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Catalytic hydrodechlorination as polishing step in drinking water treatment for the removal of chlorinated micropollutants

Julia Nieto-Sandoval[*], Macarena Munoz, Zahara M. de Pedro and Jose A. Casas

Departamento de Ingeniería Química, Universidad Autónoma de Madrid, Ctra. Colmenar km 15, 28049 Madrid, Spain

*Corresponding author phone: +34 91 497 3425; e-mail: julia.nieto-sandoval@uam.es

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Abstract

The presence of micropollutants in fresh waters represents an important challenge for drinking water treatment plants (DWTPs). In particular, the chlorinated ones are especially harmful given their high toxicity and strong bioaccumulation potential. The aim of this work is to evaluate the feasibility of catalytic hydrodechlorination (HDC) for the removal of a representative group of chlorinated micropollutants commonly found in the source waters of DWTPs: the antibiotic chloramphenicol (CAP), the anti-inflammatory diclofenac (DCF), the antibacterial agent triclosan (TCL) and the antidepressant sertraline (SRT). The complete degradation of the isolated micropollutants (3 mg L^{-1}) was achieved in 1 h reaction time using a Pd/Al_2O_3 catalyst load of 0.25 g L^{-1} and a H_2 flow rate of 50 N mL min^{-1}. The experimental data were properly described by a pseudo-first order kinetic equation, obtaining degradation rate constants in the range of 0.32-1.56 L g_{cat}^{-1} min^{-1} and activation energy values within 42-52 kJ mol^{-1}. In all cases, the final reaction products were chlorine-free compounds and thus, HDC effluents were non-toxic (<0.1 TU). Remarkably, the catalyst showed a suitable stability upon five consecutive applications. The versatility of the process was demonstrated in the treatment of the micropollutants mixture in different aqueous matrices (mineral, surface and tap waters). Strikingly, the removal rate was not affected by the presence of co-existing substances, being the micropollutants completely removed in 15 min with 1 g L^{-1} catalyst concentration. Finally, the potential of HDC for the removal of trihalomethanes, by-products formed along the oxidation step by chlorination in DWTPs, was also demonstrated.

Keywords: Catalytic hydrodechlorination; drinking water; Pd/Al_2O_3; chlorinated micropollutants.

1. Introduction

Drinking water is one of the Earth's most valuable resources. Access to safe potable water is essential to our health and thus, it is considered a basic human right. The quality of potable water required for human use must fulfil a specific regulation, which may vary among countries and regions, being in most of developed countries guaranteed by drinking water treatment plants (DWTPs). The main goals of DWTPs are the removal of natural organic matter (NOM), turbidity and microorganisms from the raw fresh water, with special control of its taste, odour and appearance. Nevertheless, in most cases the source waters of DWTPs have been directly or indirectly impacted by wastewater and thus, they also contain anthropogenic chemicals at low concentrations (ng L^{-1} – µg L^{-1}), usually known as micropollutants [1-3]. Among them, the chlorinated ones are particularly dangerous as they are characterized by a low biodegradability, long-term persistence, high toxicity and strong bioaccumulative potential [4-6].

Typical DWTPs generally involve a sequence of physical and chemical treatments that include oxidation pretreatment, coagulation-flocculation, sedimentation, filtration and disinfection. Pre-chlorination, an oxidation treatment of the raw water using chlorine agents, allows reducing significantly the load of pathogens [7]. Nevertheless, this step unavoidably leads to the generation of hazardous trihalomethanes (THMs) or chloro-derivative compounds [8, 9], due to the reaction of chlorine with NOM or micropollutants, respectively [10-13]. Coagulation, flocculation and sedimentation treatments are focused on the removal of turbidity and, afterwards, sand filtration allows removing fine residual solids. Finally, the pH of the effluent is neutralized, and a disinfection treatment is implemented to stabilize the biological quality of potable water, usually by the addition of chloramines [14-16]. Although the load of micropollutants is certainly reduced along the whole treatment, the total elimination of these substances is

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not usually achieved [14, 17]. The application of advanced polishing systems like ozonation as oxidation treatment would allow to complete the treatment but the operating conditions must guarantees the total elimination of the organic species in order to avoid the formation of more toxic organic intermediates than the initial ones [14, 18, 19]. Padhye et al. (2014) investigated the occurrence and fate of different micropollutants in a real DWTP, which included pre-ozonation, flocculation, sedimentation, ozonation, filtration and chlorination treatments. The maximum concentrations of two relevant chlorinated micropollutants *viz.* the broad-spectrum antibacterial agent triclosan (TCL) and over-the-counter anti-inflammatory diclofenac (DCF) in the source water were 106 and 24 ng L^{-1}, respectively; while 55 and 9 ng L^{-1} were quantified in the treated drinking water. Thus, the overall removal efficiency was 55% and 61% for TCL and DCF, respectively. These results are in agreement with a number of works in literature [20-22].

It is clear that micropollutants appear at very low concentrations in potable water and thus, the associated risk for human health could be considered relatively minor. However, despite its low concentration, the risk associated with prolonged exposure to this type of micropollutants is not known, so the elimination of these compounds from drinking water is an issue of growing interest. Moreover, the expected rise on freshwater demand for drinking-water supply worldwide would lead to a reduction on the temporal and spatial distances between wastewater and potable water. Consequently, the impact of micropollutants may be greater in the near future.

