilent Eclipse Plus C<sub>18</sub> column (15 cm length, 4.6 mm diameter) as stationary phase. Mixtures of acetonitrile and deionized water at different volume ratios (55/45% for TET, 60/40% for PEN, PCZ and TEB and 65/35% for IMZ and MET) were used as mobile phases. Quantification was carried out at 195 nm for IMZ, 210 nm for TET, 212 nm for PCZ and PEN, 222 nm for MET and at 223 nm for TEB. The chloride ions released along the HDC reaction were quantified by ion chromatography (Metrohm 883 IC Plus). A Metrosep A supp 5–250 column (25 cm length, 4 mm internal diameter) was used as stationary phase and an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (3.2 mM) and NaHCO<sub>3</sub> (1 mM) as mobile phase. Elemental analyses of fresh and used catalysts were carried out on a LECO CHNS-932 Elemental Analyzer.

## 2.4. Ecotoxicity tests

*Artemia salina* was used as a representative organism to assess the



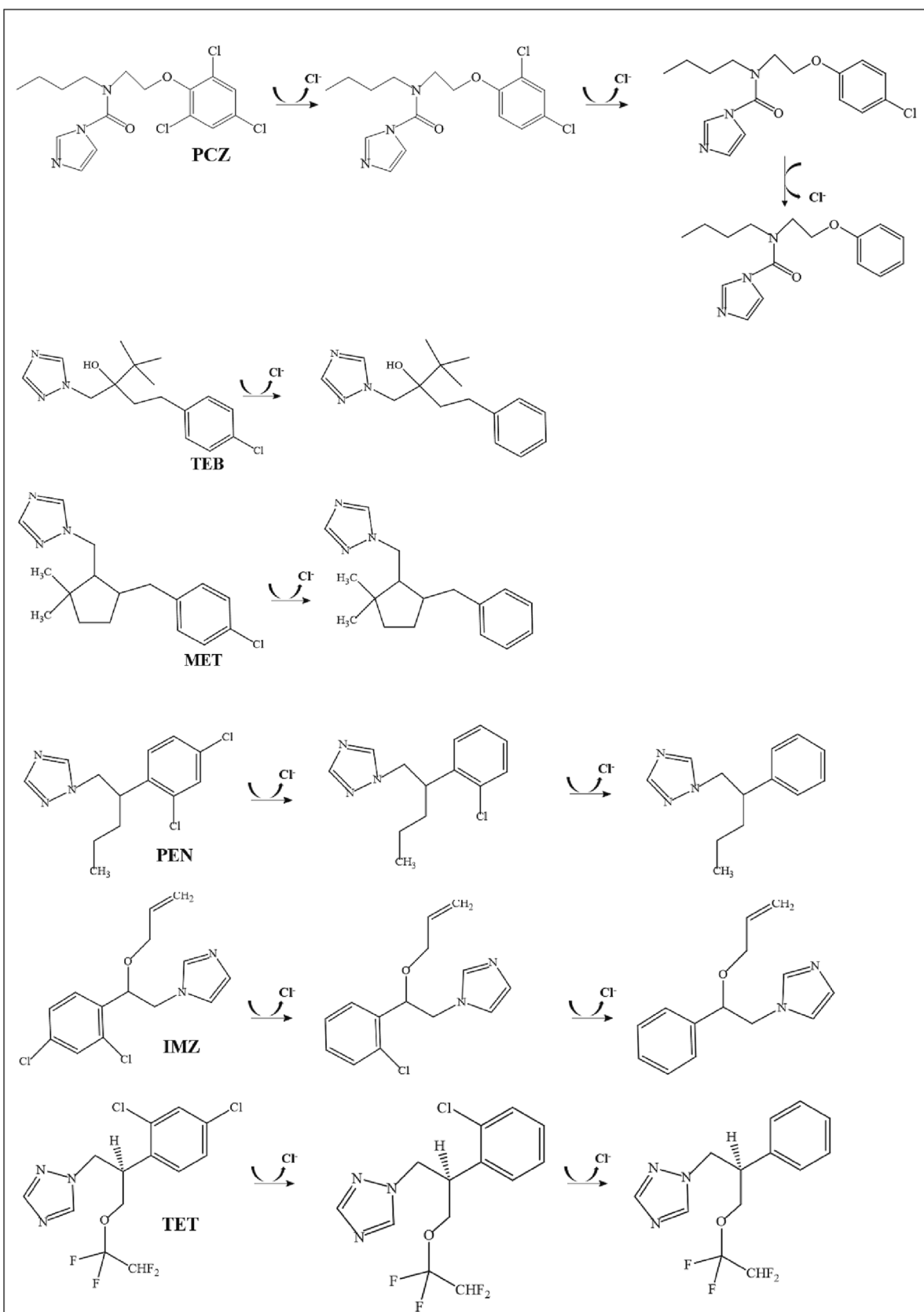
**Fig. 2.** Relationship between the HDC rate constant values at 25 °C and the pKa of azole pesticides.