Aqueous phase catalytic hydrodechlorination (HDC), an environmentally-friendly and simple system in which hydrogen reacts with the pollutants under ambient conditions giving rise to chlorine-free hydrogenated compounds, less toxic than the starting compounds, and hydrochloric acid [23, 24], could represent a promising polishing step in DWTPs although so far has been scarcely investigated for such goal [25]. This work aims
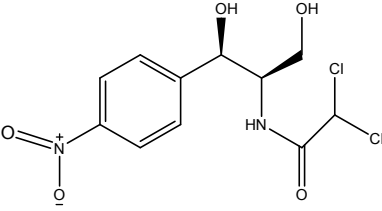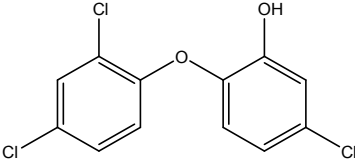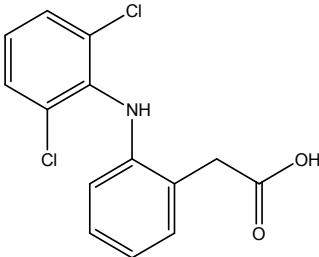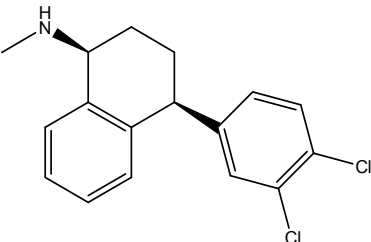
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at evaluating the feasibility of this technology for the removal of a representative group of chlorinated micropollutants frequently found in the raw sources of DWTPs (TCL, DCF, the antidepressant sertraline (SRT) and the antibiotic chloramphenicol (CAP)) [14, 26]. For such goal, each micropollutant as well as their mixture have been hydrodechlorinated using Pd/Al_2O_3 as catalyst due to its prominent role in aqueous-phase HDC [27]. The kinetics and reaction pathway of each compound have been studied. Besides, the ecotoxicity abatement along the treatment and the stability of the catalyst in consecutive runs have been analysed. As a proof of concept, relevant water matrices such as surface, mineral and tap water have been tested as reaction media. Finally, the ability of the hydrodechlorination process for the removal of THMs has been also studied.

2. Materials and methods

2.1. Materials

Diclofenac sodium salt (analytical standard), sertraline hydrochloride (98%) and chloramphenicol (98%) were provided by Sigma-Aldrich. Triclosan (≥97%) was supplied by Fluka. The main properties of the micropollutants used in this work are provided in Table 1. Acetic acid (99.5%), ortho-phosphoric acid (85%) and di-sodium hydrogen phosphate anhydrous were provided by Panreac. Acetonitrile (99.9%) and hydrogen (99.999%) were delivered by Scharlau and Praxair, respectively. The catalyst Pd/Al_2O_3 (1% wt.) was supplied by Alfa Aesar. Detailed catalyst characterization can be found in a previous work [25]. Unless otherwise indicated (tap water, mineral water and surface water), deionized water was used to carry out the experiments. Tap and surface waters were collected in the Region of Madrid and mineral water was obtained from a typical commercial brand.

Table 1. Main characteristics of the chlorinated micropollutants tested in this work.

Compound	Abbreviation	Structure	pKa	Molecular weight (g mol^{-1})
Chloramphenicol	CAP		11 [28]	323.13
Triclosan	TCL		8.14 [29]	289.54
Diclofenac	DCF		4.20 [30]	296.15
Sertraline	SRT		9.16 [31]	306.23

2.2. Experimental procedure

The experiments were operated batch-wise in a magnetically stirred glass slurry-type reactor (500 mL) continuously fed with H_2 at 50 N mL min^{-1}. Initial concentration of the isolated chlorinated micropollutants was fixed at 3 mg L^{-1}. Although it is somehow higher than the representative amounts of these micropollutants in surface waters [20, 22], it was selected to facilitate their quantification as well as to follow the evolution of the reaction intermediates and products with the available analytical techniques in the laboratory. The catalyst concentration was established at 0.25 g L^{-1}; while a catalyst load of 1 g L^{-1} was used for the treatment of the micropollutants mixture. Experiments were carried out at different temperatures from 17 to 35 ºC. The stirring velocity was fixed at 900 rpm in order to avoid external mass transfer limitations [25].

2.3. Analytical methods

The evolution of the different compounds during the HDC reactions was followed by withdrawing liquid samples from the reactor. Prior analysis, the samples were centrifuged for catalyst separation. Chlorinated micropollutants and the resulting intermediates and products were measured by HPLC-UV (Shimadzu, Prominence-i model, LC-2030C LT) using an Eclipse Plus C18 column (15 cm length, 4.6 mm diameter) (Agilent) as stationary phase. Analyses were performed at 270 nm using a mixture of acetonitrile and acetic acid aqueous solution (75 mM) as mobile phase at different volume ratios depending on the micropollutant tested (57/43%, 30/70% and 70/30% (v/v) for DCF, TCL and CAP, respectively). In the case of SRT, the analysis was carried out at 205 nm using a mobile phase that consisted of a 57/43% (v/v) mixture of phosphate buffer (Na$_2$HPO$_4$ 5 mM, H$_3$PO$_4$ 7.5 mM) and acetonitrile. The reaction intermediates and products were identified by LC/MS (SQ Agilent 6120) equipped with a quadrupole detector using the same column and analysis conditions previously described. In this case, the acetic acid solution was replaced by a formic acid one (21.7 mM) as the mobile phase. The software package LC/MSD ChemStation was used for data acquisition and processing. HCl produced during reaction was quantified as chloride by ion chromatography (Metrohm 883 Basic IC Plus). A Metrosep A supp 5-250 column (25 cm length, 4 mm internal diameter) was used as stationary phase and a 3.2 mM Na$_2$CO$_3$ aqueous solution as mobile phase. A Shimadzu TOC VSCH analyser was employed to measure the total organic carbon (TOC). Monochloramines were determined by a spectrophotometer (Hach DR3900) using the Indophenol Method (U.S. Patent 6,315,950) at 20 ºC. Trichloromethane was measured by a GC/MS (Bruker, EVOQ GC-TQ4, 436-GC model) using a Rxi- 5Sil MS column (30 m length, 0.25 mm internal diameter) and helium as

carrier gas. The injector temperature was set at 250 ºC and the column temperature was increased from 50 to 200 ºC at a ramp of 8 ºC min^{-1}. The analysis was performed in the mass range of m/z 45-200.

The ecotoxicity of the chlorinated micropollutant solutions and HDC effluents was evaluated by the Microtox toxicity test (ISO11348-3, 1998) using *Vibrio fischeri*. In this test, a photomultiplier M500 Microtox Analyzer (Azur Evironmental) was used to measure the bioluminescence after 15 min of exposure at 15ºC, previously adjusting the pH, between $6 - 8$, and the salinity, with 2% NaCl solution, of the samples. The EC_{50}, defined as the effective nominal concentration (mg L^{-1}) of the compound that reduces the intensity of light emission by 50%, was measured for the four micropollutants tested, whereas the ecotoxicity of the reaction samples was expressed as toxicity units (TUs), which is inversely proportional to EC_{50} (IC_{50} in case of complex samples), as follows in Equation 1:

$$TU = \frac{C_o \text{ (mg L}^{-1})}{EC_{50} \text{ (mg L}^{-1})} = \frac{100}{IC_{50}} \tag{1}$$

3. Results and discussion

3.1. Catalytic hydrodechlorination of relevant chlorinated micropollutants

Fig. 1 shows the evolution of the isolated micropollutants upon HDC reaction at 25 ºC. As observed, all of them were completely removed in short reaction times (below 1 h). The effect of temperature was evaluated within the range 17 - 35 ºC (see Fig. S1 of the Supplementary Material for experimental data). As expected, the increase of temperature led to faster degradation rates in all cases. In this sense, CAP was removed in 20 min at 17 ºC while only 10 min were required operating at 35 ºC. The experimental data were successfully described by a pseudo-first order kinetic equation. The resulting rate constant values are collected in Table 2. The activation energy values, calculated

according to the Arrhenius equation (see Fig. S2 for Arrhenius plot), were within the range of 42 – 52 kJ mol^{-1} (Table 2), which are similar to the ones previously reported for the degradation of other priority organochlorinated pollutants such as chlorophenols by HDC using Pd/Al$_2$O$_3$ catalysts [27, 32].
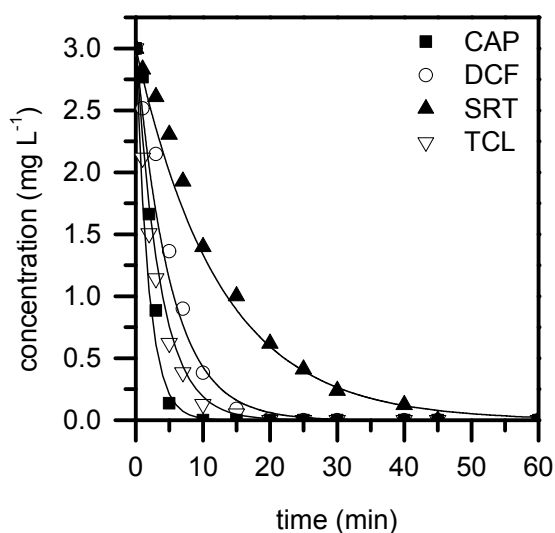

Fig. 1. Evolution of the isolated micropollutants upon HDC with Pd/Al$_2$O$_3$ ([Micropollutant]$_0$ = 3 mg L^{-1}; H$_2$ = 50 N mL min^{-1}; [Pd/Al$_2$O$_3$] = 0.25 g L^{-1}; 25 ºC). Experimental (symbols) and model fit (lines).

Table 2. Pseudo-first order constant rate and activation energy values for HDC of CAP, TCL, DCF and SRT.

Micropollutant	k (L g$_{cat}^{-1}$ min^{-1})			Ea (kJ mol^{-1})
	17 ºC	25 ºC	35 ºC	
CAP	1.08	1.56	2.94	42
TCL	0.74	1.10	2.20	45
DCF	0.46	0.78	1.62	52
SRT	0.20	0.32	0.70	52

The micropollutants reactivity towards HDC decreased in the following order: CAP>TCL>DCF>SRT. This could be explained by the number of available positions at the molecule where the nucleophilic substitution by hydrogen can take place. Previously, the hydrogen molecule undergoes a dissociative adsorption on the surface of Pd [33, 34]. In this sense, CAP showed four positions liable to be attacked, two chlorine atoms, a nitro group and an amide group. TCL was the following most reactive micropollutant, with three chlorine atoms, and finally DCF and SRT, both with two chlorine atoms. The differences among the latter could be attributed to the different pKa of these substances (Table 1). HDC experiments were carried out at natural pH (pH$_0 \sim 7$), which was reduced to values around 5.6, so the surface of Pd/Al$_2$O$_3$ was weakly positively charged along reaction taking into account its pH$_{PZC} = 8.7$ [32]. Accordingly, it presented a favourable surface to the negatively charged DCF molecule while SRT could suffer a weak electrostatic repulsion.

The evolution of the reaction intermediates and final products obtained with each micropollutant was qualitatively followed by HPLC/UV (see Fig. S3, S4 and S5 of the Supplementary Material for the experimental data). Subsequently, they were also identified by LC/MS. According to the obtained results, consecutive reaction pathways were proposed, as shown in Scheme 1. In the case of CAP, the hydrogenation of the nitro group to yield an amino one occurred previous to the hydrodechlorination of the molecule. On the other hand, TCL, DCF and SRT were stepwise hydrodechlorinated leading to the corresponding chlorine-free products. The release of chloride was confirmed by ionic chromatography, being the chlorine balances closed above 95% at the end of the reactions in all cases.