toxicity of both the target pollutants and HDC effluents. The procedure followed was reported in a previous work [21]. *Artemia salina* cysts (0.5 g) were incubated in an aquarium containing 0.47 L synthetic seawater at 30 °C, illuminated and under continuous aeration. Cysts hatched at around 24 h of incubation. Synthetic seawater consisted of 15 g synthetic sea salt (Aquaforest) dissolved in 0.47 L deionized water. The standard conditions used to evaluate the toxicity were: 30 °C, 35 g L<sup>-1</sup> synthetic sea salt, neutral pH and darkness. Five concentrations of each pesticide were tested. Three control replicates were also performed in the seawater medium alone. Each vial contained 20 organisms in 2 mL of sample and was placed in an incubator for a period of 72 h. Afterwards, nauplii were observed and dead nauplii were counted. Nauplii were considered dead if no movement was detected during 10 s of observation. The lethal concentration (LC<sub>50</sub>), defined as the concentration of the contaminant that kills 50% of the nauplii in 72 h [21,37], was used to determine the toxicity of the pesticides. Moreover, the HDC effluent samples were also evaluated, expressing the results in terms of mortality (percentage of dead nauplii after incubation).

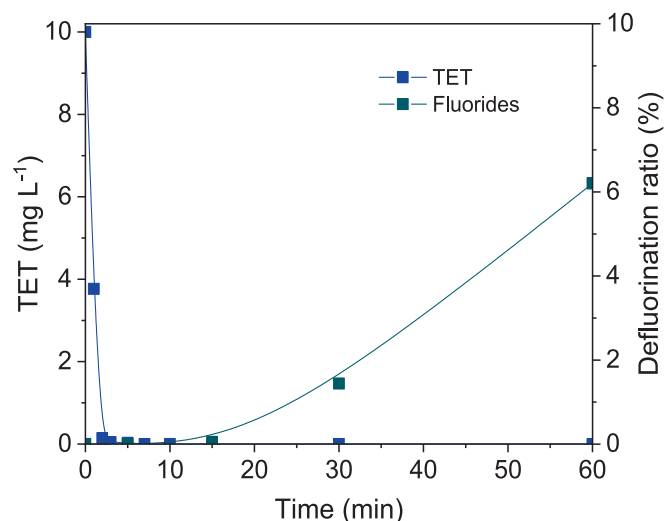
## 3. Results and discussion

### 3.1. Catalytic hydrodechlorination of chlorinated azole pesticides

Fig. 1 shows the evolution of the isolated azole pesticides (100 µg L<sup>-1</sup>) upon HDC using 0.25 g L<sup>-1</sup> Pd/Al<sub>2</sub>O<sub>3</sub> catalyst under ambient conditions. As can be seen, all pollutants were completely degraded within 15 min reaction time, although slight variations in their disappearance rates were observed. The experimental data were successfully described by a pseudo-first order kinetic equation, obtaining the following rate constant values (correlation coefficients (r<sup>2</sup>) between 0.95 and 1 were obtained in all cases): 2.60 L g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup> (TEB), 2.28 L g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup> (TET), 1.72 L g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup> (PEN and PCZ), 1.56 L g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup> (IMZ) and 1.08 L g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup> (MET). Accordingly, the pesticides reactivity towards HDC decreased following the order: TEB > TET > PEN ~ PCZ > IMZ > MET. The electrostatic interaction between the target pollutants and the catalyst surface seems to play a non-despicable role on the reactivity trend observed. Except for TEB, an almost linear correlation between the rate constant value and the pKa value of the azole pesticide was found (Fig. 2). It must be noted that, under the operating conditions tested, the catalyst surface was positively charged (pH<sub>PZC</sub> = 7.6). MET, which showed the lowest HDC rate constant, was the only compound that suffered electrostatic repulsion from the catalyst surface as it was positively charged at neutral pH (pKa = 11.6). The rest of azole pesticides were negatively charged and thus, their interaction with the