Most of prior studies dealing with the removal of the micropollutants tested in this work have been focused on the application of advanced oxidation processes, mainly

Fenton oxidation, while the use of HDC has been scarcely investigated.[35-37] All in all, the results obtained in this work can be favourably compared with those previously reported in the literature. Wang (2015) [38] studied the removal of CAP by a sequential adsorption-HDC treatment using Au-Pd nanoparticles supported on Amberlite ($[CAP]_0$=50 mg L^{-1}; [717@Au–Pd]=10 g L^{-1}; 25 ºC). The first step required 10 h to reach the equilibrium, 60% of CAP adsorbed, and the second one showed a rate constant of 0.007 L g_{cat}^{-1} min^{-1}, which is 4 times lower than the one obtained in the current work. In the same line, the removal of TCL by HDC using a novel anion-exchange-resin supported Pd catalyst under similar conditions ($[TCL]_0$=2.9 mg L^{-1}; [resin]=1 g L^{-1} with 0.2% wt. of Pd loading; 20 ºC) obtaining rate constants 14 times lower than the reached with Pd/Al$_2$O$_3$ [39]. With regard to DCF, De Corte et al. (2012) obtained rate constants two and one orders of magnitude lower than the ones reported in the current work using biogenic Pd and bimetallic biogenic Pd-Au catalysts, respectively [40]. On the other hand, similar HDC rate constants were reported by Wu (2015) [24] in the degradation of DCF over Pd/CeO$_2$ but the catalyst showed a poor stability upon consecutive uses. In the case of SRT, to the best of our knowledge there are no works dealing with its treatment by HDC although a few works can be found focused on its advanced oxidation, where similar reaction times were required to achieve its complete removal [41, 42].
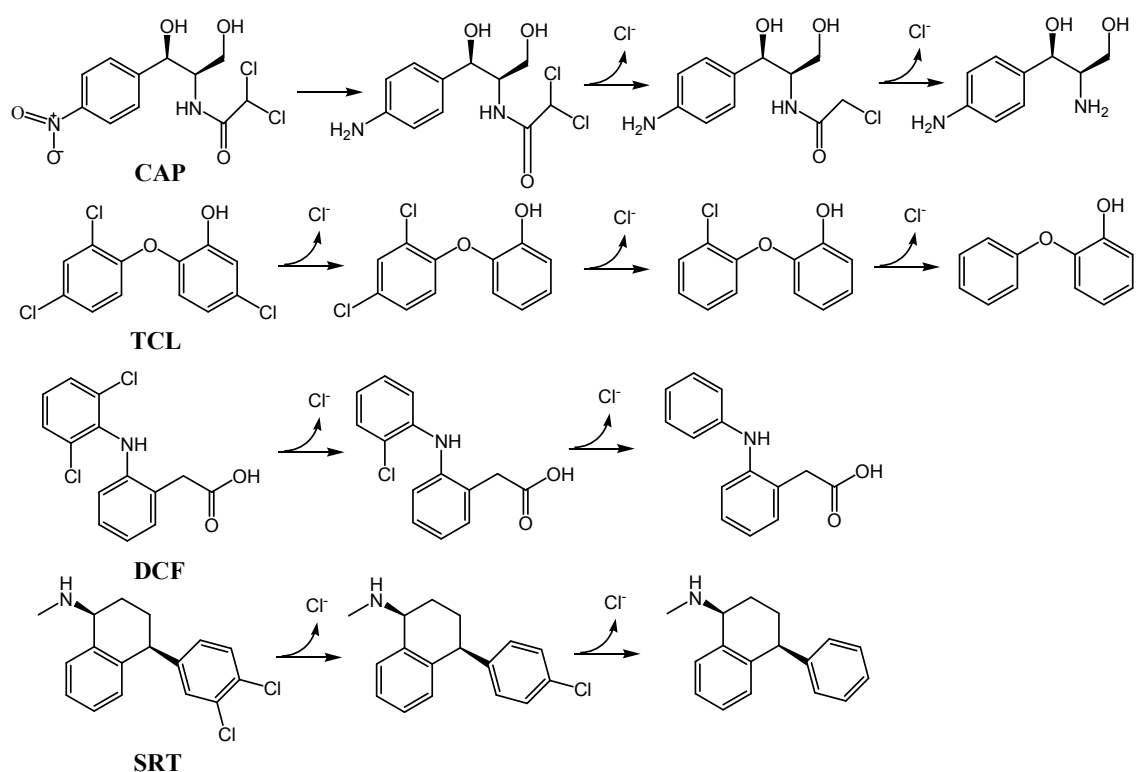
Scheme 1. Proposed reaction pathways for the HDC of CAP, TCL, DCF and SRT.

It is clear that chlorinated micropollutants will not appear isolated in real fresh waters, thus it is crucial to evaluate the degradation of a mixture of them. For such experiments, the catalyst concentration was established at 1 g L^{-1} given the higher initial load of chlorinated compounds tested (3 mg L^{-1} each). As can be seen in Fig. 2, all compounds were removed in 30 min reaction time, following the same order of reactivity previously observed. The rate constants were quite similar to those achieved when the isolated pollutants were treated (0.13, 0.51, 0.54 and 1.37 L g$_{cat}^{-1}$ min^{-1} for SRT, DCF, TCL and CAP, respectively), observing a slight inhibitory effect among them. In addition to the evolution of the concentration of the target pollutants, the abatement of ecotoxicity along reaction was also evaluated. First, the EC$_{50}$ values of the isolated compounds were calculated, obtaining values of 404, 0.25, 6.2 and 8.8 mg L^{-1} for CAP, TCL, DCF and SRT, respectively, which are close to those reported in the literature [37, 43-45]. The

ecotoxicity of the initial micropollutant mixture was calculated to be 17.4 TUs, which corresponded to the sum of the individual compounds. The ecotoxicity of the solution was progressively decreased along reaction, reaching negligible ecotoxicity values in 10 min. reaction time, which is consistent with the removal of TCL, the most toxic compound among the ones tested (Fig. 2). These results allowed to confirm that the intermediates generated upon the process showed a lower toxicity of the target compounds, being the final chlorine-free products non-toxic.
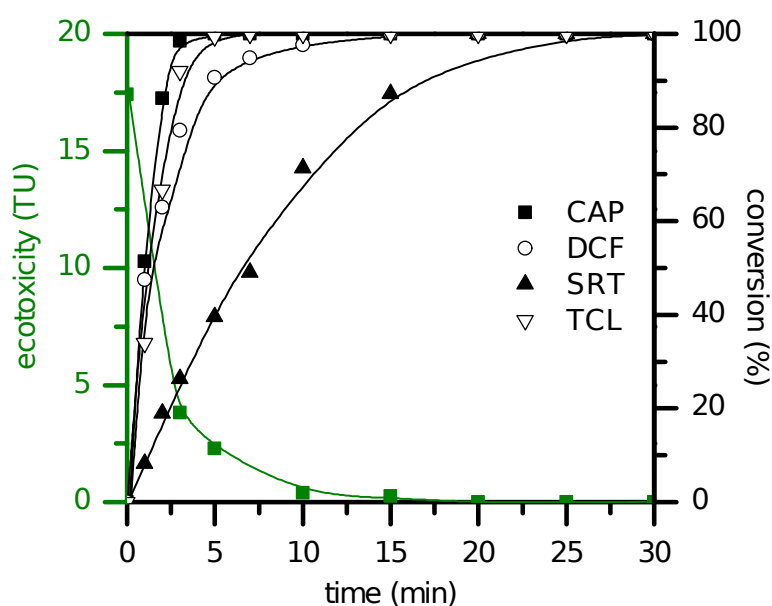
Fig. 2. Time-course of chlorinated micropollutants (treated in mixture) and ecotoxicity upon HDC ([Micropollutant]$_0$ = 3 mg L^{-1}; H$_2$ = 50 N mL min^{-1}; [Pd/Al$_2$O$_3$] = 1 g L^{-1}; 25 ºC).

3.2. Stability tests

One of the main shortcomings of HDC is the catalyst deactivation during reaction, which is mainly due to HCl poisoning, metal component leaching and by-products adsorption [46-48]. Taking into account the high cost of HDC catalysts, composed by precious metals, ensure their stability after consecutive applications is imperative. To

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assess the stability of Pd/Al_2O_3, it was submitted to five consecutive HDC runs. The rate constants obtained in each of the five trials were quite similar with all the micropollutants tested, as can be seen in Fig. 3, which demonstrates the outstanding stability of the solid. In fact, analysis of the used catalysts by TXRF allowed to discard the leaching of Pd (<1% wt.). These results are consistent with a previous work where the HDC of DCF was investigated.[25] They are also in good agreement with Yuan and Keane (2003) and de Pedro et al. (2011) [46, 49], who concluded that Pd/Al_2O_3 is a particularly resistant catalyst in the HDC of different chlorophenols.
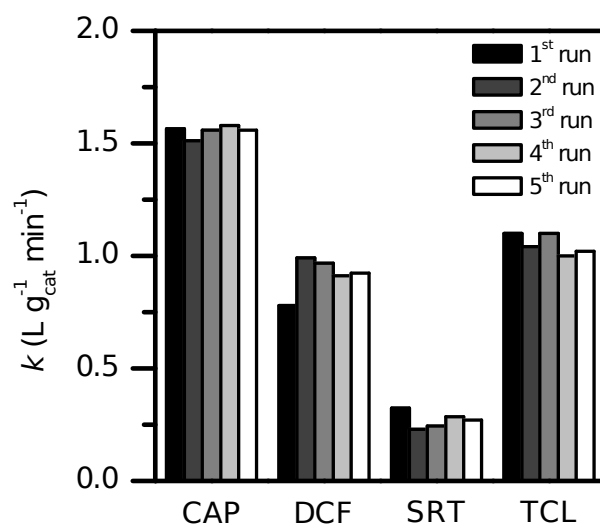

Fig. 3. Rate constant values after five consecutive HDC runs ([Micropollutant]$_0$ = 3 mg L^{-1}; H$_2$ = 50 N mL min^{-1}; [Pd/Al$_2$O$_3$] = 0.25 g L^{-1}; 25 °C).

3.3. Operation in relevant water matrices

The HDC process has proved to be effective for the degradation of chlorinated micropollutants in deionized water operating under ambient conditions. Nevertheless,

these compounds are usually found in more complex matrices, where the presence of co-existing substances could affect the performance of the system. Accordingly, different real water matrices such as surface, tap and mineral water fortified with the mixture of chlorinated micropollutants under the same operating conditions previously tested was investigated. Surface water represents one of the main sources of DWTPs. On the other hand, tap and mineral waters are also relevant matrices to be investigated as their composition is similar to the one of the finished DWTP effluent where the HDC treatment would be implemented. The main characteristics of these matrices are summarized in Table 3.

Table 3. Main characteristics of the real aqueous matrices.

Matrices	pH	TOC (mg L^{-1})	IC (mg L^{-1})	Conductivity (μS cm^{-1})	Cl$^-$ (mg L^{-1})
Mineral water	7.1	0.3	3.5	41	0.35
Tap water	7.2	2.5	2.9	67	8.7
Surface water	7.0	2.7	14.9	200	14.1

Fig. 4 shows the evolution of the chlorinated micropollutants in the real aqueous matrices tested. As observed, all of them were completely degraded in less than 15 min although slight differences were appreciated depending on the matrix tested. It should be noted that, in general, the degradation rates observed in these real matrices were slightly higher than the achieved in deionized water (Fig.2), which could be due to the neutralization of the chloride ions generated along reaction by the presence of salts [50]. In fact, whereas in deionized water, the pH decreased from 7 to 5.6, it remained practically unchanged in the real matrices. This effect was particularly relevant in the case of SRT, in line with its relatively high pKa. In fact, an additional experiment carried out in the presence of HCO$_3^-$ (29 mg L^{-1}, pH$_0$= 8) (see Fig. S6 of the Supplementary Material for experimental data) led to a significant increase of the HDC constant of SRT (0.66 L g$_{cat}^-$