**Scheme 1.** Reaction pathways proposed for the HDC of azole pesticides.



**Fig. 3.** Evolution of TET and fluoride upon HDH reaction ( $[TET]_0 = 10 \text{ mg L}^{-1}$ ;  $H_2 = 50 \text{ N mL min}^{-1}$ ;  $[Pd/Al_2O_3] = 0.25 \text{ g L}^{-1}$ ;  $55^\circ \text{C}$ ).

catalyst surface was favored. In fact, the rate constant value increased with decreasing the pKa value of the target pollutant, with the exception of TEB. This azole pesticide showed the highest rate constant value among the ones tested, which could be due to the fact that it only contains one chlorine substituent in its structure while the other azole pesticides show two or three substituents. Furthermore, it also contains a hydroxyl substituent, which could also enhance the HDC rate (Shin and Keane, 1998). In Fig. 2, despite its lower pKa, PCZ, with three chlorine substituents, showed a rate constant value exactly the same as PEN, with only two chlorine substituents, which further demonstrates that the reactivity of azole pesticides decreases with increasing the number of chlorine substituents. These results are consistent with the fact that TET, PEN and IMZ, all with two chlorine substituents, followed a clear linear trend between their pKa and rate constant values.

An additional set of experiments was carried out increasing the initial concentration of the azole pesticides up to  $10 \text{ mg L}^{-1}$  to get better insights on the reaction intermediates and products generated during the HDC process (see Fig. S1 of the Supplementary Material for experimental data). Adsorption experiments were also carried out with each of the pesticides (see Fig. S2 of the Supplementary Material for experimental data). Another experiment was carried out in the absence of the catalyst for the removal of the azole pesticides. As shown in the Fig. S3 of the Supplementary Material, as expected, none of the pesticides were removed in the presence of  $H_2$  (<5%). The analysis of the samples along reaction time by HPLC-UV allowed to determine the chemical structures of those species. The chloride ions released along the HDC reaction were quantified by ion chromatography. Accordingly, reaction pathways were proposed for the different azole compounds tested (Scheme 1). It must be highlighted that, regardless of the chemical structure of the parent compound, complete hydrodechlorination of the azole pesticides was achieved at the end of the reactions. A consecutive reaction pathway was proposed in all cases, which implies the sequential removal of all the chlorine atoms from the parent compound obtaining as final products non-chlorinated species without further hydrogenation. The evolution of the species along reaction is collected in Fig. S4-S9 of the Supplementary Material. It must be noted that TET, which apart from chlorine contains four fluorine substituents, did not suffer its complete hydrodehalogenation as fluorine substituents were not removed. This fact could be attributed to the higher C-F binding energy ( $485 \text{ kJ mol}^{-1}$ ) in comparison with the chlorine binding energy ( $339 \text{ kJ mol}^{-1}$ ) [30]. An additional experiment performed at relatively high temperature ( $55^\circ \text{C}$ ) allowed to confirm this hypothesis since an increase of the reaction temperature allows to obtain not only the complete hydrodechlorination

**Table 2**

$LC_{50}$  values and mortality of the six azole pesticides tested in this work.