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[1] min^{-1}), confirming the key role of pH on its removal rate. Finally, it should be mentioned that the fastest removal rate of micropollutants was achieved in mineral water, while tap and surface water led to similar results. This fact is consistent with the remarkably lower chloride and TOC contents of the former matrix. Chloride could interact with the catalyst, occupying active sites that can not be used by the compounds to be hydrodechlorinated [49, 51], while the presence of organic species could contribute to the fouling of the catalyst [52].
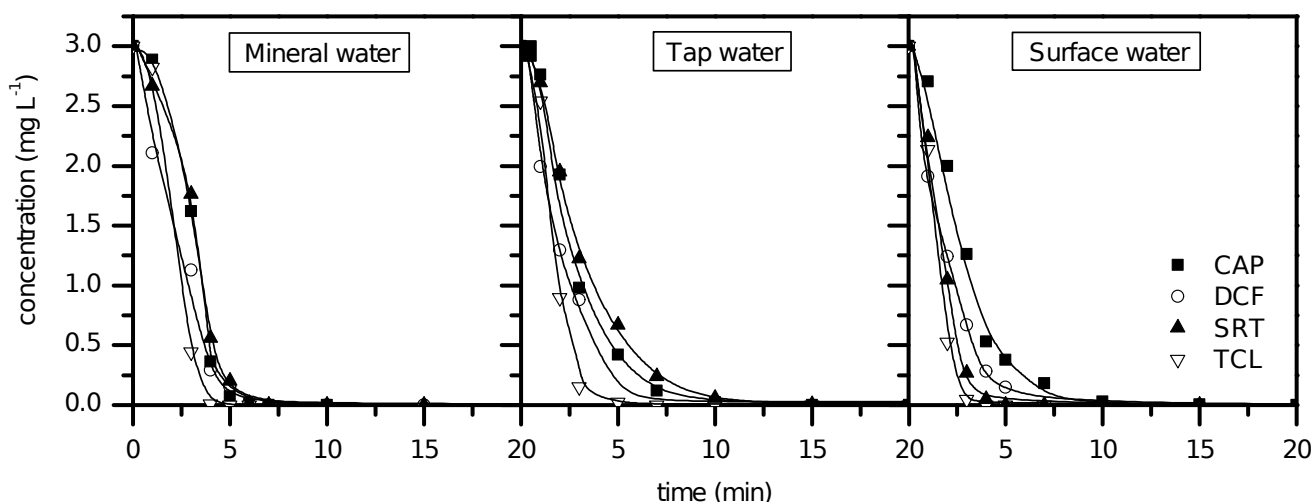
Fig. 4. Evolution of DCF, TCL, CAP and SRT mix through HDC in mineral, tap and surface water ([Micropollutant]$_0$ = 3 mg L^{-1}; H$_2$ = 50 N mL min^{-1}; [Pd/Al$_2$O$_3$] = 1 g L^{-1}; 25 ºC).

3.4. On the potential integration of HDC in DWTP

Once demonstrated the effectiveness of the HDC technology for the removal of chlorinated micropollutants from water, its potential integration in the sequential treatment of a typical DWTP was investigated. It is clear that HDC would be a polishing step and thus, it should be implemented once the load of pathogens, NOM and suspended solids have been removed in a high extent, *i.e.* after the filtration step. In first place, the

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ability of HDC for the removal of trichloromethane (TCM), the most dominant species among the THMs formed in the pre-chlorination of the raw water, was investigated. These hazardous substances are associated to important human health risks such as bladder cancer, genetic polymorphism and miscarriage [7-9]. In second place, in order to assess if HDC must be performed prior the disinfection treatment or afterwards, its possible effect on chloramines was investigated.

Fig. 5 shows the results obtained in the HDC of TCM at a relevant concentration of 100 $\mu g\ L^{-1}$ under ambient conditions and using a catalyst load of 1 g L^{-1} [53]. An additional experiment in the absence of catalyst was also performed taking into account the high volatility of this species. Remarkably, TCM was completely removed in 30 min. in the presence of catalyst, while around 90% conversion was achieved in 2 h. in its absence. In fact, the HDC rate of TCM is also significantly higher than that obtained in the HDC of the chlorinated micropollutants tested in this work. Thus, these experiments demonstrate that HDC is an effective polishing technology not only for the removal of chlorinated micropollutants but also for the harmful THMs formed in the pre-chlorination treatment.
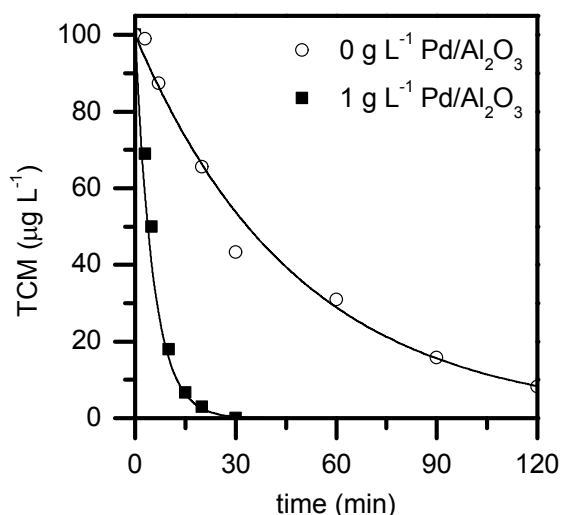

Fig. 5. Evolution of TCM upon HDC in the absence and presence of catalyst ([THM]$_0$ = 100 $\mu g\ L^{-1}$; H$_2$ = 50 N mL min^{-1}; 25 ºC). Experimental (symbols) and model fit (lines).

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Disinfection is the last common step in drinking water treatment as one of the key goals of DWTPs is to supply safe water at the tap. Chloramine is often used as disinfectant instead of chlorine due to its higher stability, which hinders the formation of harmful disinfection by-products and also warrants the disinfection action throughout the whole distribution network [54]. Additional HDC experiments were carried out using tap water, where actual monochloramine concentration was 0.97 mg_{Cl_2} L^{-1}, in the absence of catalyst and also with a concentration of 0.25 g_{cat} L^{-1}. HDC led to the complete removal of monochloramine in 30 min reaction time (see Fig. S7 of the Supplementary Material for experimental data). Even in the absence of catalyst, chloramine concentration was strongly reduced (around 70% at the same reaction time), indicating that it can be removed by stripping. On the basis of these results, the potential integration of HDC in DWTP should be accomplished prior to the disinfection step and, taking into account the generation of HCl along the treatment, it should be also performed prior pH adjustment.

4. Conclusions

This work demonstrates the feasibility of HDC for the removal of a relevant group of chlorinated micropollutants: the antibiotic chloramphenicol (CAP), the anti-inflammatory diclofenac (DCF), the antibacterial agent triclosan (TCL) and the antidepressant sertraline (SRT). The complete degradation of the micropollutants was achieved in short reaction times, obtaining chlorine-free products and, thus, non-toxic effluents. Remarkably, the catalyst showed a relatively high stability upon five consecutive runs and the versatility of the process was proved in different real aqueous matrices (mineral, surface and tap waters). Finally, the removal of trihalomethanes, by-

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products usually formed along the oxidation step in DWTPs, by HDC was also demonstrated.

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Supplementary Material

Catalytic hydrodechlorination as polishing step in drinking water treatment for the removal of chlorinated micropollutants

Julia Nieto-Sandoval*, Macarena Munoz, Zahara M. de Pedro and Jose A. Casas

Departamento de Ingeniería Química, Universidad Autónoma de Madrid, Ctra. Colmenar km 15, 28049 Madrid, Spain

*Corresponding author phone: +34 91 497 3425; e-mail: julia.nieto-sandoval@uam.es
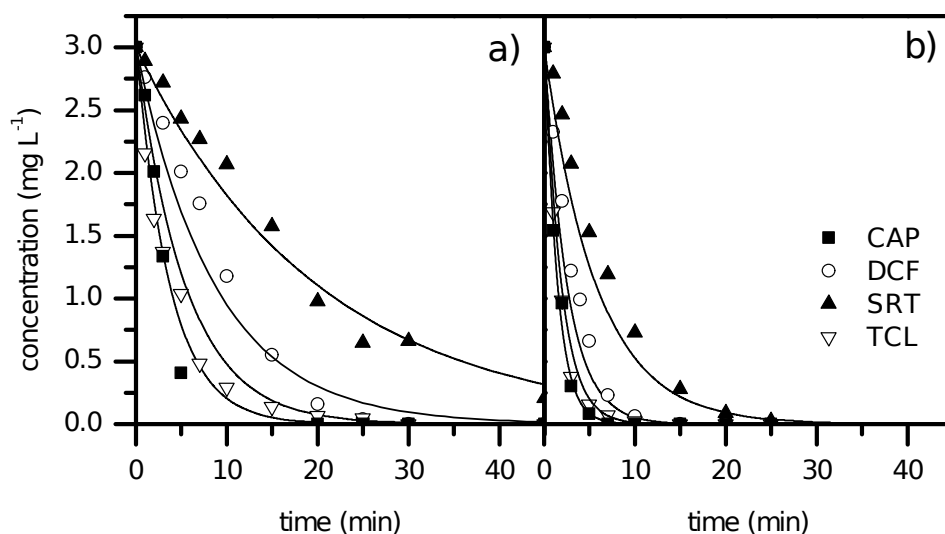
Fig. S1. Evolution of the isolated micropollutants upon HDC with Pd/Al$_2$O$_3$ (a: 17ºC, b: 35ºC) ([Micropollutant]$_0$ = 3 mg L^{-1}; H$_2$ = 50 N mL min^{-1}; [Pd/Al$_2$O$_3$] = 0.25 g L^{-1}). Experimental (symbols) and model fit (lines).
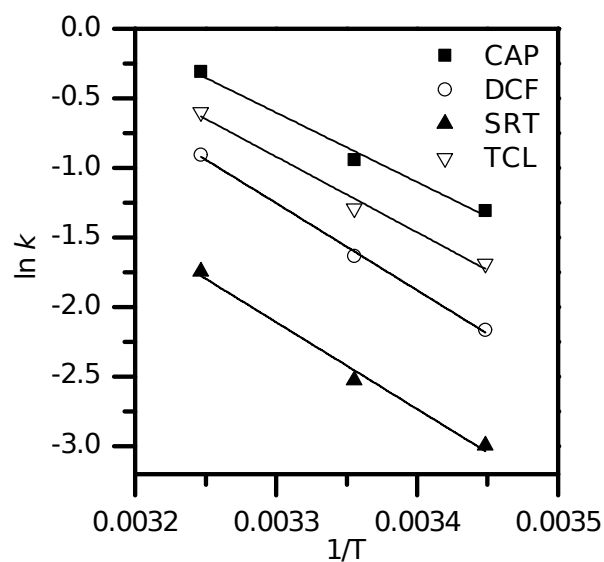
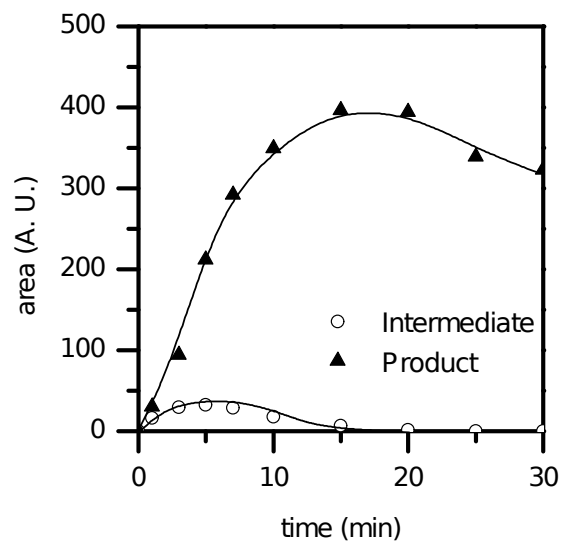**Fig. S2.** Arrhenius plot of the first order kinetics constants for each of the micropollutants tested in this work.