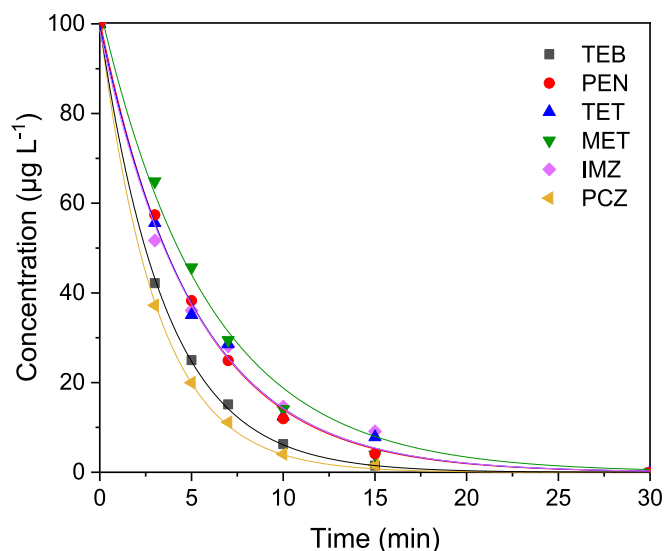
Pesticide	$LC_{50}$ (mg $L^{-1}$ )	Mortality (%)		
		72 h	Initial Solution	HDC effluent
TEB	2.5	26.4	< 0.1	>99.9
PEN	1.3	58.8	41.1	30.1
TET	3.4	26.4	8.8	66.6
MET	7.0	24.9	5.8	76.7
IMZ	0.4	58.8	32.3	45
PCZ	3.4	50.0	14.7	70.6

of TET, but also its partial hydrodefluorination (Fig. 3).

### 3.2. Ecotoxicity tests

The ecotoxicity of the azole pesticides and the final HDC effluents was analyzed using the brine shrimp *Artemia salina* lethality bioassay. *Artemia salina* is recognized as an outstanding target organism for ecotoxicity testing given its high filtration rate which makes it highly sensitive to the presence of xenobiotics [28]. Table 3 collects the ecotoxicity values of the azole pesticide tested in this work expressed as lethal concentration ( $LC_{50}$  (mg  $L^{-1}$ )) at 72 h exposure time. As can be observed, the lowest value of  $LC_{50}$  ( $0.4 \text{ mg L}^{-1}$ ) was obtained for IMZ, which indicates that this azole compound is the most toxic among the pesticides evaluated in this study. The higher lethality of IMZ can be related to its chemical structure which contains a chiral center that gives rise to two enantiomers, which, while sharing physical and chemical properties, have different biological effects [17]. These results are in agreement with some studies evaluating the  $LC_{50}$  of IMZ and PEN in trout where the resulting  $LC_{50}$  value for IMZ was  $1.1 \text{ mg L}^{-1}$  [20,33]. All in all, all the azole pesticides tested showed a remarkable ecotoxicity (being the highest  $LC_{50}$  value of  $7 \text{ mg L}^{-1}$ ) and thus, their effective elimination from water is crucial.

The ecotoxicity of the HDC effluents against *Artemia salina* nauplii was also evaluated with a set of experiments with an initial concentration of  $10 \text{ mg L}^{-1}$ . In all cases, the ecotoxicity significantly decreased after the treatment achieving values of elimination between approximately 20 to 90% (data in Table S1 of the Supplementary Material). This is consistent with the transformation of the organochlorine pollutants



**Fig. 4.** HDC of azole pesticide mixture ( $[Pesticide]_0 = 100 \text{ μg L}^{-1}$ ;  $H_2 = 50 \text{ N mL min}^{-1}$ ;  $[Pd/Al_2O_3] = 0.25 \text{ g L}^{-1}$ ;  $25^\circ \text{C}$ ). Experimental (symbols) and model fit (solid lines).

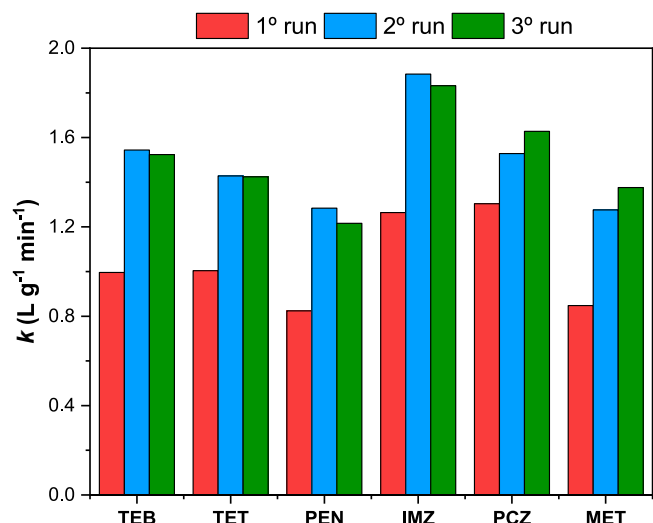


Fig. 5. Rate constant values obtained in the HDC of the isolated azole pesticides upon three consecutive HDC runs. ([Pesticide]<sub>0</sub> = 100 µg L<sup>-1</sup>; H<sub>2</sub> = 50 N mL min<sup>-1</sup>; [Pd/Al<sub>2</sub>O<sub>3</sub>] = 0.25 g L<sup>-1</sup>; 25 °C).

during the HDC reactions giving rise to chlorine-free products which usually are more biodegradable and, therefore, easier to be removed in the aquatic environment.

To further demonstrate the effectiveness of HDC in reducing the ecotoxicity of pesticides, another set of experiments were carried out with all contaminants with an initial concentration of 3 mg L<sup>-1</sup>. In this case, a significant decrease in mortality was obtained after HDC treatment regardless the pesticides (see results in Table 2). Notably, the ecotoxicity abatement in the case of TEB was complete, which allows to confirm that chlorine substituents are the mainly responsible for the ecotoxicity of azole pesticides.

### 3.3. HDC of azole pesticides mixture

Azole pesticides do not appear isolated in real aqueous matrices. For instance, in 2011, different pesticide residues were detected in water samples from the Ebro River (Spain), being IMZ and PCZ two of the most frequent azole compounds identified (70% of the samples) [8]. Several azole compounds such as TEB and propiconazole have been also detected in water samples collected at the intake point of DWTP [11].

To evaluate possible competing effects between the target pollutants upon HDC, the treatment of a pesticide mixture was accomplished. The experiments were performed with an initial concentration of each pesticide of 100 µg L<sup>-1</sup> while the catalyst concentration was established at 0.25 g L<sup>-1</sup>. As can be seen in Fig. 4, all pollutants were removed in a relatively short reaction time (<30 min), although it was somehow longer than the observed with the isolated pesticides (<15 min). Nevertheless, it must be noted that the same catalyst concentration (and H<sub>2</sub> feed) was employed to degrade the whole pollutants mixture. As for the results obtained in the treatment of the isolated pesticides, the pseudo-first order kinetic constants were obtained for the HDC of each azole compound when they were treated in mixture (correlation coefficients were above 0.95 in all cases (see Table S2 of Supplementary Material)). Competitive effects can explain the differences found in the reactivity trend observed between the treatment of isolated pesticides and the complex mixture. Again, the interaction of the pollutants with the catalyst surface due to electrostatic attraction/repulsion as well as the number of chlorine substituents present in the molecule are the main factors that explain the reactivity trend observed. In this sense, MET, whose interaction with the catalyst surface is not favored due to electrostatic repulsion, showed again the lowest rate constant value. PEN, TET and IMZ, whose interaction with the catalyst surface is favored

Table 3

Main characteristics of the real aqueous matrices.