Fig. S3. Evolution of the reaction intermediate and final product of DCF upon HDC with Pd/Al$_2$O$_3$ ([Micropollutant]$_0$ = 3 mg L^{-1}; H$_2$ = 50 N mL min^{-1}; [Pd/Al$_2$O$_3$] = 0.25 g L^{-1}; 25 °C).
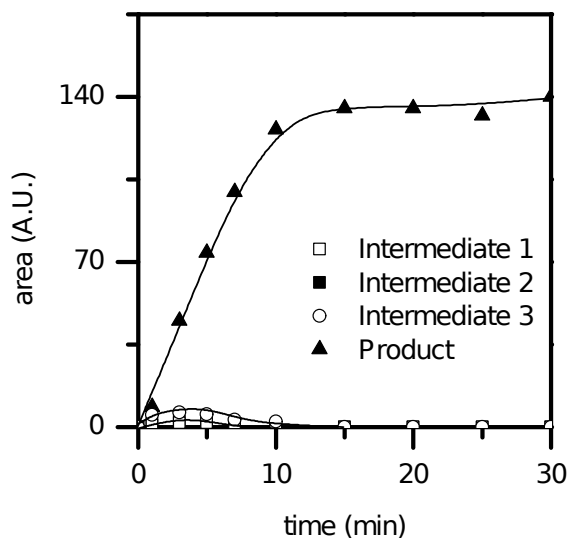
Fig. S4 Evolution of the reaction intermediate and final product of TCL upon HDC with Pd/Al$_2$O$_3$ ([Micropollutant]$_0$ = 3 mg L^{-1}; H$_2$ = 50 N mL min^{-1}; [Pd/Al$_2$O$_3$] = 0.25 g L^{-1}; 25 °C).
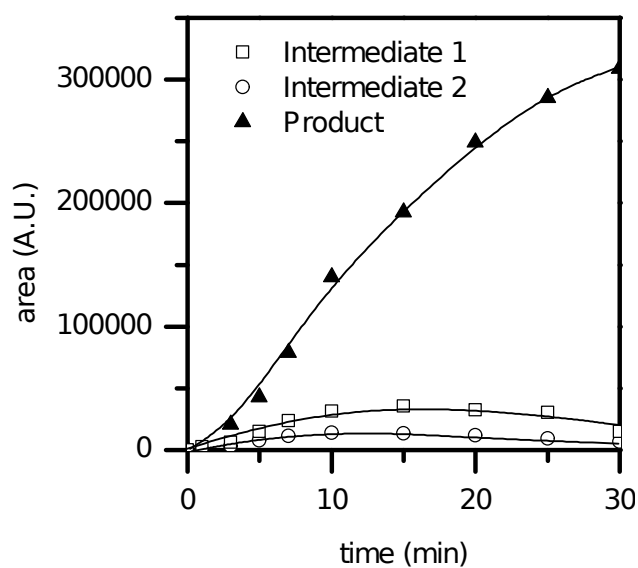
Fig. S5 Evolution of the reaction intermediate and final product of SRT upon HDC with Pd/Al$_2$O$_3$ ([Micropollutant]$_0$ = 3 mg L^{-1}; H$_2$ = 50 N mL min^{-1}; [Pd/Al$_2$O$_3$] = 0.25 g L^{-1}; 25 ºC).
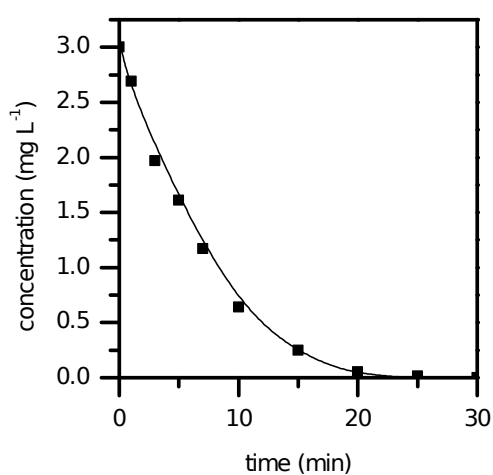
Fig. S6 Evolution of SRT upon HDC in the presence of 29 mg L^{-1} of HCO$_3^-$ ([Micropollutant]$_0$ = 3 mg L^{-1}; H$_2$ = 50 N mL min^{-1}; [Pd/Al$_2$O$_3$] = 0.25 g L^{-1}; 25 ºC).

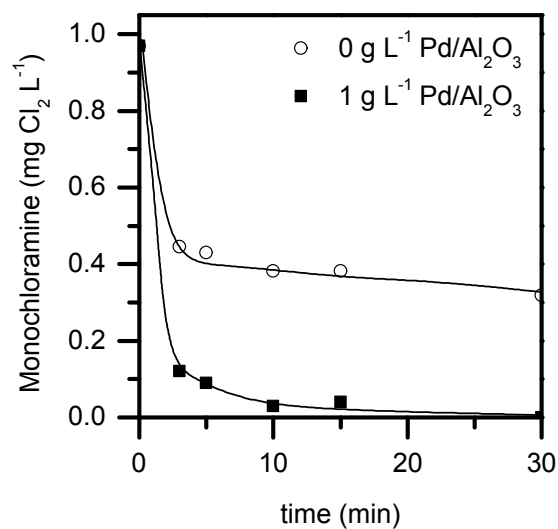**Fig. S7.** Evolution of TCM upon hydrodechlorination in the absence and presence of catalyst ([THM]$_0$ = 100 μg L^{-1}; H$_2$ = 50 N mL min^{-1}; 25 ºC). Experimental (symbols) and model fit (lines).