Parameter	Deionized water	Tap water	Surface water
pH	6.9	8	6.8
TOC (mg L <sup>-1</sup> )	0.54	2.8	2.2
IC (mg L <sup>-1</sup> )	0.11	4.3	1.6
Conductivity (µS cm <sup>-1</sup> )	0.05	80.7	48.9
Cl <sup>-</sup> (mg L <sup>-1</sup> )	0.09	12.1	14.5

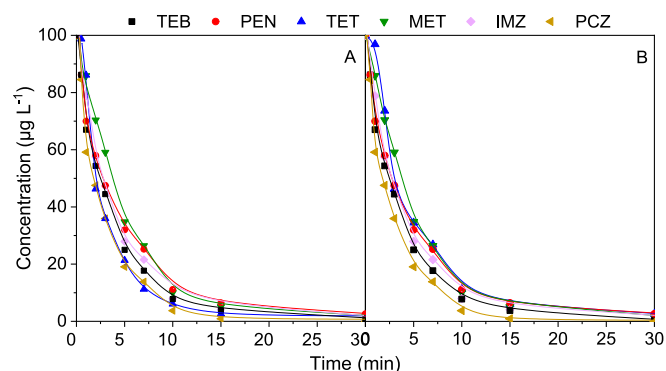
according to their pK<sub>a</sub> values and with two chlorine substituents in their structures, presented very similar rate constant values. On the other hand, in contrast to the behavior observed in the treatment of isolated pesticides, PCZ exhibited the highest rate constant value, possibly due to the fact that it contains three chlorine substituents in its structure. Although the presence of such amount of chlorine substituents could somehow decrease the HDC rate, its interaction with the Pd nanoparticles present on the catalyst surface is significantly favored and thus, it is preferentially adsorbed in comparison with the other azole pesticides present in the mixture. This is consistent with previous works of the literature where it was demonstrated that highly chlorinated species are more strongly adsorbed on Pd catalysts [22].

### 3.4. Stability tests

Catalyst deactivation represents one of the main limitations of HDC technology given the high costs of the catalysts involved. The main reasons behind this phenomenon are mainly the poisoning of Pd active centers by their interaction with the HCl released along reaction as well as the fouling (and even pore blocking) promoted by the adsorption of organic compounds onto the catalyst surface [27,34]. In this work, the stability of the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was evaluated in three consecutive HDC runs with each (isolated) azole pesticide. Fig. 5 collects the pseudo-first rate constant values obtained in the three consecutive runs. Notably, the catalyst showed a remarkable stability and no signs of deactivation were found in any case. It must be noted that, after three consecutive HDC runs, the catalyst maintained its properties practically unchanged, and palladium leaching was negligible (<0.1% wt.). In the same line, elemental analyses of the used catalyst revealed a negligible content of carbon on the catalyst surface after reaction, which allowed to discard the blocking of the Pd active centers by organic molecules along reaction (see Table S3 of Supplementary Material). These results are in good agreement with those reported in the literature using Pd/Al<sub>2</sub>O<sub>3</sub> catalysts for the removal of other chlorinated micropollutants by HDC under similar conditions [25] and confirm that Pd/Al<sub>2</sub>O<sub>3</sub> is a resistant catalyst for HDC reactions. In all cases, the lower decomposition rate observed in the first HDC run can be related to the initial adsorption step required for beginning the reaction. However, in the second and third reaction runs, organic species are adsorbed on the catalyst surface at the beginning of the run, so this stage did not slow down the initial reaction rate [23].

### 3.5. Catalytic hydrodechlorination in real aqueous matrices

To further demonstrate the feasibility of HDC for the removal of azole pesticides in drinking water, the effectiveness of the process was also evaluated using different real water samples as reaction matrices. In particular, tap water and surface water were tested. This series of experiments was carried out with the pesticide mixture. The main properties of the real aqueous matrices are summarized in Table 3. Briefly, the conductivity value of tap water is twice that of surface water. The concentration of chlorides, species which can act as poison for the Pd active centers of the catalyst, was 12.1 and 14.5 mg L<sup>-1</sup> for tap and surface water, respectively. The total organic carbon content was quite similar for the two samples (2.8 mg L<sup>-1</sup> and 2.2 mg L<sup>-1</sup> for the tap and surface water, respectively). Moreover, tap water shows a somewhat



**Fig. 6.** HDC of azole compounds mixture in tap water (A) and surface water (B) ( $[\text{Pesticide}]_0 = 100 \mu\text{g L}^{-1}$ ;  $\text{H}_2\text{O} = 50 \text{ N mL min}^{-1}$ ;  $[\text{Pd}/\text{Al}_2\text{O}_3] = 0.25 \text{ g L}^{-1}$ ;  $25^\circ\text{C}$ ).

**Table 4**

Values of the rate constant in the HDC of the azole pesticides in different water matrices.

Pesticide	$k \text{ (L g min}^{-1}\text{)}$		
	Deionized water	Tap water	Surface water
TEB	$2.6 \text{ (} r^2 = 0.95 \text{)}$	$0.76 \text{ (} r^2 = 0.98 \text{)}$	$0.96 \text{ (} r^2 = 0.99 \text{)}$
PEN	$1.72 \text{ (} r^2 = 0.97 \text{)}$	$0.72 \text{ (} r^2 = 0.99 \text{)}$	$0.88 \text{ (} r^2 = 0.98 \text{)}$
TET	$2.28 \text{ (} r^2 = 0.99 \text{)}$	$0.80 \text{ (} r^2 = 0.98 \text{)}$	$0.80 \text{ (} r^2 = 0.92 \text{)}$
MET	$1.08 \text{ (} r^2 = 0.97 \text{)}$	$0.88 \text{ (} r^2 = 0.99 \text{)}$	$0.88 \text{ (} r^2 = 0.99 \text{)}$
IMZ	$1.56 \text{ (} r^2 = 0.97 \text{)}$	$1.04 \text{ (} r^2 = 0.99 \text{)}$	$1.04 \text{ (} r^2 = 0.98 \text{)}$
PCZ	$1.72 \text{ (} r^2 = 0.99 \text{)}$	$1.08 \text{ (} r^2 = 0.99 \text{)}$	$1.08 \text{ (} r^2 = 0.98 \text{)}$

higher pH which is consistent with its higher carbonate content (measured as inorganic carbon (IC) concentration).

The evolution of the azole pesticides along the HDC reactions in the different reaction matrices is shown in Fig. 6. As can be seen, complete degradation of the pesticides was achieved in all cases regardless of the reaction aqueous matrices, which demonstrates the versatility of the system. In fact, the rate constant values obtained were quite similar to the achieved in deionized water. Accordingly, the low carbon content as well as the presence of co-existing species in these water matrices do not seem to hinder the activity of the catalytic system (see Table 3). As can be shown, the activity decreased in tap water and surface water (see Table 4) could be mainly attributed to the higher conductivity, and therefore, higher ions concentration, since they can compete for Pd catalytic centers. Yuan & Keane, [35], studied the hydrodechlorination (HDC) of 2,4-dichlorophenol (2,4-DCP) and 2-chlorophenol (2-CP) on 1% Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub> under minimal mass transport conditions. The HDC of 2,4-DCP generated HCl and 2-CP as a partially dechlorinated intermediate, which was further hydrodechlorinated to cyclohexanone.

According to this work, inhibitory effects due to the presence of HCl were observed on the activity of the catalyst during the HDC reaction, while the selectivity towards the reaction products was maintaining unchanged.

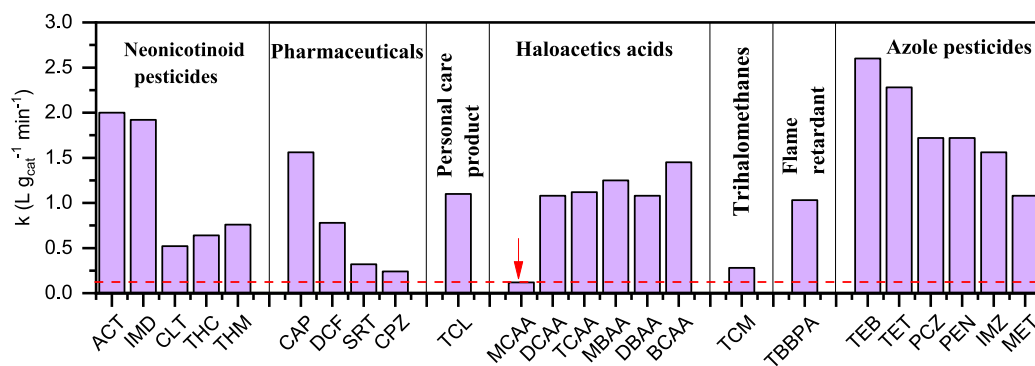
### 3.6. HDC of azole pesticides in the context of EU Watch Lists micropollutants

HDH is an efficient and versatile process, as it can be applied to different families of micropollutants included in the different EU Watch Lists such as pharmaceuticals, pesticides or personal hygiene products, among others, or even the haloacetic acids, recently included in the Directive 2020/2184 on the quality of water intended for human consumption. Depending on the nature of the organohalogen compounds, such as the type and number of halogen substituents, their reactivity to the HDH process would be different. Fig. 7 compares the pseudo-first apparent rate constant values obtained in the HDH of the halogenated azole pesticides with those obtained in the HDH of different representative halogenated groups of micropollutants [26]. It can be seen that the azole pesticides are quite reactive towards HDC in comparison with neonicotinoid pesticides, pharmaceuticals and haloacetic acids. TEB and TET are the most reactive compounds in this group, while MET is the least reactive azole pesticide. Nonetheless, the reactivity of MET is notably higher than that of other halogenated micropollutants such as the haloacetic acid MCAA, the pharmaceuticals SRT and CPZ or the trihalomethanes. All these low reactivity micropollutants, specially MCAA, can be used as indicators of the effectiveness of the HDH treatment, since their complete elimination guarantees that the rest of the halogenated micropollutants have been effectively converted.

All in all, it must be highlighted that all the compounds included in Fig. 7 were completely eliminated in short reaction times (most of them in about 30 min of reaction time) with rate constants ranging from 0.12 to  $2.6 \text{ L g}_{\text{cat}}^{-1} \text{ min}^{-1}$ , so this technology can be proposed as a viable alternative for the abatement of a wide variety of halogenated micropollutants in DWTPs.

## 4. Conclusions

The feasibility of HDC for the removal of a representative group of chlorinated azole pesticides recently included in the EU Watch List has been demonstrated. Notably, complete degradation of all compounds was achieved in a short reaction time (<15 min) operating under ambient conditions and neutral pH. This group of micropollutants was quite reactive towards HDC in comparison with neonicotinoid pesticides, pharmaceuticals and chloroacetic acids. Furthermore, azole pesticides were completely dechlorinated along reaction, achieving in all cases chlorine-free reaction products. This transformation allowed to dramatically reduce the ecotoxicity of the effluents despite the high ecotoxic character of all pesticides. Notably, the catalyst was fairly



**Fig. 7.** Pseudo-first order rate constant values obtained in the HDC of representative groups of micropollutants included in the EU Watch Lists ( $[\text{Pollutant}]_0 = 100 \mu\text{g L}^{-1}$ ;  $[\text{H}_2]_0 = 50 \text{ N mL min}^{-1}$ ;  $[\text{Pd}/\text{Al}_2\text{O}_3] = 0.25 - 1.0 \text{ g L}^{-1}$ ).

stable upon three consecutive HDC runs, maintaining its properties practically unchanged. The versatility of the catalytic system was finally demonstrated in real aqueous matrices (DWTP and tap water), where the effects of the presence of co-existing substances were practically negligible.

### CRedit authorship contribution statement

**Raúl B. del Olmo:** Writing – original draft, Investigation, Methodology, Visualization. **Julia Nieto-Sandoval:** Writing – review & editing. **Macarena Munoz:** Conceptualization, Writing – original draft, Supervision. **Zahara M. de Pedro:** Conceptualization, Writing – review & editing, Supervision. **Jose A. Casas:** Resources, Writing – review & editing, Supervision, Project administration, 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

No data was used for the research described in the article.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2023.124393>.

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